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Synthetic, structural, and mechanistic studies of palladium complexes supported by sterically encumbering m-terphenyl isocyanides

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Synthetic, Structural, and Mechanistic Studies of Palladium Complexes Supported by Sterically Encumbering \textit{m}\textendash{}Terphenyl Isocyanides

A dissertation submitted in partial satisfaction of the requirements for the degree Doctor of Philosophy

in

Chemistry

by

Liezel Ann Labios

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2012
The Dissertation of Liezel Ann Labios is approved, and it is acceptable in quality and form for publication on microfilm and electronically:

Chair

University of California, San Diego

2012
For my favorite parents Norma and Bert Labios, with immense gratitude and love.
“Brick walls are there for a reason. The brick walls are not there to keep us out. The brick walls are there to give us a chance to show how badly we want something. Because the brick walls are there to stop the people who don’t want it badly enough.”

– Randy Pausch (The Last Lecture)
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LIST OF ABBREVIATIONS

Å = Angstrom (10^{-10} m)

a = unit cell axis a

Anal. = combustion analysis (elemental)

Ar = aryl

α = unit cell angle α, orientation of magnetic nuclei aligned with an external magnetic field

b = unit cell axis b

β = unit cell angle β, position two atoms removed, orientation of magnetic nuclei aligned against an external magnetic field

br = broad

C_{ipso} = arene ring carbon attached to the substituent

C_{iso} = terminal isocyanide carbon

CNR = isocyanide

CO = carbon monoxide, carbonyl

COD = 1,5-cyclooctadiene (C_{8}H_{12})

Cp = cyclopentadienyl (C_{5}H_{5})

Cy = cyclohexyl (cyclo-C_{6}H_{11})

c = unit cell axis c

calcd. = calculated

cm^{-1} = wavenumber

°C = degrees Celsius

d = doublet, days, deuterated
DFT = Density Functional Theory

Dipp = 2,6-di-isopropylphenyl (2,6-i^Pr_2C_6H_3)

δ = chemical shift

η^n = hapticity of a ligand with n contiguous atoms bound to a metal center

E = energy, main group atom

EI = electron impact

equiv = equivalents

Et_2O = diethyl ether

eV = electron volts

GC-MS = Gas Chromatography – Mass Spectrometry

GoF = Goodness of Fit

g = grams

γ = unit cell angle γ

HOMO = Highest Occupied Molecular Orbital

HRMS = High Resolution Mass Spectrometry

Hz = Hertz (s⁻¹)

h = hours

IR = Infrared

i^Pr = isopropyl (CH(CH_3)_2)

J = NMR coupling constant, magnetic coupling constant

^nJ = n^th bond NMR coupling constant

κ^n = hapticity of a ligand with n non-contiguous atoms bound to a metal center

K = degrees Kelvin
kcal = kilocalories

L = ligand (neutral), liters

LDA = lithium di-isopropylamide

LUMO = Lowest Unoccupied Molecular Orbital

M = transition metal, mega- (10^6), molar (mol/L)

Me = methyl (CH₃)

(Me₃Si)₂O = bis-trimethylsilyl ether

MeCN = acetonitrile

Mes = mesityl, 2,4,6-trimethylphenyl (2,4,6-Me₃C₆H₂)

MO = Molecular Orbital

m = meta position

m = multiplet, mili- (10⁻³)

min = minutes

mol = moles

µ = bridging ligands, absorption coefficient (crystallography), magnetic moment

NMR = Nuclear Magnetic Resonance

ν = infrared stretching frequency

OTf = triflate, trifluoromethylsulfonate ([OSO₂CF₃])

o = ortho position

Ph = phenyl (C₆H₅)

p = para position

ppm = parts per million

π = pi
q = quartet

R = organic group, alkyl group

R = residual value (crystallography)

RT = room temperature

S = singlet electronic state

S = electronic spin

SOF = Site Occupancy Factor

SOMO = Singly Occupied Molecular Orbital

SQUID = Superconducting Quantum Interference Device

s = singlet, seconds

σ = sigma

T = temperature, triplet electronic state

THF = tetrahydrofuran

t = triplet

Tol = toluene, tolyl (C7H8)

t-Bu = tertiary-butyl (C(CH3)3)

Tripp = tri-isopropylphenyl (2,4,6-iPr3C6H2)

V = unit cell volume

VT = variable temperature

X = halide or pseudo halide

XAS = X-ray Absorption Spectroscopy

Xyl = xylyl

Z = number of molecules in unit cell
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ABSTRACT OF THE DISSERTATION

Synthetic, Structural, and Mechanistic Studies of Palladium Complexes Supported by Sterically Encumbering m-Terphenyl Isocyanides

by

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Doctor of Philosophy in Chemistry

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Professor Joshua S. Figueroa, Chair

The two-coordinate binary Pd(0) isocyanide monomer Pd(CN\text{Ar Dipp}_2)\text{2} was prepared using the sterically encumbering m-terphenyl isocyanide ligand CN\text{Ar Dipp}_2 (\text{Ar Dipp}_2 = 2,6-(2,6-\text{Pr})_2\text{C}_6\text{H}_2)\text{2C}_6\text{H}_3). Building upon the isolobal relationship between π-acidic isocyanides and CO, Pd(CN\text{Ar Dipp}_2)\text{2} was targeted as a stable analogue to the highly reactive binary carbonyl species Pd(CO)\text{2}. The electron-rich nature of
Pd(CNArDipp²)₂ was demonstrated by its reactivity towards electrophilic and Lewis acidic substrates such as I₂, MeOTf, and TlOTf.

In addition, the ability of Pd(CNArDipp²)₂ to oxidatively add across C–Br bonds of aryl bromides made it a promising catalyst precursor for organic cross-coupling reactions. Pd(CNArDipp²)₂ mediated the Suzuki-Miyaura cross-coupling of unactivated aryl bromides and aryl boronic acids with 1 mol % catalyst loading at room temperature. Moderate activity was observed with Pd(CNArDipp²)₂, and was attributed to the presence of an unnecessary equivalent of ligand on the complex. Kinetic studies on the oxidative addition step provided evidence for a dissociative mechanism, which thereby implied the involvement of a monoligated [Pd(0)L] species. Synthetic approaches to complexes containing a 1:1 L/Pd ratio culminated in the isolation and structural characterization of [Pd(η²-Dipp-μ-CNArDipp)]₃. This complex is a trinuclear aggregate of [Pd(0)L] and is catalytically competent in Suzuki-Miyaura cross-coupling reactions. Most notably, [Pd(η²-Dipp-μ-CNArDipp)]₃ exemplifies the ability of sterically encumbering π-acidic isocyanide ligands to stabilize the highly reactive and electron-rich monoligated [Pd(0)L] species.

Further, Pd(CNArDipp²)₂ was employed to probe the coordination chemistry of redox non-innocent ArNO ligands. Remarkably, addition of 2 equiv of PhNO to Pd(CNArDipp²)₂ generated the complex Pd(κ¹-N-PhNO)₂(CNArDipp²)₂, which is the first metal complex containing (η¹-N-PhNO)⁺⁻ units to be structurally characterized. Magnetic susceptibility measurements and broken symmetry calculations confirmed the singlet diradical electronic structure of this complex in the solid state. However, spectroscopic studies indicated that Pd(κ¹-N-PhNO)₂(CNArDipp²)₂ can only be
observed at low temperature in solution. Complexation of two ArNO units to Pd(CNAr$^{\text{Dipp2}}$)$_2$ in solution at room temperature was achieved using $p$-OCH-$C_6H_4$NO. The resulting complex Pd(κ$^1$-$N$-$p$-OCH-$C_6H_4$NO)$_2$(CNAr$^{\text{Dipp2}}$)$_2$ also exhibited paramagnetism in solution, unlike its PhNO derivative. Additional ArNO derivatives of Pd(CNAr$^{\text{Dipp2}}$)$_2$ were isolated and characterized, and the chemistry pertaining to these compounds is discussed.
1.1 Introduction

Low-coordinate, transition metal isocyanide complexes have aroused significant curiosity within our group for their potential to serve as stable models of unsaturated metal carbonyl species. Representative molecules of the latter class include Mo(CO)₄, Ni(CO)₃, and Fe(CO)₄, which are highly reactive and have primarily been studied in the gas phase or in low temperature matrix isolation experiments.¹,² The inherent reactivity of the unsaturated metal carbonyls stems from their low-coordinate, electron-rich nature and has prevented their successful study in the condensed phase. Consequently, definitive structural characterization of the unsaturated metal carbonyls has not been previously accomplished and information pertaining to their reaction chemistry is limited. Thus, obtaining stable and isolable analogues of these molecules can help elucidate their reactivity patterns as well as their structural and electronic properties. This pursuit has ultimately led to the construction of novel low-coordinate transition metal isocyanides, which effectively
function as mimics of the reactive unsaturated metal carbonyls. In this chapter, the historical developments behind this chemistry are outlined, and general strategies towards low-coordinate transition metal isocyanide complexes follow.

1.2 Unsaturated Metal Carbonyls

The chemistry of metal carbonyls was introduced with the discovery of Ni(CO)₄ by Mond and co-workers in 1890. In this report, Ni(CO)₄ was produced by heating metallic Ni between 350 °C and 450 °C under a current of CO gas. Attempts to obtain carbonyl compounds of other metals using this protocol were unsuccessful. Shortly thereafter in 1891, modified methods were employed which presumably resulted in the generation of Fe(CO)₄ and Fe(CO)₅. Since then, metal carbonyls have increasingly become the subject of numerous photochemical, spectroscopic, and synthetic studies. A particular area of interest surrounds the photodissociation of metal carbonyls to generate coordinatively unsaturated species, which are reputedly the active intermediates in various catalytic transformations. For example, Grant and co-workers observed that pulsed-laser irradiation of Fe(CO)₅ catalyzed the isomerization and hydrogenation of olefins, presumably via the generation of Fe(CO)₃ as the active species. Similarly, Yardley and co-workers proposed that laser photolysis of Cr(CO)₆ generated Cr(CO)₃ and Cr(CO)₂ as catalytic intermediates for olefin isomerization. Other reports have established Co₂(CO)₈ as a catalyst precursor for hydroformylation and carbonylation reactions. In these processes, either HCo(CO)₃ or Co(CO)₄ is implicated as the active intermediate.
Unsaturated metal carbonyls have also attracted attention due to their unique coordination properties. Spectroscopic and theoretical studies of the group 6 metal carbonyls, for example, revealed that these species possessed unconventional molecular geometries according to VSEPR and valence-bond models. The transient species Mo(CO)$_4$, Mo(CO)$_3$, and Mo(CO)$_2$, which are generated from the photodissociation of Mo(CO)$_6$, are expected to exhibit square planar (D$_{4h}$), trigonal planar (D$_{3h}$), and linear (C$_{∞v}$) geometries, respectively. Instead, these species were discovered to possess cis-divacant octahedral (C$_{2v}$), trigonal pyramidal (C$_{3v}$), and bent (C$_{2v}$) geometries (Figure 1.1). Other examples include Ni(CO)$_3$ and Fe(CO)$_4$, which are expected to adopt trigonal pyramidal (C$_{3v}$) and tetrahedral (T$_d$) geometries, but were instead reported to display trigonal planar (D$_{3h}$) and distorted tetrahedral (C$_{2v}$) geometries, respectively (Figure 1.1). These geometries were reasoned as a result of maximum π-back donation based on molecular orbital theory predictions and angular overlap methods by Burdett.

The combination of their inherent reactivity with their unusual structural features makes the unsaturated metal carbonyls targets for more detailed study. However, despite the developments within the chemistry of unsaturated metal carbonyls, direct structural, mechanistic and kinetic information pertaining to these species still remains unknown. Much of the difficulty in procuring such data stems from the highly reactive and transient nature of these species. Thus, the necessity exists for stable and isolable analogues of unsaturated metal carbonyls that can be handled and observed in the condensed phase. Due to the isolobal relationship between carbon monoxide (C≡O) and isocyanides (C≡N‒R), the latter species have
been well recognized as appropriate ligand models for carbonyls in transition metal complexes.\textsuperscript{29-32} Both CO and CNR moieties act as $\sigma$-donors through donation of the lone pair on carbon to an empty metal d$\sigma$ orbital, and as $\pi$-acceptors via $\pi$-back donation from a filled metal d$\pi$ orbital to an empty CO or CNR $\pi^*$ orbital. Molecular orbital representations of the M(CO) and M(CNR) fragments illustrate these interactions (Figure 1.2).

**Figure 1.1.** Predicted geometries for select unsaturated metal carbonyl species. Top: Photodissociation of Mo(CO)$_6$ to Mo(CO)$_4$, Mo(CO)$_3$, and Mo(CO)$_2$. Bottom-left: Ni(CO)$_3$. Bottom-right: Fe(CO)$_4$.

**Figure 1.2.** Molecular Orbital representations of the isolobal M(CO) and M(CNR) fragments. In each diagram, only one of the two mutually orthogonal sets of $\pi$ orbitals is shown.
1.3 Transition Metal Isocyanides

These electronic similarities have thus enabled the use of isocyanides as alternative ligands to CO in transition metal complexes. The resultant isocyanide analogues exhibit differing solubility features with structural and spectroscopic attributes that make them appealing models to study. For example, numerous transition metal isocyanides have been structurally characterized by X-ray diffraction, thus providing concrete evidence for their design and formulation. Isocyanide complexes additionally have the advantage of being detected via $^1$H NMR spectroscopy and exhibit strong $\nu_{\text{CN}}$ stretching frequencies in IR spectroscopy. The $\nu_{\text{CN}}$ stretches of terminal isocyanides are generally within the 1900 to 2200 cm$^{-1}$ range, while those of bridging isocyanides appear between 1500 and 1900 cm$^{-1}$. IR spectral data can also help assess the relative $\sigma$-donating and $\pi$-accepting ability of isocyanide ligands within various metal complexes. For example, isocyanides coordinated to metal centers in higher oxidation states serve as $\sigma$-donors. Donation of electron density from the lone pair orbital of the CN $\sigma$ system, which consists of significant antibonding character, induces strengthening of the CN bond. This results in $\nu_{\text{CN}}$ stretches that are higher in energy than those of the uncoordinated isocyanides. Higher energy $\nu_{\text{CN}}$ stretches are also seen in metal complexes containing both isocyanide and CO ligands, due to the lower $\pi$-accepting ability of isocyanides relative to CO. Conversely, isocyanides function as $\pi$-acceptors when coordinated to low valent metal centers. Here, $\pi$-back donation from the metal into an empty CN $\pi^*$ orbital weakens the CN bond, giving rise to lower energy $\nu_{\text{CN}}$ stretches than in the free
isocyanides. Such is also observed in isocyanide complexes containing phosphine ligands, which are better σ-donors than isocyanides.

Several isocyanide analogues of homoleptic, zerrovalent metal carbonyls have been prepared. The first of these complexes was reported in 1950 by Klages and Monkeneyer\textsuperscript{33} and Hieber and Böckley,\textsuperscript{34} who independently prepared Ni(CNPh)\textsubscript{4} from substitution reactions with Ni(CO)\textsubscript{4}. Successful isolations of group 6 isocyanides M(CNPh)\textsubscript{6} (M = Cr, Mo, W) were later achieved by Gray and co-workers.\textsuperscript{35} Previously, Bamford and co-workers had investigated Mo(CNPh)\textsubscript{6} and W(CNPh)\textsubscript{6} as free radical sources to initiate vinyl polymerization.\textsuperscript{36} It was shown that in comparison to their carbonyl counterparts,\textsuperscript{37} the isocyano complexes of Mo and W were more active initiators in the presence of CCl\textsubscript{4} for the polymerization of methyl methacrylate. Isocyano analogues of the hydroformylation and carbonylation precatalyst Co\textsubscript{2}(CO)\textsubscript{8} have also been isolated. The syntheses of Co\textsubscript{2}(CN(2,6-Xyl))\textsubscript{8} and Co\textsubscript{2}(CN\textsuperscript{t}Bu)\textsubscript{8} had been reported around the same time by Yamamoto and Yamazaki\textsuperscript{38,39} and by Green and co-workers,\textsuperscript{40,41} respectively. Interestingly, similar activities were not observed between the isocyanide and carbonyl complexes. For instance, Co\textsubscript{2}(CN(2,6-Xyl))\textsubscript{8} instead served as a catalyst for the oligomerization and co-oligomerization of active methylene compounds with isocyanides.\textsuperscript{42}

The chemistry of homoleptic, zerrovalent transition metal isocyanide complexes indeed holds promise for elucidating the reaction chemistry of metal carbonyls. Yet, despite the developments in the realm of transition metal isocyanide chemistry, examples of homoleptic isocyanide complexes with lower coordination numbers than their carbonyl analogues have remained obscure. The problem stems from the use of
unencumbering isocyanide ligands within these complexes. Thus, sterically tuning the R group of the isocyanides to create more encumbering ligand structures can foster coordinatively unsaturated environments. By exploiting such steric features in conjunction with the π-acidity of isocyanides, we sought to achieve the stabilization of low-coordinate, electron-rich metal centers and thus harness the desired reactivity manifested by the unsaturated metal carbonyls.

1.4 Low-Coordinate Transitional Metal Complexes Supported by \textit{m}-Terphenyl Isocyanides

To construct sterically encumbering isocyanides for our purposes, our group has employed the \textit{m}-terphenyl framework. This ligand structure has garnered much attention particularly by Robinson,\textsuperscript{43-45} Power,\textsuperscript{46-48} and Protasiewicz.\textsuperscript{49-51} Their works have collectively focused on three main \textit{m}-terphenyl variants: Ar\textsuperscript{Mes2} (Ar\textsuperscript{Mes2} = 2,6-(2,4,6-Me\textsubscript{3}C\textsubscript{6}H\textsubscript{2})\textsubscript{2}C\textsubscript{6}H\textsubscript{3}), Ar\textsuperscript{Dipp2} (Ar\textsuperscript{Dipp2} = 2,6-(2,6-(\textsuperscript{i}Pr)\textsubscript{2}C\textsubscript{6}H\textsubscript{2})\textsubscript{2}C\textsubscript{6}H\textsubscript{3}), and Ar\textsuperscript{Tripp2} (Ar\textsuperscript{Tripp2} = 2,6-(2,4,6-(\textsuperscript{i}Pr)\textsubscript{3}C\textsubscript{6}H\textsubscript{2})\textsubscript{2}C\textsubscript{6}H\textsubscript{3}) (Figure 1.3). The space-filling models of their respective coordination complexes illustrate the varying degrees of steric protection offered by each unit around the metal center (Figure 1.3). Apparently, the flanking mesityl (Mes) rings in Ar\textsuperscript{Mes2} provide the least steric protection for the metal center. Increased coverage around the metal center is achieved with the bulkier di-isopropyl phenyl (Dipp) derivative, and even more so with the presence of additional isopropyl units in the tri-isopropyl phenyl (Tripp) derivative. Indeed, steric variations among the \textit{m}-terphenyl frameworks have been shown to affect the coordination geometry of
metal complexes. Power demonstrated the ability an \textit{m}-terphenyl with increased steric pressure, 3,5-\textit{i}Pr\textsubscript{2}-Ar\textit{Tripp}\textsuperscript{2}, to stabilize two-coordinate Cr(I) monomers\textsuperscript{52,53} whereas the less encumbering Ar\textit{Dipp}\textsuperscript{2} enabled the formation of a dinuclear Cr complex with fivefold bonding between the two metal centers (Figure 1.4)\textsuperscript{47}.

**Figure 1.3.** Top: Substituted \textit{m}-terphenyl frameworks shown in order of increasing steric bulk from left to right: Ar\textit{Mes}\textsuperscript{2}, Ar\textit{Dipp}\textsuperscript{2}, and Ar\textit{Tripp}\textsuperscript{2}. Bottom: Space-filling models of the \textit{m}-terphenyl units coordinated to metal centers (blue).

**Figure 1.4.** Cr complexes supported by the \textit{m}-terphenyl ligands Ar\textit{Dipp}\textsuperscript{2} and 3,5-\textit{i}Pr\textsubscript{2}-Ar\textit{Tripp}\textsuperscript{2}. Adapted from references 48, 52, and 53.

The chemistry of the \textit{m}-terphenyl framework is not just limited to the \textit{\sigma}\textsubscript{aryl}s described above. Various \textit{m}-terphenyls functionalized at the C\textsubscript{ipso} on the central ring have been utilized as supporting ligands for transition metal complexes, including
amido,\textsuperscript{54} aryloxide,\textsuperscript{55,56} carboxylate,\textsuperscript{57-60} and imido,\textsuperscript{61,62} and $\alpha$-ketocarboxylate\textsuperscript{63} derivatives. Meanwhile, there have only been three reports of $m$-terphenyl isocyanides as supporting ligands for transition metal complexes prior to the time our group had begun exploring this chemistry. Nagashima and co-workers employed $m$-terphenyl isocyanides as ancillary groups in the Ni-catalyzed polymerization of ethylene,\textsuperscript{64} while Ito and Sawamura explored their use in Rh-catalyzed hydrosilylation of ketones.\textsuperscript{65,66} However, these reports did not provide definitive structural data of the presumed metal isocyanide species.

Pursuit of $m$-terphenyl isocyanide chemistry within our group began with the synthesis, isolation, and characterization of the bis-mesityl $m$-terphenyl isocyanide $\text{CNAr}^\text{Mes2}$. In 2008, we reported its use as a sterically encumbering support for monovalent Cu centers.\textsuperscript{67} Inspired by previous reports of $X\text{Cu(CNR)}_n$ ($X$ = halide or pseudohalide) species containing sterically unencumbering isocyanides,\textsuperscript{68,69} initial studies within our group were intended to demonstrate the ability of $m$-terphenyl isocyanides to promote low-coordination geometries. Indeed, treatment of CuCl with 2 equiv of $\text{CNAr}^\text{Mes2}$ generated the three-coordinate, bis-isocyanide complex $\text{ClCu(CNAr}^\text{Mes2})_2$ (Scheme 1.1).\textsuperscript{67} Prior to this, the only other monomeric bis-isocyanide Cu(I) halide complex that had been structurally characterized was $\text{ClCu(CN}^{t\text{Bu}})_2$.\textsuperscript{70} Most of the other structurally characterized Cu bis-isocyanide complexes were shown to exist as bridging halide dimers.\textsuperscript{71,72} It is thus evident that the $\text{CNAr}^\text{Mes2}$ ligand provides enough steric protection to prevent the formation of multinuclear Cu complexes.
Scheme 1.1. Synthesis of $\text{ClCu(CNAr}^{\text{Mes2}}\text{)}_2$.

The more encumbering $\text{CNA}^{\text{Dipp2}}$ ligand was subsequently reported in 2009 and its ligation properties were compared to that of the $\text{CNA}^{\text{Mes2}}$ ligand. This study featured Cu(I), Ag(I), and Mo(0) centers as coordination platforms from which the relative steric pressures enforced by the isocyanide ligands could be evaluated. Crystallographic characterization of the resultant complexes revealed that tris-isocyanide formation was readily achieved with $\text{CNA}^{\text{Mes2}}$ but not with $\text{CNA}^{\text{Dipp2}}$. Several representative complexes are depicted in Figure 1.5. In the example of Cu(I), treatment of $(\text{C}_6\text{H}_6)\text{[CuOTf]}_2$ with 3 equiv of $\text{CNA}^{\text{Mes2}}$ in THF afforded the tris-isocyanide salt $\text{[(THF)Cu(CNA}^{\text{Mes2}}\text{)}_3\text{]OTf}$ (Figure 1.5, 1a). The analogous reaction using $\text{CNA}^{\text{Dipp2}}$ generated the bis-isocyanide salt $\text{[(THF)\text{2Cu(CNA}^{\text{Dipp2}}\text{)}_2\text{]OTf}$ (Figure 1.5, 1b), which resisted binding of a third isocyanide ligand. Similar ligation patterns were observed in reactions with Ag(I). It was initially thought that the relatively larger Group 11 congener could accommodate three $\text{CNA}^{\text{Dipp2}}$ ligands. Instead, treatment of AgOTf with the $\text{CNA}^{\text{Mes2}}$ and $\text{CNA}^{\text{Dipp2}}$ units produced the tris-isocyanide salt $\text{[(Et}_2\text{O)Ag(CNA}^{\text{Mes2}}\text{)}_3\text{]OTf}$ (Figure 1.5, 2a) and the bis-isocyanide complex ($\kappa^2$-TfO)$\text{Ag(CNA}^{\text{Dipp2}}\text{)}_2$ (Figure 1.5, 2b), respectively. Lastly, zerovalent Mo centers were also prone to this behavior towards the $m$-terphenyl isocyanides, as exemplified
by the formation of \textit{fac-Mo(CO)}_3(CNAr^{Mes2})_3 (Figure 1.5, 3a) and \textit{trans-Mo(CO)}_4(CNAr^{Dipp2})_2 (Figure 1.5, 3b). In all cases, complexes already containing two CNAr^{Dipp2} ligands were unable to accommodate a third. It is therefore apparent that CNAr^{Dipp2} creates a more sterically congested environment around metal centers.

Further, the \textit{m}-terphenyl isocyanide ligands provided access to low-coordinate complexes that structurally mimic unsaturated metal carbonyl species. For instance, one of the goals was to generate a zerovalent Ni tris-isocyanide complex (Ni(CNR)_3) which would serve as an analogue to the elusive Ni(CO)_3. Interest in the latter species is born from its presumed role as the active intermediate in reactions mediated by Ni(CO)_4. Complexes of the type Ni(CNR)_4 do indeed exist and are also proposed to generate reactive three-coordinate species (Ni(CNR)_3) in solution. Like their zerovalent tri-carbonyl counterparts, Ni(CNR)_3 species have thus far not been isolated.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Cu(I), Ag(I), and Mo(0) complexes [(THF)Cu(CNAr^{Mes2})_3]OTf (1a), [(THF)_2Cu(CNAr^{Dipp2})_2]OTf (1b), [(Et_2O)Ag(CNAr^{Mes2})_3]OTf (2a), (κ^2-TfO)Ag(CNAr^{Dipp2})_2 (2b), \textit{fac-Mo(CO)}_3(CNAr^{Mes2})_3 (3a), and \textit{trans-Mo(CO)}_4(CNAr^{Dipp2})_2 (3b).}
\end{figure}
or experimentally confirmed. Accordingly, the tris-isocyanide complex \( \text{Ni(CNAr}^{\text{Mes2}})_{3} \) was cleanly achieved through a synthesis in which Tl(I) was utilized as a coordination site protecting agent for the Ni center.\(^{79}\) Crystallographic characterization of \( \text{Ni(CNAr}^{\text{Mes2}})_{3} \) revealed a trigonal planar (D\(_{3h}\)) coordination geometry, which is consistent with the predicted geometry for \( \text{Ni(CO)}_{3} \) (Figure 1.6).\(^{24,25,28}\) Surprisingly, a Ni tris-isocyanide complex \( \text{Ni(CNAr}^{\text{Dipp2}})_{3} \) was also obtained with the CNAr\(^{\text{Dipp2}}\) ligand. Structural characterization of \( \text{Ni(CNAr}^{\text{Dipp2}})_{3} \) likewise featured a trigonal planar coordination geometry about the metal center (Figure 1.6).\(^{80}\) Based on the ability of CNAr\(^{\text{Dipp2}}\) to prevent binding of a third isocyanide ligand on the Cu(I), Ag(I), and Mo(0) platforms, the formation of \( \text{Ni(CNAr}^{\text{Dipp2}})_{3} \) seemed anomalous. However, the steric protection provided by the CNAr\(^{\text{Dipp2}}\) ligand was similar to that observed in the previous examples. \( \text{Ni(CNAr}^{\text{Dipp2}})_{3} \) was unable to accommodate a fourth isocyanide ligand, whereas its dimesityl derivative \( \text{Ni(CNAr}^{\text{Mes2}})_{3} \) added an extra equivalent of CNAr\(^{\text{Mes2}}\) to form the tetrakis-isocyanide complex \( \text{Ni(CNAr}^{\text{Mes2}})_{4} \) (Scheme 1.2).\(^{79}\)

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**Figure 1.6.** Homoleptic zerovalent tris-isocyanide Ni complexes \( \text{Ni(CNAr}^{\text{Mes2}})_{3} \) and \( \text{Ni(CNAr}^{\text{Dipp2}})_{3} \).
Scheme 1.2. Addition of CNAr\textsuperscript{Mes2} to Ni(CNAr\textsuperscript{Mes2})\textsubscript{3} to generate Ni(CNAr\textsuperscript{Mes2})\textsubscript{4}.

The increased steric protection achieved by the CNAr\textsuperscript{Dipp2} ligand with respect to the less encumbering CNAr\textsuperscript{Mes2} derivative is indeed evident. More notably, analogues of the elusive Ni(CO)\textsubscript{3} species were successfully isolated using the sterically encumbering m-terphenyl isocyanides. These developments prompted us to explore other group 10 metal platforms from which to construct homoleptic, low-coordinate zerovalent isocyanide complexes. In particular, we were interested in preparing a reactive two-coordinate bis-isocyanide complex of zerovalent Pd to serve as a model of the binary carbonyl Pd(CO)\textsubscript{2}. Like other binary Pd(0) carbonyls, Pd(CO)\textsubscript{2} is a highly unstable species which has primarily been observed in the gas phase and matrix isolation techniques.\textsuperscript{81} Similarly, the chemistry of their homoleptic Pd(0) isocyanide counterparts (Pd(CNR)\textsubscript{n}) has thus far remained undeveloped. We therefore envisioned that the steric and \pi-acidic properties of CNAr\textsuperscript{Dipp2} would provide access to stable low-coordinate, electron-rich binary Pd(0) isocyanides. Moreover, the pursuit of a two-coordinate binary Pd(0) isocyanide complex as an analogue to Pd(CO)\textsubscript{2} would open up new opportunities for catalysis and substrate activation chemistry. The chemistry of Pd(CNAr\textsuperscript{Dipp2})\textsubscript{2} and other novel Pd complexes supported by the CNAr\textsuperscript{Dipp2} ligand is accordingly described in the following chapters.
1.5 References


Chapter 2

Synthesis and Reactivity of an Isolable Homoleptic Palladium(0) Bis-Isocyanide Monomer

2.1 Introduction

The chemistry of homoleptic zerovalent isocyanide complexes of the group 10 metals dates back to the preparation of Ni(CNPh)₄ in 1950 by Klages and Monkemeyer¹ and by Hieber and Böckley.² Ni(CNPh)₄ was initially generated from a substitution reaction between Ni(CO)₄ and phenylisocyanide. Since then, various strategies to obtain homoleptic isocyanide complexes of transition metals in the zerovalent state have been presented.³ In the context of the group 10 metals, numerous methods towards zerovalent isocyanide complexes have been described for Ni. This included an alternative synthesis for Ni(CNPh)₄ from nickelocene and phenylisocyanide reported by Behrens and Meyer.⁴ Other zerovalent [Ni(CNR)ₙ] derivatives were generated from the disproportionation of Bellucci’s salt, K₄[Ni₂(CN)₆], in the presence of isocyanides.⁵ Structural evidence for these supposed monomeric species was not published until 2004 by Hahn and co-workers,⁶ who reported the first crystallographically characterized zerovalent tetrakis-isocyanide
complexes Ni(CNR)$_4$ (R = Ph, 2,6-Xyl, C$_6$H$_4$-2-NO$_2$).

However, previous synthetic strategies towards zerovalent, coordinatively unsaturated, mononuclear group 10 metal isocyanides were unsuccessful. Preparations employing 2:1 molar ratios of isocyanide to metal generated products which were initially presumed to have the empirical formulation “M(CNR)$_2$”. Interestingly, structural data instead revealed the formation of multinuclear complexes as exemplified by Ni$_4$(CN$_{tBu}$)$_7$[7,8] and the triangulo-Pt$_3$ complex [Pt$_3$(μ-CN$_{tBu}$)$_3$(CN$_{tBu}$)$_3$]$_9$ (Figure 2.1). The isolation of the latter from Pt(COD)$_2$ and 2 equiv of tBuNC led the authors to conclude that similar reactions formed other trinuclear derivatives of the type [Pt$_3$(CNR)$_6$] (R = Me, Et, Cy).$^9$ Analogous attempts to isolate the presumed bis-isocyanide “Pd(CNR)$_2$” (R = Ph, p-Tol, C$_6$H$_4$-4-OMe, Cy, tPr) species were reported by Malatesta$^{10,11}$ and Fischer and Werner.$^{12}$ Additionally, Otsuka and co-workers$^{13}$ had observed the formation of peroxo compounds M(O$_2$)(CNR)$_2$ (M = Ni, Pd) when the corresponding zerovalent isocyanide precursors were exposed to air. While this implicated the existence of monomeric Pd(0) isocyanide complexes, structural evidence for such species was still lacking.

Based on the previous observations made in the cases of Ni and Pt, subsequent proposals increasingly favored the formation of trinuclear Pd isocyanide clusters.$^{14,15}$ Concrete evidence for these complexes was first presented by Francis and co-workers in 1984 with the crystallographic characterization of triangulo-[Pd(μ-CNCy)(CNCy)]$_3$ (Figure 2.1).$^{16}$ This complex features terminal and bridging isocyanide ligands on each metal center, in analogy to the previously observed trimeric Pt isocyanides. In all
cases, the use of unencumbering isocyanides to support these metal centers likely encourages aggregation of the reduced fragments to higher nuclearity clusters.

![Group 10 "M(CNR)\textsubscript{2}" Complexes](image)

**Figure 2.1.** Multinuclear complexes of the group 10 metals supported by unencumbering isocyanides. Adapted from references 7-9 and 16.

Herein we report the isolation of a monomeric, coordinatively unsaturated isocyanide complex of Pd(0) utilizing the sterically encumbering \(m\)-terphenyl CNA\textsubscript{ArDipp}\textsuperscript{2} ligand. As demonstrated in the previous chapter, the combined \(\pi\)-acidic and steric properties of the CNA\textsubscript{ArDipp}\textsuperscript{2} ligand stabilized an electron-rich, coordinatively unsaturated tris-isocyanide compound, Ni(CNA\textsubscript{ArDipp}\textsuperscript{2})\textsubscript{3},\textsuperscript{17} as an analogue to Ni(CO)\textsubscript{3}. Accordingly, we reasoned that CNA\textsubscript{ArDipp}\textsuperscript{2} would unlock the gateway to a two-coordinate isocyano analogue of the elusive Pd(CO)\textsubscript{2}\textsuperscript{18} species. Further, we were interested to explore the \(\pi\)-acidic CNA\textsubscript{ArDipp}\textsuperscript{2} ligand as a counterpoint to the well studied \(\sigma\)-donating phosphine (PR\textsubscript{3})\textsuperscript{19,20} and N-heterocyclic carbene (NHC)\textsuperscript{21-25} ligands for the stabilization of zerovalent PdL\textsubscript{2}.
2.2 Synthesis and Characterization of Pd(CNAr\textsuperscript{Dipp})\textsubscript{2} (2)

Treatment of PdCl\textsubscript{2}(COD) (COD = 1,5-cyclooctadiene) in THF with 2.0 equiv of CNAr\textsuperscript{Dipp} generated trans-PdCl\textsubscript{2}(CNAr\textsuperscript{Dipp})\textsubscript{2} (1, Scheme 2.1), which was isolated and structurally characterized by X-ray diffraction (Figure 2.2). Reduction of trans-PdCl\textsubscript{2}(CNAr\textsuperscript{Dipp})\textsubscript{2} (1) with excess Mg\textsuperscript{0} in an Et\textsubscript{2}O/THF mixture afforded Pd(CNAr\textsuperscript{Dipp})\textsubscript{2} (2, Scheme 2.1). While X-ray diffraction confirmed the monomeric nature of Pd(CNAr\textsuperscript{Dipp})\textsubscript{2} (2) (Figure 2.3), spectroscopic data provided evidence for its zerovalent state. First, features pertaining to a hydride moiety are absent in the \textsuperscript{1}H NMR and IR spectra of Pd(CNAr\textsuperscript{Dipp})\textsubscript{2} (2). Furthermore, the $\nu_{CN}$ stretches of Pd(CNAr\textsuperscript{Dipp})\textsubscript{2} (2) (2073 and 2011 cm\textsuperscript{-1}, KBr) are significantly lower in energy than that of its divalent precursor trans-PdCl\textsubscript{2}(CNAr\textsuperscript{Dipp})\textsubscript{2} (1) (2202 cm\textsuperscript{-1}, KBr). This is consistent with considerable $\pi$-back donation to the isocyanide ligands in Pd(CNAr\textsuperscript{Dipp})\textsubscript{2} (2). Other noteworthy features include the relatively shorter average

\[
\text{Scheme 2.1. Synthesis of PdCl}_2(\text{CNAr}^{\text{Dipp}})_2 \ (1) \text{ and } \text{Pd(CNAr}^{\text{Dipp}})_2 \ (2).
\]
Figure 2.2. Molecular structure of one crystallographically independent molecule of PdCl₂(CNArDipp₂)₂ (1). Selected bond distances (Å) and angles (°): Pd1–C1 = 1.977(3); Pd1–C2 = 1.978(3); Pd1–Cl₁ = 2.2996(10); Pd1–Cl₂ = 2.29866(10); C₁–Pd₁–C₂ = 179.09(12); Cl₁–Pd₁–Cl₂ = 179.45(3).

Figure 2.3. Molecular structure of Pd(CNArDipp₂)₂ (2). Selected bond distances (Å) and angles (°): Pd₁–C₁ = 1.928(4); Pd₁–C₂ = 1.932(4); C₁–Pd₁–C₂ = 169.81(16); C₁–N₁–C₃ = 163.6(4); C₂–N₂–C₄ = 174.1(4).

Pd–C iso bond distances crystallographically observed in Pd(CNArDipp₂)₂ (2) (1.930(3) Å av) compared to those in trans-PdCl₂(CNArDipp₂)₂ (1) (1.976(2) Å av). These also demonstrate π-back donation in Pd(CNArDipp₂)₂ (2). In contrast, zerovalent metal complexes containing σ-donating ligands exhibit M–L bond distances that are longer...
than those of their corresponding divalent derivatives. Bending of the C‒N‒C angle is indeed observed for one of the isocyanide ligands (∠(C1–N1–C3) = 163.6(4)°), yet it is interesting to note that the C‒N‒C angle for the other CNAr\textsuperscript{Dipp}\textsubscript{2} stays almost linear (∠(C2–N2–C4) = 174.1(4)°).

DFT calculations were conducted on the model compound Pd(CNAr\textsuperscript{Ph}\textsubscript{2})\textsubscript{2} to illustrate the expected π-back bonding interactions between Pd and the CNAr\textsuperscript{Dipp}\textsubscript{2} ligands. The computational model Pd(CNAr\textsuperscript{Ph}\textsubscript{2})\textsubscript{2} differs from Pd(CNAr\textsuperscript{Dipp}\textsubscript{2})\textsubscript{2} (2) by the absence of the isopropyl substituents on the flanking aryl rings (Figure 2.4). Small differences between the key structural parameters of Pd(CNAr\textsuperscript{Ph}\textsubscript{2})\textsubscript{2} and Pd(CNAr\textsuperscript{Dipp}\textsubscript{2})\textsubscript{2} (2) listed in Table 2.1 indicate that Pd(CNAr\textsuperscript{Ph}\textsubscript{2})\textsubscript{2} serves as a sufficient computational model. The Molecular Orbitals of Pd(CNAr\textsuperscript{Ph}\textsubscript{2})\textsubscript{2} in Figure 2.5 depict two mutually orthogonal π-back bonding interactions (HOMO-3 and HOMO-4), and is indicative of significant π-back donation in Pd(CNAr\textsuperscript{Dipp}\textsubscript{2})\textsubscript{2} (2).

Figure 2.4. Optimized geometry of the computational model Pd(CNAr\textsuperscript{Ph}\textsubscript{2})\textsubscript{2}.
Table 2.1. Comparison of Computational vs. Experimental Structures for Pd(CNAr\text{Ph}_2)\textsubscript{2} and Pd(CNAr\text{Dipp}_2)\textsubscript{2} (2)

<table>
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<tr>
<th>Parameter/Complex</th>
<th>Pd(CNAr\text{Ph}_2)\textsubscript{2} Calc</th>
<th>Pd(CNAr\text{Dipp}_2)\textsubscript{2} Xray</th>
<th>% Difference</th>
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<tr>
<td>d(Pd–C\textsubscript{iso})</td>
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<td>1.930(3) Å av</td>
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<td>∠(C1–Pd–C2)</td>
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<td>169.81(16)°</td>
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<tr>
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<td>163.6(4)°</td>
<td>2.5</td>
</tr>
<tr>
<td>∠(C2–N1–C4)</td>
<td>178.2°</td>
<td>174.1(4)°</td>
<td>2.4</td>
</tr>
</tbody>
</table>

Figure 2.5. Molecular Orbitals of Pd(CNAr\text{Ph}_2)\textsubscript{2} depicting its d-orbital splitting diagram and Pd–CNR π back-bonding interactions.
The $\pi$-acidic CNAr$^{\text{Dipp2}}$ ligands impart considerable thermal and kinetic stability to Pd(CNAr$^{\text{Dipp2}}$)$_2$ (2) in solution. For example, $^1$H NMR monitoring of a solution of Pd(CNAr$^{\text{Dipp2}}$)$_2$ (2) in C$_6$D$_6$ heated at 80 °C shows no decomposition within 5 d. Additionally, the CNAr$^{\text{Dipp2}}$ ligands provide enough steric protection to maintain a coordinatively unsaturated environment about the metal center. FTIR spectroscopy reveals that an equimolar mixture of Pd(CNAr$^{\text{Dipp2}}$)$_2$ (2) and CNAr$^{\text{Dipp2}}$ in C$_6$D$_6$ at room temperature does not produce a Pd tris-isocyanide complex (Figure 2.6). Further, the $^1$H NMR spectrum of this mixture displays broadened signals (2.64 and 1.24 ppm) indicating fast isocyanide ligand exchange at room temperature (Figure 2.7). The $^1$H NMR spectra of Pd(CNAr$^{\text{Dipp2}}$)$_2$ (2) and CNAr$^{\text{Dipp2}}$ in C$_6$D$_6$ are both shown separately for reference (Figure 2.8). Variable temperature studies in toluene-$d_8$ further illustrate that this exchange is still rapid on the $^1$H NMR time scale, even at increasingly lower temperatures (Figure 2.9). Decoalescence of the signals begins to

Figure 2.6. FTIR spectrum of a 1:1 Pd(CNAr$^{\text{Dipp2}}$)$_2$/CNAr$^{\text{Dipp2}}$ mixture in C$_6$D$_6$ (NaCl windows).
Figure 2.7. $^1$H NMR (400 MHz) spectrum of a 1:1 Pd(CNArDipp$^2$)$_2$/CNArDipp$^2$ mixture in C$_6$D$_6$.

Figure 2.8. $^1$H NMR (400 MHz) spectra of Pd(CNArDipp$^2$)$_2$ (top) and CNArDipp$^2$ (bottom) in C$_6$D$_6$. 
occur near −40 °C, yet the signals remain relatively broadened even down to −80 °C (Figure 2.9). It is worth mentioning that while the formation of a tris-isocyanide species at lower temperatures cannot be completely dismissed, our studies concern the reactivity of Pd(CNArDipp2)2 (2) at ambient conditions.

![Diagram](image)

**Figure 2.9.** VT-NMR stacked plot (aliphatic region) for a 1:1 Pd(CNArDipp2)2/CNArDipp2 mixture in toluene-d8.

### 2.3 Reactivity of Pd(CNArDipp2)2 (2) Towards Small Molecule Substrates

The low-coordinate, electron-rich nature of Pd(CNArDipp2)2 (2) renders it reactive towards a variety of small molecules and electronically unsaturated substrates. For example, Pd(CNArDipp2)2 (2) is readily oxidized by 1 equiv of I2 in Et2O to provide divalent trans-PdI2(CNArDipp2)2 (3, Scheme 2.2). The molecular structure of trans-PdI2(CNArDipp2)2 (3) is shown in Figure 2.10. Similar to its dichloride derivative trans-PdCl2(CNArDipp2)2 (1), the diiodide trans-PdI2(CNArDipp2)2 (3) exhibits a higher
Scheme 2.2. Reaction pinwheel for Pd(CNAr$^{Dipp^2}$)$_2$ with I$_2$, MeOTf, TIOTf, and organic halides.

Figure 2.10. Molecular structure of one crystallographically independent molecule of Pd$_2$(CNAr$^{Dipp^2}$)$_2$ (3). Selected bond distances (Å) and angles (°): Pd1–C1 = 1.971(4); Pd1–C2 = 1.972(4); Pd1–I1 = 2.5948(6); Pd1–I2 = 2.5972(6); C1–Pd1–C2 = 179.12(19); I1–Pd1–I2 = 179.171(18).
energy $v_{CN}$ stretch (2184 cm$^{-1}$, KBr) and relatively longer Pd–C$_{iso}$ bond distances (1.971(1) Å av), demonstrating decreased π-back donation to the isocyanide ligands. Pd(CNAr$^{Dipp^2}$)$_2$ (2) also readily reacts with electrophilic substrates. As analyzed by $^1$H NMR spectroscopy, treatment of Pd(CNAr$^{Dipp^2}$)$_2$ (2) with MeOTf in C$_6$H$_6$ generates an unstable species, which gradually converts to a new product. Signals corresponding to two chemically inequivalent CNAr$^{Dipp^2}$ ligands were observed in the $^1$H NMR spectrum of the latter, indicative of molecular asymmetry. Crystallographic characterization of this product, after dissolution in THF, revealed formation of the iminoacyl complex [(THF)Pd($\eta^{2}$-C$_N$-(MeC=NAr$^{Dipp^2}$)(CNAr$^{Dipp^2}$))OTf (4, Figure 2.11). Based on the known ability of L$_n$M(R)(CNR') species to undergo migratory insertion to form iminoacyl complexes,$^{26}$ the unstable precursor formed immediately upon addition of MeOTf to Pd(CNAr$^{Dipp^2}$)$_2$ (2) is likely a species with the formulation

![Figure 2.11. Molecular structure of [(THF)Pd($\eta^{2}$-C$_N$-(MeC=NAr$^{Dipp^2}$)(CNAr$^{Dipp^2}$))OTf (4). Selected bond distances (Å) and angles (°): Pd1–C1 = 1.961(3); Pd1–C2 = 1.931(3); Pd1–N2 = 2.123(2); Pd1–O1 = 2.1652(18); C1–Pd1–C2 = 107.57(11); C1–Pd1–N2 = 142.77(9); C1–Pd1–O1 = 95.93(9); N2–Pd1–O1 = 121.24(7); C2–N2–C34 = 138.9(2).](image-url)
Conversion to the iminoacyl [(THF)Pd(η²-C,N-(MeC=NArDipp²)(CNArDipp²))OTf (4) still occurred under typical low temperature crystallization conditions (−35 °C) and has precluded isolation of presumed intermediate 5 thus far.

Treatment of Pd(CNArDipp²)₂ (2) with 1 equiv of the Lewis-acidic substrate TlOTf generated the Lewis acid-base adduct [TlPd(CNArDipp²)₂]OTf (6, Scheme 2.2). The molecular structure of [TlPd(CNArDipp²)₂]OTf (6) depicts a one-coordinate Tl(I) center directly bound to Pd with a Pd–Tl separation of 2.8551(12) Å (Figure 2.12). Pd(0)–Tl(I) distances of 2.7914(6) and 2.7678(6) Å have been reported by Catalano in zerovalent Pd metallocryptands encapsulating Tl(I) ions.²⁷ These complexes were considered to exhibit strong Pd(0)–Tl(I) interactions based on their proximity in value to the sum of the Pd–Tl covalent radii (2.76 Å).²⁷ The relatively longer Pd–Tl distance in [TlPd(CNArDipp²)₂]OTf (6) suggests a dative interaction between the Lewis basic Pd

![Figure 2.12. Molecular structure of [TlPd(CNArDipp²)₂]OTf (6). Selected bond distances (Å) and angles (°): Pd1–Tl1 = 2.8551(12); Pd1–C1 = 1.962(7); Pd1–C2 = 1.940(8); Tl1–O1 = 2.825; Tl1–O2 = 3.024; C1–Pd1–C2 = 163.3(3); C1–Pd1–Tl1 = 97.34(16); C2–Pd1–Tl1 = 94.78(18).]
center and Tl(I) ion. Donation of electron density to Tl(I) seemingly results in fairly decreased \( \pi \)-back donation to the isocyanide ligands. This is evident in the higher energy \( \nu_{CN} \) stretch (2107 cm\(^{-1}\)) and moderately longer Pd–C\(_{iso}\) bond distances (1.951(15) Å av) in \([\text{TIPd(CNAr}^{\text{Dipp2}})_{2}]\text{OTf}\) (6) compared to those in Pd(CNAr\(^{\text{Dipp2}}\))\(_2\) (2). Additionally, very slight bending is observed for the CNAr\(^{\text{Dipp2}}\) ligands (\( \angle(C1–N1–C4) = 171.1(5)^\circ \), \( \angle(C2–N2–C7) = 167.5(5)^\circ \)) in \([\text{TIPd(CNAr}^{\text{Dipp2}})_{2}]\text{OTf}\) (6). While these data indicate the presence of an oxidized Pd center in \([\text{TIPd(CNAr}^{\text{Dipp2}})_{2}]\text{OTf}\) (6), the dative interaction to the Tl(I) ion does not affect the formal oxidation state of the metal. This is demonstrated by the normalized Pd K-edge XAS of PdCl\(_2\)(CNAr\(^{\text{Dipp2}}\))\(_2\) (1), Pd(CNAr\(^{\text{Dipp2}}\))\(_2\) (2), and \([\text{TIPd(CNAr}^{\text{Dipp2}})_{2}]\text{OTf}\) (6) (Figure 2.13). Indeed, the Pd K-edge energies of Pd(CNAr\(^{\text{Dipp2}}\))\(_2\) (2) (24343.2 eV) and \([\text{TIPd(CNAr}^{\text{Dipp2}})_{2}]\text{OTf}\) (6) (24343.3 eV) are similar, confirming a Pd oxidation state of zero for the latter complex. For comparison, the rising edge energy of divalent PdCl\(_2\)(CNAr\(^{\text{Dipp2}}\))\(_2\) (1) is \(~3\) eV higher in energy (24346.5 eV), consistent with a 2 unit increase in oxidation state.

### 2.4 Oxidative Addition of Organic Halides to Pd(CNAr\(^{\text{Dipp2}}\))\(_2\) (2)

As expected, Pd(CNAr\(^{\text{Dipp2}}\))\(_2\) (2) is also active towards oxidative addition of C–Cl and C–Br bonds. Reactions of Pd(CNAr\(^{\text{Dipp2}}\))\(_2\) (2) with benzyl chloride and MesBr in Et\(_2\)O afforded \( \text{trans-PdCl(Bz)}(\text{CNAr}^{\text{Dipp2}})_{2} \) (7) (Bz = benzyl) (Figure 2.14) and \( \text{trans-PdBr(Mes)}(\text{CNAr}^{\text{Dipp2}})_{2} \) (8) (Figure 2.15), respectively (Scheme 2.2).
Interestingly, trans-PdBr(Mes)(CNAr\textsuperscript{Dipp\textsubscript{2}}\textsubscript{2}) (8) remains stable in solution at room temperature over several days and is resistant toward migratory insertion processes even up to 80 °C. Such stability is noteworthy because divalent group 10 metal complexes are known to form iminoacyls via migratory insertion to isocyanides.\textsuperscript{28-30} This suggested that Pd(CNAr\textsuperscript{Dipp\textsubscript{2}}\textsubscript{2}) (2) could serve as a catalyst precursor for organic cross-coupling reactions involving aryl bromides. While σ-donating PR\textsubscript{3} and NHC units, which are considered to facilitate the rate of oxidative addition, have typically been employed as supporting groups in Pd-catalyzed cross-coupling transformations,\textsuperscript{19,23-25,31} π-acidic ligands have thus far received limited attention.
Figure 2.14. Molecular structure of PdCl(Bz)(CNAr\textsuperscript{Dipp2})\textsubscript{2} (7). Selected bond distances (Å) and angles (°): Pd1–C1 = 1.976(4); Pd1–C2 = 1.993(3); Pd1–C3 = 2.088(3); Pd1–Cl1 = 2.3914(10); C1–Pd1–C2 = 167.17(15); C3–Pd1–Cl1 = 173.48(12).

Figure 2.15. Molecular structure of PdBr(Mes)(CNAr\textsuperscript{Dipp2})\textsubscript{2} (8). Selected bond distances (Å) and angles (°): Pd1–C1 = 1.946(3); Pd1–C2 = 1.973(3); Pd1–C5 = 2.025(3); Pd1–Br1 = 2.5069(4); C1–Pd1–C2 = 169.35(12); C5–Pd1–Br1 = 176.10(9).

Since monocoordinated Pd(0)L species are presumably the active catalysts in organic cross-coupling reactions,\textsuperscript{32} we reasoned that CNAr\textsuperscript{Dipp2} could stabilize such a low-coordinate, electron-rich intermediate. The catalytic competency of
Pd(CNArDipp)\textsubscript{2} (2) was accordingly investigated in the Suzuki-Miyaura cross-coupling reaction.\textsuperscript{33-35} This was chosen as our experimental platform for its tolerance to a wide variety of functional groups, its use of organoboron reagents, which are widely available and convenient to handle, its ability to proceed under mild conditions, and its relatively non-toxic workup. Preliminary experiments showed that 5 mol % of Pd(CNArDipp)\textsubscript{2} (2) catalyzed the cross-coupling of MesBr with phenyl boronic acid (PhB(OH)\textsubscript{2}) using K\textsubscript{3}PO\textsubscript{4} as base in THF within 8 h at room temperature to produce 2,4,6-trimethylbiphenyl in 94 % isolated yield (Scheme 2.3). Similarly, cross-coupling between 2-bromotoluene and PhB(OH)\textsubscript{2} generated 2-methylbiphenyl in 95 % isolated yield (Scheme 2.3). Continued studies of the cross-coupling chemistry involving Pd(CNArDipp)\textsubscript{2} (2) are discussed further in Chapter 3.

Scheme 2.3. Preliminary Suzuki-Miyaura cross-coupling reactions mediated by 5 mol % Pd(CNArDipp)\textsubscript{2} (2) at room temperature.
2.5 Bond Reduction in Electronically Unsaturated Substrates

The reactions between Pd(CNAr\textsubscript{Dipp\textsuperscript{2}})\textsubscript{2} (2) and electronically unsaturated substrates E=E' resulted in adducts featuring bond reduction of the latter substrates. Addition of 1 equiv of O\textsubscript{2} to Pd(CNAr\textsubscript{Dipp\textsuperscript{2}})\textsubscript{2} (2) in THF at $-78 \degree C$ generated the peroxo complex Pd($\eta^2$-O\textsubscript{2})(CNAr\textsubscript{Dipp\textsuperscript{2}})\textsubscript{2} (9, Scheme 2.4). Unsaturated Pd(0)L\textsubscript{2} complexes are known to react with dioxygen to produce Pd($\eta^2$-O\textsubscript{2})L\textsubscript{2} complexes as demonstrated by Otsuka\textsuperscript{36}, Stahl\textsuperscript{37,38} and Nolan\textsuperscript{39,40}. Similar to other structurally characterized $\eta^2$-peroxo Pd(II) complexes\textsuperscript{36-38}, Pd($\eta^2$-O\textsubscript{2})(CNAr\textsubscript{Dipp\textsuperscript{2}})\textsubscript{2} (9) features a

Scheme 2.4. Reaction pinwheel for Pd(CNAr\textsubscript{Dipp\textsuperscript{2}})\textsubscript{2} with electronically unsaturated substrates.
Figure 2.16. Molecular structure of Pd(\(\eta^2\)-O\(_2\))(CNAr\(^{Dipp}\))\(_2\) (9). Selected bond distances (Å) and angles (°): Pd1–C1 = 1.980(4); Pd–C2 = 1.98(4); Pd1–O1 = 1.987(3); Pd1–O2 = 1.978(3); O1–O2 = 1.415(4); C1–Pd1–C2 = 101.20(18); O1–Pd1–C1 = 110.85(14); O2–Pd1–C2 = 106.15(16); C1–N1–C37 = 169.7(4); C2–N2–C3 = 168.9(4).

Side-on coordinated, reduced O–O moiety (d(O1–O2) = 1.415(4) Å) (Figure 2.16).

Pd(CNAr\(^{Dipp}\))\(_2\) (2) effected similar bond reduction on azoarenes (Ar–N=N–Ar). Treatment of Pd(CNAr\(^{Dipp}\))\(_2\) (2) with 1.0 equiv of azo-(Ar\(^{F1}\))\(_2\) (Ar\(^{F1}\) = C\(_6\)H\(_4\)-4-CF\(_3\)) afforded Pd(\(\eta^2\)-N\(_2\)-Ar\(^{F1}\)NAr\(^{F1}\))(CNAr\(^{Dipp}\))\(_2\) (10, Scheme 2.4), in which the aryl groups bound to the nitrogen atoms are positioned \(\text{trans}\) to each other (Figure 2.17). Likewise, treatment of Pd(CNAr\(^{Dipp}\))\(_2\) with 1 equiv of azo-(Ar\(^{F2}\))\(_2\) (Ar\(^{F2}\) = C\(_6\)H\(_3\)-3,5-(CF\(_3\))\(_2\)) afforded Pd(\(\eta^2\)-N\(_2\)-Ar\(^{F2}\)NAr\(^{F2}\))(CNAr\(^{Dipp}\))\(_2\) (11, Scheme 2.4 and Figure 2.18). Compounds 10 and 11 are reminiscent of \(\pi\)-bound azobenzene complexes such as Ni(PhN=NPh)(CN\(^t\)Bu)\(_2\)\(^{41-44}\) and Fe(PhN=NPh)(dmpe)\(_2\)\(^{45,46}\) which have been considered as structural models for proposed metal-bound diazene [M(\(\text{HN}={\text{NH}}\))] intermediates in dinitrogen fixation. The N–N bond distances observed in Pd(\(\eta^2\)-N\(_2\)-Ar\(^{F1}\)NAr\(^{F1}\))(CNAr\(^{Dipp}\))\(_2\) (10) and Pd(\(\eta^2\)-N\(_2\)-Ar\(^{F2}\)NAr\(^{F2}\))(CNAr\(^{Dipp}\))\(_2\)
(11) $(d(N1-N2) = 1.374(4) \text{ and } 1.379(6) \text{ Å, respectively})$ are within the range of N–N bond distances in other side-on coordinated azoarene complexes (1.340–1.449 Å).\textsuperscript{47-53}

Figure 2.17. Molecular structure of Pd$(\eta^2-N,N$-$\text{ArF}_1$)$\text{ArF}_2$)(CNArDipp\textsubscript{2})\textsubscript{2} (10). Selected bond distances (Å) and angles (°): Pd1–C1 = 2.005(4); Pd1–C2 = 2.008(4); Pd1–N1 = 2.075(3); Pd1–N2 = 2.092(3); N1–N2 = 1.374(4); C1–Pd1–C2 = 109.39(14); C1–Pd1–N1 = 105.27(12); C2–Pd1–N2 = 108.26(12); C1–N3–C3 = 174.6(4); C2–N4–C33 = 175.2(3).

Figure 2.18. Two views of the molecular structure of Pd$(\eta^2-N,N$-$\text{ArF}_2$)$\text{ArF}_2$)(CNArDipp\textsubscript{2})\textsubscript{2} (11). Selected bond distances (Å) and angles (°): Pd1–C1 = 1.983(5); Pd1–C2 = 2.013(6); Pd1–N1 = 2.070(4); Pd1–N2 = 2.051(4); N1–N2 = 1.379(6); C1–Pd1–C2 = 98.9(2); C1–Pd1–N2 = 108.14(19); C2–Pd1–N1 = 114.22(19); C1–N3–C3 = 163.2(5); C2–N4–C33 = 164.3(5).
In analogy to the reduction of O=O and N=N bonds, Pd(CNArDipp\textsuperscript{2})\textsubscript{2} (2) induced N=O bond lengthening in nitrosobenzene (PhNO). Treatment of Pd(CNArDipp\textsuperscript{2})\textsubscript{2} (2) with 1 equiv of PhNO generated Pd(\eta\textsuperscript{2}-O,N-PhNO)(CNArDipp\textsuperscript{2})\textsubscript{2} (12, Scheme 2.4) in which the coordinated N–O bond distance is 1.349(3) Å (Figure 2.19). More noteworthy, however, is the reaction between Pd(CNArDipp\textsuperscript{2})\textsubscript{2} (2) and 2 equiv of PhNO to afford the complex Pd(\kappa\textsuperscript{1}-N-PhNO)\textsubscript{2}(CNArDipp\textsuperscript{2})\textsubscript{2} (13, Scheme 2.4). The molecular structure of Pd(\kappa\textsuperscript{1}-N-PhNO)\textsubscript{2}(CNArDipp\textsuperscript{2})\textsubscript{2} (13), which exhibits crystallographic inversion symmetry, notably features a square planar coordination geometry, indicative of a complex containing a divalent Pd center (Figure 2.20). Pd(\kappa\textsuperscript{1}-N-PhNO)\textsubscript{2}(CNArDipp\textsuperscript{2})\textsubscript{2} (13) also gives rise to \nu_{\text{CN}} stretches (2188, 2146 and 2111 cm\textsuperscript{-1}, KBr) that are higher in energy compared to those of Pd(CNArDipp\textsuperscript{2})\textsubscript{2} (2). Further, the crystallographic structure of Pd(\kappa\textsuperscript{1}-N-PhNO)\textsubscript{2}(CNArDipp\textsuperscript{2})\textsubscript{2} (13) exhibits a \textit{d}(Pd–C_{\text{iso}}) bond distance of 2.004(2) Å, which is significantly longer than those of Pd(CNArDipp\textsuperscript{2})\textsubscript{2} (2). The structure also displays a lack of bending within the isocyanide ligands (\angle(C1–N2–C2) = 174.6(2)\textdegree). These spectroscopic and structural parameters are reflective of decreased \pi-back donation to the CNArDipp\textsuperscript{2} ligands, thus supporting the existence of a divalent Pd center. Lastly, the N–O bond distance of Pd(\kappa\textsuperscript{1}-N-PhNO)\textsubscript{2}(CNArDipp\textsuperscript{2})\textsubscript{2} (13) (1.291(2) Å) is longer than that observed for monomeric nitrosoarene compounds (d(N–O) = 1.18 – 1.24 Å\textsuperscript{54} and shorter than that of Pd(\eta\textsuperscript{2}-O,N-PhNO)(CNArDipp\textsuperscript{2})\textsubscript{2} (12). It is also worth noting that the N–O bond distance of Pd(\kappa\textsuperscript{1}-N-PhNO)\textsubscript{2}(CNArDipp\textsuperscript{2})\textsubscript{2} (13) is longer than that in Balch’s complex, PdCl\textsubscript{2}(\kappa\textsuperscript{1}-N-
PhNO\textsubscript{2} \((d(N–O) = 1.209(3) \text{ Å})\), in which the Pd center is coordinated to two neutral PhNO ligands.\textsuperscript{55,56}

**Figure 2.19.** Molecular structure of Pd(\(\eta^2\)-O,N-PhNO)(CNAr\textsubscript{Dipp2})\textsubscript{2} (12). Selected bond distances (Å) and angles (°): Pd1–C1 = 1.985(2); Pd1–C2 = 2.033(2); Pd1–N1 = 2.072(2); Pd1–O1 = 2.0369(17); N1–O1 = 1.349(3); C1–Pd1–C2 = 108.61(9); C1–Pd1–N1 = 109.21(8); C2–Pd1–O1 = 103.56(8); C1–N2–C3 = 169.7(2); C2–N3–C33 = 177.6(2).

**Figure 2.20.** Molecular structure of Pd(\(\kappa^1\)-N-PhNO\textsubscript{2})(CNAr\textsubscript{Dipp2})\textsubscript{2} (13). Selected bond distances (Å) and angles (°): Pd–C1 = 2.004(2); Pd1–N1 = 2.0108(19); N1–O1 = 1.291(2); C1–Pd1–C1' = 179.997(1); N1–Pd1–N1' = 179.996(1); C1–Pd1–N1 = 89.64(8); C1–Pd1–N1' = 90.35(8); C1–N2–C2 = 174.60(19).
These data collectively imply a one-electron reduction of each PhNO ligand in Pd(κ¹-N-PhNO)₂(CNArDipp²) (13) from the Pd center. Consequently, two electronic descriptions are proposed (Scheme 2.5): 1) a singlet diradical description⁵⁷ in which each PhNO unit is reduced to its O-centered nitroxyl radical, and 2) a closed-shell representation featuring a \((\sigma)^4(\pi)^4(\pi^*)^2\) singlet ground state containing nondegenerate \(\pi^*\) orbitals \(a_g\) and \(a_u\) in \(C_i\) symmetry. In accord with this latter description, spin-restricted, closed-shell DFT calculations were conducted on the computational model Pd(κ¹-N-PhNO)₂(CNArPh²)₂ depicted in Figure 2.21. A comparison of the key structural parameters between the experimental compound Pd(κ¹-N-PhNO)₂(CNArDipp²) (13) and the model Pd(κ¹-N-PhNO)₂(CNArPh²)₂ is listed in Table 2.2. While spin-restricted, closed-shell DFT calculations on the \(S = 0\) state of Pd(κ¹-N-PhNO)₂(CNArPh²)₂ agree with the latter MO description (Figure 2.22), additional information is necessary to definitively distinguish between the closed-shell and the singlet diradical electronic structures. Detailed studies of the nitroso compounds Pd(κ¹-N-PhNO)₂(CNArDipp²) (13) and Pd(η²-O,N-PhNO)(CNArDipp²) (12) are accordingly presented in Chapter 4.

**Scheme 2.5.** Proposed electronic representations for Pd(κ¹-N-PhNO)₂(CNArDipp²) (13).
Figure 2.21. Optimized geometry of the computational model Pd(κ\(^1\)-N-PhNO\(_2\))(CNAr\(^{Ph2}\))\(_2\).

Table 2.2. Comparison of Computational vs. Experimental Structures for Pd(κ\(^1\)-N-PhNO\(_2\))(CNAr\(^{Ph2}\))\(_2\) and Pd(κ\(^1\)-N-PhNO\(_2\))(CNAr\(^{Dipp2}\))\(_2\) (13).

<table>
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<th>Parameter</th>
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<th>Pd(κ(^1)-N-PhNO(_2))(CNAr(^{Dipp2}))(_2)</th>
<th>% Difference</th>
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* Possesses crystallographic inversion symmetry.
2.6 Conclusions

Isolation of the first monomeric, zerovalent bis-isocyanide complex of the group 10 metals, Pd(CNArDipp₂)₂ (2), was achieved with the sterically encumbering m-terphenyl isocyanide CNArDipp₂. As a counterpoint to other zerovalent PdL₂ complexes (L = PR₃, NHC), Pd(CNArDipp₂)₂ (2) exemplifies the ability of π-acidic isocyanide ligands to stabilize a reduced metal center. Reactivity studies of Pd(CNArDipp₂)₂ (2)
towards a wide variety of small molecule substrates demonstrated its coordinatively unsaturated and electron-rich nature. For example, Pd(CNAr^{Dipp2})_2 (2) is readily oxidized by I_2 and is active towards electrophilic and Lewis acidic substrates. More notably, Pd(CNAr^{Dipp2})_2 (2) is catalytically competent in Suzuki-Miyaura cross-coupling reactions between aryl bromides and aryl boronic acids. The limited attention given to π-acidic ligands in Pd-catalyzed cross-coupling chemistry has indeed spurred further investigations of Pd(CNAr^{Dipp2})_2 (2) as a catalyst precursor. These studies are described in Chapter 3. Lastly, reduction of various electronically unsaturated substrates is effected by Pd(CNAr^{Dipp2})_2 (2). Most interesting is the addition of 2 units of PhNO to Pd(CNAr^{Dipp2})_2 (2), forming Pd(κ^1-N-PhNO)(CNAr^{Dipp2})_2 (13). Two electronic descriptions of the latter complex are initially proposed: a singlet diradical ground state, and a closed-shell representation featuring a (σ)^4(π)^4(π^*)^2 singlet ground state. Detailed investigations of Pd(κ^1-N-PhNO)(CNAr^{Dipp2})_2 (13), its corresponding mono-nitrosoarene counterpart Pd(η^2-O,N-PhNO)(CNAr^{Dipp2})_2 (12), and additional nitrosoarene derivatives are presented in Chapter 4.

2.7 Synthetic Procedures

General considerations. All manipulations were carried out under an atmosphere of dinitrogen using standard Schlenk and glovebox techniques. Solvents were dried and deoxygenated according to standard procedures. Benzene-\textit{d}_6 and toluene-\textit{d}_8 (Cambridge Isotope Laboratories) were degassed and stored over 4 Å
molecular sieves for 2 d prior to use. The isocyanide ligand CNArDipp$_2$ was prepared as described previously.$^{58}$ Thallium triflate (TlOTf) was prepared from thallium ethoxide (TlOEt) and triflic acid (HOSO$_2$CF$_3$) in n-pentane. Celite 405 (Fisher Scientific) was dried under vacuum (24 h) at a temperature above 250 °C and stored in the glovebox prior to use. KBr (FTIR grade from Aldrich) was stirred overnight in anhydrous THF, filtered and dried under vacuum (24 h) at a temperature above 250 °C and stored in the glovebox prior to use. All other reagents were purchased from commercial sources and used as received.

Solution $^1$H, $^{13}$C{$^1$H} and $^{19}$F{$^1$H} NMR spectra were recorded on Varian Mercury 300 and 400 spectrometers, a Varian X-Sens500 spectrometer, and a Jeol ECA 500 spectrometer. $^1$H and $^{13}$C{$^1$H} chemical shifts are reported in ppm relative to SiMe$_4$ ($^1$H and $^{13}$C δ = 0.0 ppm) with reference to residual solvent resonances of 7.16 ppm ($^1$H) and 128.06 ppm ($^{13}$C) for C$_6$D$_6$, 2.08 ppm ($^1$H) for toluene-$d_8$. $^{19}$F{$^1$H} NMR spectra were referenced externally to neat trifluoroacetic acid, F$_3$CC(O)OH (δ = −78.5 ppm vs. CFCl$_3$ = 0.0 ppm). FTIR spectra were recorded on a Thermo-Nicolet iS10 FTIR spectrometer. Samples were prepared as either KBr pellets or as C$_6$D$_6$ solutions injected into a ThermoFisher solution cell equipped with NaCl windows. For solution FTIR spectra, solvent peaks were digitally subtracted from all spectra by comparison with an authentic spectrum obtained immediately prior to that of the sample. Combustion analyses were performed by Robertson Microlit Laboratories of Madison, NJ (USA). High-resolution mass spectrometry (HRMS) analyses were performed by the UCSD Chemistry and Biochemistry Molecular MS Facility.
Synthesis of \textit{trans-}PdCl\textsubscript{2}(CNAr\textsuperscript{Dipp\textsubscript{2}}\textsubscript{2}) (1). To a stirred slurry of PdCl\textsubscript{2}(COD) (0.840 g, 2.94 mmol, COD = 1,5-cyclooctadiene) in THF (40 mL) was added CNAr\textsuperscript{Dipp\textsubscript{2}} (2.550 g, 6.03 mmol, 2.05 equiv). The reaction mixture was stirred for 3 h, and then all volatile materials were removed under reduced pressure. The residue was then slurried in \textit{n}-pentane (10 mL), stirred for 5 min and then dried \textit{in vacuo} for 3 consecutive cycles. Dissolution of the resulting pale-yellow solid in THF (25 mL) followed by filtration and storage at −35 °C overnight resulted in pale yellow crystals which were collected and dried \textit{in vacuo}. Yield: 2.257 g, 2.20 mmol, 75%. \textsuperscript{1}H NMR (400.1 MHz, C\textsubscript{6}D\textsubscript{6}, 20 °C): \(\delta = 7.34\) (t, 4H, \(J = 8\) Hz, \textit{p}-Dipp), 7.19 (d, 8H, \(J = 8\) Hz, \textit{m}-Dipp), 6.89 (d, 4H, \(J = 8\) Hz, \textit{m}-Ph), 6.84 (t, 2H, \(J = 8\) Hz, \textit{p}-Ph), 2.51 (septet, 8H, \(J = 8\) Hz, CH(CH\textsubscript{3})\textsubscript{2}), 1.35 (d, 24H, \(J = 8\) Hz, CH(CH\textsubscript{3})\textsubscript{2}), 1.03 (d, 24H, \(J = 8\) Hz, CH(CH\textsubscript{3})\textsubscript{2}) ppm. \textsuperscript{13}C\{\textsuperscript{1}H\} NMR (100.6 MHz, C\textsubscript{6}D\textsubscript{6}, 20 °C): \(\delta = 146.4, 140.5, 133.1, 130.1, 130.0, 129.8, 127.9, 127.6, 31.5\) (CH(CH\textsubscript{3})\textsubscript{2}), 24.9 (CH(CH\textsubscript{3})\textsubscript{2}), 24.1 (CH(CH\textsubscript{3})\textsubscript{2}), 21.7 (\textit{m}-CH\textsubscript{3}) ppm (extended scanning (12 h) failed to locate the C\textsubscript{iso} \textsuperscript{13}C resonance for this complex). FTIR (KBr pellet): (\(\nu\textsuperscript{CN}\)) 2202 cm\textsuperscript{−1} also 2962, 2926, 2867, 1580, 1463, 1412, 1383, 1363, 1056, 825, 797, 754 cm\textsuperscript{−1}. Anal. calcd. for C\textsubscript{62}H\textsubscript{74}Cl\textsubscript{2}N\textsubscript{2}Pd: C, 72.68; H, 7.28; N, 2.73. Found: C, 72.78; H, 7.36; N, 2.71.

Synthesis of Pd(CNAr\textsuperscript{Dipp\textsubscript{2}}\textsubscript{2}) (2). To a stirred solution of \textit{trans-}PdCl\textsubscript{2}(CNAr\textsuperscript{Dipp\textsubscript{2}}\textsubscript{2}) (2.257 g, 2.20 mmol) in 4:1 Et\textsubscript{2}O/THF (50 mL total) was added activated magnesium turnings (0.803 g, 33.04 mmol, 15 equiv). The reaction mixture was stirred for 6 h and gradually changed in color from pale-yellow to orange. The
resulting solution was decanted away from the residual magnesium turnings and then
dried under reduced pressure. The residue was then slurried in n-pentane (10 mL),
stirred for 5 min and then dried in vacuo for 3 consecutive cycles. The resulting
orange residue was then extracted with Et$_2$O (3 x 100 mL) and filtered through Celite.
The filtrate was evaporated to dryness under reduced pressure and the remaining solid
was dissolved in THF (15 mL), filtered, layerred with n-pentane (10 mL) and stored at
−35 °C for 3 d, whereupon orange crystals were obtained. Yield: 1.537 g, 1.61 mmol,
73 %. $^1$H NMR (400.1 MHz, C$_6$D$_6$, 20 °C): δ = 7.31 (t, 4H, J = 8 Hz, p-Dipp), 7.18
(d, 8H, J = 8 Hz, m-Dipp), 6.91 (m, 6H, m-Ph and p-Ph), 2.62 (septet, 8H, J = 8 Hz,
CH(CH$_3$)$_2$), 1.23 (d, 24H, J = 8 Hz, CH(CH$_3$)$_2$), 1.10 (d, 24H, J = 8 Hz, CH(CH$_3$)$_2$)
ppm. $^{13}$C {$^1$H} NMR (100.6 MHz, C$_6$D$_6$, 20 °C): δ = 160.7 (C≡N), 146.5, 139.5, 134.8,
129.6, 129.4, 123.3, 31.4 (CH(CH$_3$)$_2$), 24.6 (CH(CH$_3$)$_2$), 24.4 (CH(CH$_3$)$_2$) ppm. FTIR
(KBr pellet): (νCN) 2073 and 2011 cm$^{-1}$ also 2961, 2924, 2865, 1458, 1261, 1102,
1056, 1022, 804, 791, 753 cm$^{-1}$. Anal. calcd. for C$_{62}$H$_{74}$N$_2$Pd: C, 78.08; H, 7.82; N,
2.94. Found: C, 78.36; H, 8.09; N, 2.74.

**Synthesis of trans-PdI$_2$(CNAr$^{Dipp^2}$)$_2$ (3).** To a stirred solution of
Pd(CNAr$^{Dipp^2}$)$_2$ (0.100 g, 0.105 mmol) in Et$_2$O (5 mL) was added I$_2$ (0.027 g, 0.105
mmol, 1.0 equiv). The reaction mixture was stirred for 1 h during which orange
precipitate formed. All volatile materials were removed under reduced pressure and
the resulting orange powder was dissolved in THF, filtered, and stored at −35 °C
overnight to produce orange crystals, which were collected and dried in vacuo. Yield:
0.083 g, 0.069 mmol, 66%. Crystals suitable for X-ray analysis were obtained by slow evaporation of a solution of trans-PdI₂(CNArDipp₂)₂ in THF at room temperature for 3 d. ¹H NMR (400.1 MHz, C₆D₆, 20 °C): δ = 7.36 (t, 4H, J = 8 Hz, p-Dipp), 7.20 (d, 8H, J = 8 Hz, m-Dipp), 6.88-6.79 (m, 6H, m-Ph and p-Ph), 2.57 (septet, 8H, J = X Hz, CH(CH₃)₂), 1.37 (d, 24H, J = 7 Hz, CH(CΗ₃)₂), 1.03 (d, 24H, J = 7 Hz, CH(CH₃)₂) ppm. ¹³C{¹H} NMR (125.7 MHz, C₆D₆, 20 °C): δ = 146.4, 140.4, 133.7, 130.3, 130.1, 129.9, 128.4, 123.9, 31.5 (CH(CH₃)₂), 24.8 (CH(CH₃)₂), 24.5 (CH(CH₃)₂) ppm (extended scanning (12 h) failed to locate the C iso ¹³C resonance for this complex). FTIR (KBr pellet): (νCN) 2184 cm⁻¹ also 2961, 2925, 2867, 1595, 1581, 1460, 1411, 1383, 1362, 1253, 1056, 1046, 797, 754 cm⁻¹. Anal. calcd. for C₆₂H₇₄I₂N₂Pd: C, 61.67; H, 6.18; N, 2.32. Found: C, 61.92; H, 6.00; N, 2.25.

**Synthesis of [(THF)Pd(η²-C,N-(MeC=NArDipp₂)(CNArDipp₂))OTf (4).** To a stirred solution of Pd(CNArDipp₂)₂ (0.050 g, 0.052 mmol) in 2:1 Et₂O/THF (3 mL total) was added a solution of MeOTf (0.009 g, 0.052 mmol, 1.0 equiv) in Et₂O (2 mL). The solution immediately turned yellow in color and was stirred for 3 h, after which the solvents were removed under reduced pressure. The resulting residue was stirred in a solution of 4:1 n-pentane/toluene (5 mL total) and concentrated under reduced pressure to induce precipitation of a yellow solid, which was isolated by filtration and dried in vacuo. This resulted in an analytically pure sample lacking coordinated THF. Yield: 0.043 g, 0.038 mmol, 73%. Crystals suitable for X-ray analysis were grown from a 1:1 THF/toluene solution at −35 °C. ¹H NMR (300.1 MHz, C₆D₆, 20 °C): δ =
7.45–7.39 (m, 7H, p-Dipp, m-Dipp, and m-Ph), 7.28–7.23 (m, 7H, m-Dipp and m-Ph), 7.15 (m, 2H, p-Ph), 6.86 (d, 2H, J = 8 Hz, m-Ph), 2.47 (septet, 4H, J = 7 Hz, CH(CH₃)₂), 2.39 (septet, 4H, J = 7 Hz, CH(CH₃)₂), 1.20 (d, 3H, (CH₃)(C=NarDipp²)), 1.15 (d, 12H, J = 7 Hz, CH(CH₃)₂), 1.13 (d, 12H, J = 7 Hz, CH(CH₃)₂), 1.07 (d, 12H, J = 7 Hz, CH(CH₃)₂), 1.00 (d, 12H, J = 7 Hz, CH(CH₃)₂) ppm. ¹³C{¹H} NMR (100.6 MHz, C₆D₆, 20 °C): δ = 155.0 ((CH₃)C=NArDipp²), 146.6, 143.0, 142.5, 140.4, 133.2, 131.0, 130.7, 130.0, 129.5, 129.4, 125.5, 124.2, 122.3, 31.5 (CH(CH₃)₂), 31.0 (CH(CH₃)₂), 25.3 ((CH₃)C=NArDipp²), 24.4 (CH(CH₃)₂), 24.3 (CH(CH₃)₂), 23.4 (CH(CH₃)₂) ppm (extended scanning (12 h) failed to locate the second C iso ¹³C resonance for this complex). ¹⁹F{¹H} NMR (282.3 MHz, C₆D₆, 20 °C) δ = −77.8 ppm. FTIR (KBr pellet): (νCN) 2182 and 1711 cm⁻¹ also 3062, 2961, 2928, 2869, 1459, 1363, 1275, 1264, 1224, 1151, 1065, 1031, 824, 796, 761, 638 cm⁻¹. Anal. calcd. for C₆₄H₇₇F₃N₂O₃SPd: C, 68.77; H, 6.94; N, 2.51. Found: C, 69.01; H, 7.01; N, 2.52.

**Synthesis of [TlPd(CNArDipp²)₂]OTf (6).** To a solution of Pd(CNArDipp²)₂ (0.068 g, 0.069 mmol) in Et₂O (3 mL) was added a slurry of TIOTf (0.026 g, 0.073 mmol, 1.05 equiv) in Et₂O (2 mL). The reaction mixture was stirred for 4 h and then the solvent was removed under reduced pressure. The resulting residue was extracted with Et₂O (2 mL) and filtered. Storage of this solution at −35 °C overnight produced orange crystals, which were collected and dried *in vacuo*. Yield: 0.068 g, 0.059 mmol, 57 %. ¹H NMR (300.1 MHz, C₆D₆, 20 °C): δ = 7.42 (t, 4H, J = 8 Hz, p-Dipp), 7.28 (d, 8H, J = 8 Hz, m-Dipp), 6.82 (m, 6H, m-Ph and p-Ph), 2.52 (septet, 8H, J = 7 Hz,
CH(CH₃)₂, 1.26 (d, 24H, J = 7 Hz, CH(CH₃)₂), 1.07 (d, 24H, J = 7 Hz, CH(CH₃)₂) ppm. ¹³C{¹H} NMR (125.7 MHz, C₆D₆, 20 °C): δ = 164.0 (C≡N), 147.2, 139.4, 134.7, 130.2, 129.8, 129.2, 123.9, 31.5 (CH(CH₃)₂), 24.5 (CH(CH₃)₂), 24.4 (CH(CH₃)₂) ppm.

¹⁹F{¹H} NMR (282.3 MHz, C₆D₆, 20 °C) δ = −78.3 ppm. FTIR (KBr pellet): (νCN) 2107 cm⁻¹ also 2963, 2868, 1449, 1283, 1235, 1174 cm⁻¹. Anal. calcd. for C₆₃H₇₅F₃N₂O₃SPdTl: C, 57.84; H, 5.78; N, 2.14. Found: C, 57.57; H, 5.52; N, 2.18.

**Synthesis of trans-PdCl(Bz)(CNArDipp)₂ (7).** To a solution of Pd(CNArDipp)₂ (0.100 g, 0.105 mmol) in THF (2 mL) was added a solution of benzyl chloride (0.013 g, 0.105 mmol, 1.0 equiv) in THF (2 mL). The reaction mixture was stirred for 10 min and changed in color from orange to pale yellow. All volatile materials were removed under reduced pressure and the resulting pale yellow solid was dissolved in a 1:1 Et₂O mixture (2 mL total). Filtration of this solution followed by storage at −35 °C for 12 h produced colorless crystals, which were collected and dried in vacuo. Yield: 0.032 g, 0.030 mmol, 29 %. ¹H NMR (400.1 MHz, C₆D₆, 20 °C): δ = 7.37 (t, 4H, J = 8 Hz, p-Dipp), 7.23 (d, 8H, J = 8 Hz, m-Dipp), 7.00–6.88 (m, 9H, m-Ph, p-Ph, m-Bz and p-Bz), 6.30 (dd, 2H, J = 8 Hz, o-Bz), 2.64 (septet, 8H, J = 8 Hz, CH(CH₃)₂), 2.39 (s, 2H, CH₂), 1.35 (d, 24H, J = 8 Hz, CH(CH₃)₂), 1.08 (d, 24H, J = 8 Hz, CH(CH₃)₂) ppm.

¹³C{¹H} NMR (125.7 MHz, C₆D₆, 20 °C): δ = 149.5, 146.5, 144.5, 140.0, 133.8, 130.2, 130.0, 129.7, 129.3, 127.0, 123.8, 123.1, 31.5 (CH(CH₃)₂), 24.9 (CH(CH₃)₂), 24.2 (CH(CH₃)₂), 12.8 (PhCH₂) ppm (extended scanning (12 h) failed to locate the Ciso ¹³C resonance for this complex). FTIR (KBr pellet): (νCN) 2154 cm⁻¹ also 3060, 2960,
2927, 2868, 1459, 1363, 1179, 1056, 806, 756 cm$^{-1}$. Anal. calcd. for C$_{69}$H$_{81}$ClN$_2$Pd: C, 76.72; H, 7.56; N, 2.59. Found: C, 76.47; H, 7.81; N, 2.36.

**Synthesis of trans-PdBr(Mes)(CNAr$_{Dipp}$)$_2$ (8).** To a solution of Pd(CNAr$_{Dipp}$)$_2$ (0.100 g, 0.105 mmol) in Et$_2$O (2 mL) was added MesBr (16 μL, 0.105 mmol, 1.0 equiv). The reaction mixture was stirred for 20 h and gradually changed in color from orange to pale yellow. All volatile materials were removed under reduced pressure and the resulting residue was extracted with Et$_2$O (2 mL) and filtered. Storage of this solution at $-35$ °C overnight produced pale yellow crystals, which were collected and dried *in vacuo*. Yield: 0.068 g, 0.059 mmol, 57 %. $^1$H NMR (300.1 MHz, C$_6$D$_6$, 20 °C): $\delta = 7.33$ (t, 4H, $J = 6$ Hz, $p$-Dipp), 7.15 (d, 8H, $J = 6$ Hz, $m$-Dipp), 6.82 (m, 6H, $m$-Ph and $p$-Ph), 6.45 (s, 2H, $m$-Mes), 2.45 (septet, 8H, $J = 6$ Hz, CH(CH$_3$)$_2$), 2.27 (s, 3H, $p$-CH$_3$), 1.69 (s, 6H, $o$-CH$_3$), 1.18 (d, 24H, $J = 6$ Hz, CH(CH$_3$)$_2$), 0.98 (d, 24H, $J = 6$ Hz, CH(CH$_3$)$_2$) ppm. $^{13}$C($^1$H) NMR (100.6 MHz, C$_6$D$_6$, 20 °C): $\delta = 146.5, 145.5, 142.4, 139.7, 133.8, 132.3, 130.0, 129.8, 129.0, 127.5, 126.7, 123.5, 31.4$ (CH(CH$_3$)$_2$), 25.8 ($p$-Mes), 24.9 (CH(CH$_3$)$_2$), 24.2 (CH(CH$_3$)$_2$), 20.8 ($o$-Mes) ppm (extended scanning (12 h) failed to locate the C$_{iso}$ $^{13}$C resonance for this complex). FTIR (KBr pellet): ($\nu$$_{CN}$) 2177 cm$^{-1}$ also 3059, 2961, 2867, 1459, 1415, 1385, 1363, 1055, 755 cm$^{-1}$. Anal. calcd. for C$_{71}$H$_{85}$BrN$_2$Pd: C, 73.97; H, 7.43; N, 2.43. Found: C, 73.70; H, 7.66; N, 2.35.
Synthesis of \( \text{Pd}(\eta^2\text{-O}_2)(\text{CNArDipp}_2)_2 \) (9). To a cooled \((-78~°C)\) solution of \( \text{Pd(CNArDipp}_2)_2 \) (0.081 g, 0.083 mmol) in THF (5 mL) under partial vacuum was added dry dioxygen (2.3 mL, 0.087 mmol, 1.05 equiv) via syringe. Upon addition, the cold bath was removed and the reaction mixture was allowed to warm to room temperature whereupon it gradually changed in color from orange to pale yellow-green. The reaction mixture was stirred an additional hour and then all volatile materials were removed under reduced pressure. Dissolution of the resulting pale yellow-green residue in THF, followed by filtration and storage at \(-35~°C\) for 2 d produced yellow crystals, which were collected and dried \( \text{in vacuo} \). Yield: 0.053 g, 0.052 mmol, 63 %. \(^1\)H NMR (400.1 MHz, \( \text{C}_6\text{D}_6 \), 20 °C): \( \delta = 7.33 \) (t, 4H, \( J = 8 \) Hz, \( p\text{-Dipp} \)), 7.18 (d, 8H, \( J = 8 \) Hz, \( m\text{-Dipp} \)), 6.87 (m, 6H, \( m\text{-Ph} \) and \( p\text{-Ph} \)), 2.53 (septet, 8H, \( J = 7 \) Hz, \( \text{CH(CH}_3)_2 \)), 1.20 (d, 24H, \( J = 7 \) Hz, \( \text{CH(CH}_3)_2 \)) ppm. \(^{13}\)C\(^{1}\)H NMR (125.7 MHz, \( \text{C}_6\text{D}_6 \), 20 °C): \( \delta = 153.1 \) (C≡N), 146.2, 139.7, 133.8, 130.0, 129.8, 129.2, 128.3, 123.7, 31.4 (CH(CH\(_3\)_2)), 24.6 (CH(CH\(_3\)_2)), 24.3 (CH(CH\(_3\)_2)) ppm. FTIR (KBr pellet): \( (\nu\text{CN}) 2175, 2149 \) cm\(^{-1}\) also 3067, 2961, 2927, 2867, 1576, 1459, 1391, 1355, 1169, 1056, 805, 789, 754 cm\(^{-1}\). Anal. calcd. for \( \text{C}_{62}\text{H}_{74}\text{N}_2\text{O}_2\text{Pd} \): C, 75.55; H, 7.57; N, 2.84. Found: C, 77.62; H, 7.64; N, 2.79.

Synthesis of azo-(Ar\(^{1}\)F\(_2\))\(_2\).\(^{59}\) To a rapidly stirred solution of 4-trifluoromethylaniline (0.39 mL, 3.10 mmol) in glacial acetic acid (2 mL) was added 30% aqueous H\(_2\)O\(_2\) (0.88 mL, 7.75 mmol, 2.5 equiv). The reaction mixture was stirred for 20 h, then water (3 mL) was added and the product was extracted with Et\(_2\)O (3 x 2
mL). The organic layers were combined, dried over magnesium sulfate, filtered, and concentrated under reduced pressure. Storage of the resulting solution at −35 °C overnight produced red-orange crystals, which were collected and dried *in vacuo*. The isolated solid consisted of a mixture of azo-(ArF\(_1\))\(_2\) and azoxy-(ArF\(_1\))\(_2\) as determined by GC-MS analysis. \(^1\)H NMR (500.1 MHz, C\(_6\)D\(_6\), 20 °C): δ = 7.93 (d, 4H, \(J = 9\) Hz), 7.86 (d, 4H, \(J = 9\) Hz) ppm. HRMS (EI) \(m/z\) calcd. for C\(_{14}\)H\(_8\)N\(_2\)F\(_6\): 318.0586. Found: (M)\(^+\), 318.0589.

**Synthesis of azo-(ArF\(_2\))\(_2\)**.\(^{60}\) To a rapidly stirred solution of 3,5-bis(trifluoromethyl)aniline (0.48 mL, 3.10 mmol) in glacial acetic acid (2 mL) was added 30% aqueous H\(_2\)O\(_2\) (0.88 mL, 7.75 mmol, 2.5 equiv). The reaction mixture was stirred for 20 h, then water (3 mL) was added and the product was extracted with Et\(_2\)O (3 x 2 mL). The organic layers were combined, dried over magnesium sulfate, filtered, and concentrated under reduced pressure. Storage of the resulting solution at −35 °C overnight produced red-orange crystals, which were collected and dried *in vacuo*. The isolated solid consisted of a mixture of azo-(ArF\(_2\))\(_2\) and azoxy-(ArF\(_2\))\(_2\) as determined by GC-MS analysis. \(^1\)H NMR (500.1 MHz, C\(_6\)D\(_6\), 20 °C): δ = 8.42 (s, 4H), 8.04 (s, 2H) ppm. HRMS (EI) \(m/z\) calcd. for C\(_{16}\)H\(_6\)N\(_2\)F\(_{12}\): 454.0334. Found: (M)\(^+\), 454.0330.

**Synthesis of Pd(η\(^2\)-N,N-Ar\(^{F1}\)NNAr\(^{F1}\})(CNArDipp\(^2\))\(_2\) (10)**. To a solution of Pd(CNArDipp\(^2\))\(_2\) (0.100 g, 0.105 mmol) in Et\(_2\)O (5 mL) was added azo-(ArF\(_1\))\(_2\) (0.037 g, 0.115 mmol, 1.1 equiv). The reaction mixture turned red-orange in color upon addition
and was stirred for 30 min, then solvent was removed under reduced pressure. The resulting residue was extracted with \(n\)-pentane (2 mL), filtered, and stored at \(-35^\circ \text{C}\) for 3 d to produce red-orange crystals, which were collected and dried \textit{in vacuo}. Yield: 0.032 g, 0.025 mmol, 24 %. \(^1\)H NMR (500.1 MHz, \(\text{C}_6\text{D}_6\), 20 \(^\circ\)C): \(\delta = 7.43\) (d, 4H, \(J = 8\) Hz, \(m\)-Ar\(^F\)), 7.36 (d, 4H, \(J = 8\) Hz, \(o\)-Ar\(^F\)), 7.27 (t, 4H, \(J = 8\) Hz, \(p\)-Dipp), 7.13 (d, 8H, \(J = 8\) Hz, \(m\)-Dipp), 6.88 (m, 6H, \(m\)-Ph and \(p\)-Ph), 2.59 (septet, 8H, \(J = 7\) Hz, \(\text{CH(CH}_3\text{)}_2\)), 1.17 (d, 24H, \(J = 7\) Hz, \(\text{CH(CH}_3\text{)}_2\)), 1.08 (d, 24H, \(J = 7\) Hz, \(\text{CH(CH}_3\text{)}_2\) ppm. \(^{13}\)C\{\(^1\)H\} NMR (125.7 MHz, \(\text{C}_6\text{D}_6\), 20 \(^\circ\)C): \(\delta = 159.6\) (C≡N), 155.9 (NN-\(\text{C}_{\text{ipso}}\)), 146.6, 139.4, 134.6, 130.3 (q, \(J_{\text{CF}} = 32\) Hz), 129.9, 129.6, 126.4 (q, \(J_{\text{CF}} = 4\) Hz), 125.0 (q, \(J_{\text{CF}} = 272\) Hz, CF\(_3\)), 123.5, 123.4, 31.4 (CH(CH\(_3\))\(_2\)), 24.5 (CH(CH\(_3\))\(_2\)), 24.3 (CH(CH\(_3\))\(_2\) ppm. \(^{19}\)F\{\(^1\)H\} NMR (282.3 MHz, \(\text{C}_6\text{D}_6\), 20 \(^\circ\)C) \(\delta = -62.8\) ppm. FTIR (KBr pellet): (\(\nu\text{C=N}\)) 2144 and 2119 cm\(^{-1}\) also 3062, 2962, 2927, 2685, 1606, 1459, 1417, 1363, 1322, 1161, 1134, 1064, 858, 757 cm\(^{-1}\). Satisfactory combustion analysis was not obtained.

**Synthesis of Pd(\(\eta^2\)-N,N-Ar\(^{F_2}\)NNAr\(^{F_2}\))(CNAr\(^{Dipp}\))\(_2\) (11).** To a solution of Pd(CNAr\(^{Dipp}\))\(_2\) (0.100 g, 0.105 mmol) in Et\(_2\)O (5 mL) was added azo-(Ar\(^{F_2}\))\(_2\) (0.052 g, 0.115 mmol, 1.1 equiv). The reaction mixture turned red-orange in color upon addition and was stirred for 30 min, then solvent was removed under reduced pressure. The resulting residue was extracted with \(n\)-pentane (2 mL), filtered, and stored at \(-35^\circ \text{C}\) overnight to produce red-orange crystals, which were collected and dried \textit{in vacuo}. Yield: 0.027 g, 0.019 mmol, 18 %. \(^1\)H NMR (400.1 MHz, \(\text{C}_6\text{D}_6\), 20 \(^\circ\)C): \(\delta = 7.73\) (m,
6H, o-ArF$_2$ and p-ArF$_2$), 7.25 (t, 4H, $J = 8$ Hz, p-Dipp), 7.14 (d, 8H, $J = 8$ Hz, m-Dipp), 6.88 (m, 6H, m-Ph and p-Ph), 2.59 (septet, 8H, $J = 7$ Hz, CH(CH$_3$)$_2$), 1.17 (d, 24H, $J = 7$ Hz, CH(CH$_3$)$_2$), 1.08 (d, 24H, $J = 7$ Hz, CH(CH$_3$)$_2$), 1.08 (d, 24H, $J = 7$ Hz, CH(CH$_3$)$_2$), ppm. $^{13}$C{$_1$H} NMR (100.6 MHz, C$_6$D$_6$, 20 °C): $\delta = 158.8$ (C≡N), 153.1 (NN-C$_{ipso}$), 146.4, 139.5, 134.5, 132.8 (q, $^2J_{CF} = 34$ Hz), 130.1, 129.6, 123.6 (q, $^1J_{CF} = 273$ Hz, CF$_3$), 123.4, 31.3 (CH(CH$_3$)$_2$), 24.6 (CH(CH$_3$)$_2$), 24.4 (CH(CH$_3$)$_2$), ppm. $^{19}$F{$_1$H} NMR (282.3 MHz, C$_6$D$_6$, 20 °C) $\delta = -63.3$ ppm. FTIR (KBr pellet): ($\nu$CN) 2140, 2118 cm$^{-1}$ also 3091, 3067, 2965, 2928, 2870, 1464, 1376, 1364, 1281, 1263, 1186, 1168, 1135, 937, 908, 848, 759, 730, 700, 683 cm$^{-1}$. Satisfactory combustion analysis was not obtained.

**Synthesis of Pd($\eta^2$-$O,N$-PhNO)(CNAr$_{Dipp^2}$)$_2$ (12).** To a solution of Pd(CNAr$_{Dipp^2}$)$_2$ (0.050 g, 0.052 mmol) in benzene (2 mL) was added a solution of PhNO (0.006 g, 0.052 mmol, 1.0 equiv) in benzene (2 mL). Upon addition, the reaction mixture turned red in color. The reaction mixture was stirred for 3 h, and then the solvent was removed under reduced pressure. To the resulting residue was added a 3:1 $n$-pentane/bis(trimethylsilyl) ether solution (0.6 mL total). Filtration and slow evaporation of this solution overnight at room temperature produced dark red crystals suitable for X-ray analysis, which were collected and dried $in vacuo$. Yield: 0.027 g, 0.025 mmol, 48 %. $^1$H NMR (500.1 MHz, C$_6$D$_6$, 20 °C): $\delta = 7.30$ (t, 6H, $J = 8$ Hz, p-Dipp and o-PhNO), 7.18 (d, 8H, $J = 8$ Hz, m-Dipp), 7.12 (t, 2H, $J = 8$ Hz, m-PhNO), 7.05 (t, 1H, $J = 8$ Hz, p-PhNO), 6.89 (m, 6H, m-Ph and p-Ph), 2.61 (septet, 8H, $J = 7$ Hz, CH(CH$_3$)$_2$), 1.22 (d, 24H, $J = 7$ Hz, CH(CH$_3$)$_2$), 1.10 (d, 24H, $J = 7$ Hz,
CH(CH_3)_2) ppm. $^{13}$C{^1H} NMR (125.7 MHz, C_6D_6, 20 °C): $\delta = 162.6$ (ON–C_ipso), 159.1 (C≡N), 146.4, 139.4, 134.3, 130.1, 129.8, 128.6, 128.5, 128.4, 128.2, 127.9, 123.6, 123.3, 120.6, 31.4 (CH(CH_3)_2), 24.6 (CH(CH_3)_2), 24.4 (CH(CH_3)_2) ppm. FTIR (KBr pellet): (v_{CN}) 2149, 2105 cm$^{-1}$ also 3062, 2962, 2868, 1458, 1384, 1363, 1253, 1132, 1046.5, 914, 807, 793, 759 cm$^{-1}$. Anal. calcd. for C_{68}H_{79}N_3OPd: C, 76.99; H, 7.51; N, 3.96. Found: C, 75.61; H, 7.55; N, 3.94.

**Synthesis of Pd(κ¹-N-PhNO)_2(CNArDipp) (13).** To a solution of Pd(CNArDipp)_2 (0.150 g, 0.153 mmol) in benzene (2 mL) was added a solution of PhNO (0.034 g, 0.314 mmol, 2.05 equiv) in benzene (2 mL). Upon addition, the reaction mixture immediately changed in color from orange to dark red. The reaction mixture was stirred for 30 min and all volatile materials were removed under reduced pressure. Dissolution of the resulting dark residue in Et_2O, followed by filtration and storage at $−35 ^\circ$C overnight produced greenish-black crystals suitable for X-ray analysis, which were collected and dried in vacuo. Yield: 0.118 g, 0.100 mmol, 66 %.

$^1$H NMR (400.1 MHz, C_6D_6, 20 °C): $\delta = 7.44$ (m, 4H, PhNO), 7.30 (t, 4H, J = 8 Hz, p-Dipp), 7.17 (d, 8H, J = 8 Hz, m-Dipp), 7.00 (m, 6H, PhNO), 6.89 (m, 6H, m-Ph and p-Ph), 2.61 (septet, 8H, J = 7 Hz, CH(CH_3)_2), 1.23 (d, 24H, J = 7 Hz, CH(CH_3)_2), 1.10 (d, 24H, J = 7 Hz, CH(CH_3)_2) ppm. $^{13}$C{^1H} NMR (125.7 MHz, C_6D_6, 20 °C): $\delta = 164.3$ (ON–C_ipso), 159.0 (C≡N), 146.4, 139.4, 134.3, 130.0, 129.8, 128.9, 128.6, 123.6, 120.6, 31.4 (CH(CH_3)_2), 24.6 (CH(CH_3)_2), 24.4 (CH(CH_3)_2) ppm. FTIR (KBr pellet): (v_{CN}) 2185, 2144 and 2113 cm$^{-1}$, also 3060, 2961, 2926, 2867, 1571, 1460, 1450,
1317, 1177, 1056, 757 cm\(^{-1}\). Anal. calcd. for C\(_{74}H_{84}N_4O_2Pd\): C, 76.10; H, 7.25; N, 4.80. Found: C, 76.07; H, 7.42; N, 4.62.

2.8 Isocyanide Exchange Reactions

**Reaction between Pd(CNAr\(^{\text{Dipp2}}\))\(_2\) (2) and an additional equivalent of CNAr\(^{\text{Dipp2}}\).** To a solution of Pd(CNAr\(^{\text{Dipp2}}\))\(_2\) (0.015 g, 0.015 mmol) in C\(_6\)D\(_6\) (0.5 mL) was added a solution of CNAr\(^{\text{Dipp2}}\) (0.007 g, 0.016 mmol, 1.07 equiv) in C\(_6\)D\(_6\) (0.3 mL). The reaction mixture was analyzed by \(^1\)H NMR spectroscopy ca. 10 min after addition. \(^1\)H NMR spectra taken 1 h, 4 h, and 20 h after addition were identical.

**Variable temperature \(^1\)H NMR studies on a 1:1 Pd(CNAr\(^{\text{Dipp2}}\))\(_2\)/CNAr\(^{\text{Dipp2}}\) mixture.** To a solution of Pd(CNAr\(^{\text{Dipp2}}\))\(_2\) (0.025 g, 0.026 mmol) in toluene-\(d_8\) (0.5 mL) was added a solution of CNAr\(^{\text{Dipp2}}\) (0.011 g, 0.026 mmol, 1.0 equiv) in toluene-\(d_8\) (0.3 mL). A series of \(^1\)H NMR spectra were then recorded for this sample from −80 °C to +20 °C at 10 °C intervals.

**Supplemental ambient temperature (20 °C) \(^1\)H NMR (400.1 MHz) data for Pd(CNAr\(^{\text{Dipp2}}\))\(_2\) and CNAr\(^{\text{Dipp2}}\) in toluene-\(d_8\):**

Pd(CNAr\(^{\text{Dipp2}}\))\(_2\), \(\delta = 7.26\) (t, 2H, \(J = 8\) Hz, \(p\)-Dipp), 7.13 (d, 4H, \(J = 8\) Hz, \(m\)-Dipp), 6.92 (t, 1H, \(J = 8\) Hz, \(p\)-Ph), 6.91 (d, 2H, \(J = 8\) Hz, \(m\)-Ph), 2.58 (septet, 4H, \(J =\)
8 Hz, \(\text{CH(CH}_3\text{)}_2\), 1.20 (d, 12H, \(J = 8\) Hz, \(\text{CH(CH}_3\text{)}_2\)), 1.08 (d, 12H, \(J = 8\) Hz, \(\text{CH(CH}_3\text{)}_2\)) ppm.

\(\text{CNAr}^{\text{Dipp}}\) \(\delta = 7.27\) (t, 2H, \(J = 8\) Hz, \(p\)-Dipp), 7.15 (d, 4H, \(J = 8\) Hz, \(m\)-Dipp), 6.96 (s, 3H, \(J = 8\) Hz, \(m\)-Ph and \(p\)-Ph), 2.66 (septet, 4H, \(J = 8\) Hz, \(\text{CH(CH}_3\text{)}_2\)), 1.27 (d, 12H, \(J = 8\) Hz, \(\text{CH(CH}_3\text{)}_2\)), 1.09 (d, 12H, \(J = 8\) Hz, \(\text{CH(CH}_3\text{)}_2\)) ppm.

### 2.9 Suzuki-Miyaura Cross-Coupling Reactions Mediated by \(\text{Pd(CNAr}^{\text{Dipp}})\text{)}_2\) (2)

**Procedure to produce 2,4,6-trimethylbiphenyl.** A mixture of \(\text{Pd(CNAr}^{\text{Dipp}})\text{)}_2\) (0.0024 g, 5 mol%), \(\text{K}_3\text{PO}_4\) (0.318 g, 1.5 mmol, 3.0 equiv), phenylboronic acid (0.122 g, 1.0 mmol, 2.0 equiv), 2-bromomesitylene (0.076 mL, 0.5 mmol), and \(\text{THF}(2.0\text{ mL})\) was magnetically stirred in a sealed 25 mL Airfree® storage vessel under argon at room temperature for 8 h. The solvent was removed under reduced pressure to give a residue that was dissolved in water (6 mL) and extracted with hexane (3 x 2 mL). The organic layers were combined and concentrated under reduced pressure to give crude 2,4,6-trimethylbiphenyl that was purified by flash chromatography, eluting with hexane. Yield of run 1: 0.091 g, 0.46 mmol, 92 %. Yield of run 2: 0.095 g, 0.48 mmol, 96 %. \(^1\text{H NMR (300.1 MHz, C}_6\text{D}_6, 20^\circ\text{C})}: \delta = 7.48-7.45 \text{ (m, 1H)}, 7.24–7.19 \text{ (m, 2H), 7.07–7.05 \text{ (m, 2H), 6.87 \text{ (s, 2H), 2.21 \text{ (s, 3H, p-CH}_3\text{), 2.04 \text{ (s, 6H, o-CH}_3\text{)}} \text{ ppm. HRMS (EI) m/z calcd. for C}^{15}\text{H}^{16}: (M)^+, 196.1252. \text{ Found: 196.1248.}
Procedure to produce 2-methylbiphenyl. A mixture of Pd(CNArDipp$_2$)$_2$ (0.0024 g, 5 mol%), K$_3$PO$_4$ (0.318 g, 1.5 mmol, 3.0 equiv), phenylboronic acid (0.122 g, 1.0 mmol, 2.0 equiv), 2-bromotoluene (0.060 mL, 0.5 mmol), and THF (2.0 mL) was magnetically stirred in a sealed 25 mL Airfree® storage vessel under argon at room temperature for 8 h. The solvent was removed under reduced pressure to give a residue that was dissolved in water (6 mL) and extracted with hexane (3 x 2 mL). The organic layers were combined and concentrated under reduced pressure to give crude 2,4,6-trimethylbiphenyl that was purified by flash chromatography, eluting with hexane. Yield of run 1: 0.081 g, 0.48 mmol, 96 %. Yield of run 2: 0.079 g, 0.47 mmol, 94 %. $^1$H NMR (300.1 MHz, C$_6$D$_6$, 20 °C): $\delta =$ 7.24–7.11 (m, 9H), 2.15 (s, 3H, o-$\text{C}_3\text{H}_3$) ppm. HRMS (EI) $m/z$ calcd. for C$_{13}$H$_{12}$: (M)$^+$, 168.0939. Found: 196.1248.
2.10 Computational Details

Density Functional Theory calculations were performed with the Amsterdam Density Functional (ADF) program suite,\textsuperscript{61,62} version 2007.01.\textsuperscript{63} For all atoms, the triple-\(\zeta\) Slater-type orbital TZ2P ADF basis set was utilized without frozen cores. Relativistic effects were included by use of the zero-order regular approximation (ZORA).\textsuperscript{64,65} The local density approximation of Vosko \textit{et al.}\textsuperscript{66} (VWN) was coupled with the generalized gradient approximation corrections described by Becke\textsuperscript{67} and Perdew\textsuperscript{68,69} for electron exchange and correlation, respectively. Crystallographic atomic coordinates were used as input where appropriate. Optimized geometries and

\begin{figure}[h]
  \centering
  \includegraphics[width=\textwidth]{figure224.png}
  \caption{HRMS (EI) of 2-methylbiphenyl.}
\end{figure}
molecular orbitals were visualized with the ADFView graphical routine of the ADF-GUI.\textsuperscript{70}

DFT calculations were performed on a home-built 72-CPU (1 x 8 master, 8 x 8 slave) Rocks 4.3 Linux cluster featuring Intel Xeon E5335 Quad-Core 2.00 GHz processors. Job control was implemented with the Sun Grid Engine v. 5.3.

\textbf{2.11 Crystallographic Structure Determinations}

\textbf{General considerations.} Single crystal X-ray structure determinations were carried out at low temperature on a Bruker P4, Platform, or Kappa Diffractometer equipped with a Bruker APEX detector. All structures were solved by direct methods with SIR 2004\textsuperscript{71} and refined by full-matrix least-squares procedures utilizing SHELXL-97.\textsuperscript{72} Crystallographic data collection and refinement information are listed in Tables 2.3-2.6. The crystal structures of Pd(η\textsuperscript{2}-N,N-Ar\textsuperscript{F1}NNAr\textsuperscript{F1})(CNAr\textsuperscript{Dipp2})\textsubscript{2} (10) and Pd(η\textsuperscript{2}-N,N-Ar\textsuperscript{F2}NNAr\textsuperscript{F2})(CNAr\textsuperscript{Dipp2})\textsubscript{2} (11) contain trifluoromethylphenyl-group positional disorder, which was modeled and refined. The crystal structure of 11 additionally contains di-isopropylphenyl-group positional disorder, which was also modeled and refined.
Table 2.3. Crystallographic Data Collection and Refinement Information for trans-PdCl₂(CNAr\text{Dipp}²)₂, Pd(CNAr\text{Dipp}²)(CNAr\text{Dipp}²)\cdot\text{THF}, and trans-PdI₂(CNAr\text{Dipp}²)₂.

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Table 2.4. Crystallographic Data Collection and Refinement Information for [(THF)Pd(Η²-C,N-(MeC=NAr\text{Dipp}²))(CNAr\text{Dipp}²)OTf•THF, [TIPd(CNAr\text{Dipp}²)₂]OTf, and trans-PdCl(Bz)(CNAr\text{Dipp}²)₂•THF.

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### Table 2.5. Crystallographic Data Collection and Refinement Information for trans-PdBr(Mes)(CNArDipp2)2•Et2O, Pd(n²-O2)(CNArDipp2)2, and Pd(η²-N,N- (ArF1NNArF1)(CNArDipp2)2.

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### Table 2.6. Crystallographic Data Collection and Refinement Information for Pd(η²-N,N-ArF²NNArF²)(CNArDipp2)2, Pd(η²-O,N-PhNO)(CNArDipp2)2, and Pd(κ²-N-PhNO)2(CNArDipp2)2•Et2O.

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2.12 References


2.13 Acknowledgments

Chapter 2 is adapted with permission from Labios, L. A.; Millard, M. D.; Rheingold, A. L.; and Figueroa, J. S. “Bond Activation, Substrate Addition and Catalysis by an Isolable Two-Coordinate Pd(0) Bis-Isocyanide Monomer” *Journal of the American Chemical Society*, 2009, 131, 11318-11319. Copyright 2009 American Chemical Society. The dissertation author is the primary author of this paper.
Chapter 3

Generation and Stabilization of a Catalytically Active Palladium(0) Mono-Isocyanide Intermediate in Suzuki-Miyaura Cross-Coupling Reactions

3.1 Introduction

The widespread utility of palladium-catalyzed cross-coupling reactions for the formation of carbon-carbon, carbon-nitrogen, and carbon-oxygen bonds has inspired numerous advancements in catalysis chemistry. Cross-coupling reactions are indeed prevalent in the syntheses of pharmaceutical drug molecules, natural products, and polymers. Such applications have sparked interest in constructing new metal complexes and supporting ligands to pave avenues towards more complex molecules. Additionally, various strategies have been developed over the past 20 years to expand the substrate scope, lower the catalyst loadings, and increase the product yields of these transformations.

The use of electron-rich and sterically demanding phosphine ligands has historically proven to be successful in attaining such goals. In 1998, Littke and Fu
reported a method for Pd-catalyzed Suzuki cross-couplings of unactivated aryl chlorides that involved P'TBu₃ as the ligand.³ This study was one of the first to demonstrate efficient coupling of unactivated aryl chlorides,¹² which are known to be difficult cross-coupling partners. Within that same year, Buchwald and co-workers reported a highly active Pd catalyst system employing an aminophosphine ligand (A, Figure 3.1) for room temperature Suzuki coupling and amination reactions of unactivated aryl chlorides.⁴ Additional dialkylphosphanylbiaryl derivatives of this ligand (Figure 3.1) were subsequently shown to permit much lower catalyst loadings (0.000001‒0.02 mol % Pd)¹³ and wider substrate scopes¹⁴,¹⁵ while achieving high yields in the aforementioned coupling reactions. The efficacy of phosphine ligands in these reactions is ascribed to their electron-rich nature, which is widely thought to facilitate oxidative addition, particularly across strong C‒Cl bonds.

![Figure 3.1. Dialkylphosphanyl ligands featured in cross-coupling studies by Buchwald and co-workers. Adapted from references 9, 13‒15.](Image)

With the wide variety of phosphine-based catalytic systems employed in cross-coupling chemistry, it is surprising that only a few reports describe the use of preformed Pd(0) phosphine complexes as catalysts. Beller and co-workers claimed the first example, wherein 1,6-diene-stabilized zerovalent Pd(PR₃) precatalysts were synthesized and isolated prior to use (Figure 3.2).¹⁶ Building off their preliminary
success with Pd$_2$(dba)$_3$/P$_t$Bu$_3$ (dba = dibenzylideneacetone) as a catalyst system for Negishi coupling of electron-rich aryl chlorides, Dai and Fu\textsuperscript{17} investigated the catalytic activity of Pd(P$_t$Bu$_3$)$_2$.\textsuperscript{18} The findings of this study demonstrated that the ready-made Pd(0) precatalyst performed just as effectively and was used to obtain hindered biaryls in relatively high yields (76–96 %).\textsuperscript{17} The most notable example is Buchwald’s SPhos-Pd(dba) (SPhos = 2-(2’,6’-dimethoxybiphenyl)-dicyclohexylphosphine) complex, which has been structurally characterized.\textsuperscript{19–21} SPhos-Pd(dba) indeed exhibited remarkable catalytic activity and stability (vide infra) in Suzuki-Miyaura coupling reactions to produce tri- and tetra-ortho-substituted biaryls at low catalyst loadings.

![Figure 3.2. Preformed zerovalent 1,6-diene-stabilized Pd phosphine precatalysts for cross-coupling. Adapted from reference 16.](image)

Catalytic systems featuring bulky N-heterocyclic carbene (NHC) ligands have also gained prestige within the realm of cross-coupling chemistry. While they share similar $\sigma$-donating characteristics as phosphine ligands, NHCs have been shown to impart higher thermal and kinetic stability to zerovalent Pd complexes.\textsuperscript{22,23} Indeed, numerous homoleptic bis(NHC) complexes of Pd(0) have been isolated and structurally characterized. Such complexes date back to the late 1990s with Pd(I’Bu)$_2$ (I’Bu = 1,3-di-tert-butylimidazol-2-ylidene) (E, Figure 3.3), which was prepared by
Cloke and co-workers via metal vapor synthesis.\textsuperscript{24} A noteworthy feature of \( \text{Pd}(\text{tBu})_2 \) is its resistance towards thermal degradation by ligand dissociation processes, making it an ideal candidate for catalytic applications. More sterically hindered \( \text{Pd(NHC)}_2 \) derivatives were subsequently prepared (complexes F-I, Figure 3.3) and employed as precatalysts in cross-coupling reactions.\textsuperscript{6,9,25,26} One such example is \( \text{Pd(1Ad)}_2 \) (1Ad = 1,3-bis(adamantyl)imidazol-2-ylidene) (F, Figure 3.3), which was reported as the first of its kind to exhibit high catalytic activity for Suzuki coupling of aryl chlorides at ambient temperature.\textsuperscript{8}

![Figure 3.3. Zerovalent Pd(NHC)$_2$ precatalysts for cross-coupling. Adapted from references 5–7, 22–24.](image)

With the advent of such efficient ligand platforms, increasing attention has centered on ascertaining the nature of the catalytically active species in cross-coupling reactions. Previous investigations by Fu\textsuperscript{27} and Nolan\textsuperscript{28}, for example, have
demonstrated that cross-coupling reactions were most efficient when a 1:1 ratio of ligand to Pd was employed. Further, Hartwig and co-workers\textsuperscript{29} have reported extremely high catalytic activity for the Pd mono-phosphine dimer $\text{Pd}_2(\mu$-Br)$_2(\text{PrBu}_3)_2$\textsuperscript{30,31} in amination and Suzuki-Miyaura cross-coupling reactions. These observations are attributed to the formation of monoligated [Pd(0)L] species, which are proposed to serve as the catalytically active intermediates in cross-coupling reactions.\textsuperscript{26-28,32,33} These species are generated via ligand dissociation from their 14-electron Pd(0)L$_2$ precursors. Once generated, [Pd(0)L] presumably mediates the subsequent oxidative addition, transmetalation, and reductive elimination steps in cross-coupling reactions (Scheme 3.1).

\begin{center}
\textbf{Scheme 3.1.} General mechanism for cross-coupling reactions mediated by the presumed catalytically active species Pd(0)L.
\end{center}

To access these reactive intermediates, ligand construction has focused on steric stabilization of low-coordinate, zerovalent Pd centers. Representative examples
of phosphine and NHC ligands that have been sterically tuned to promote ligand
dissociation on Pd(0)L₂ complexes and thereby favor the formation of monoligated
[Pd(0)L]²⁻²⁸,³²,³³ are illustrated in Figures 3.1 and 3.3, respectively. Indeed, the high
catalytic activities described above for systems featuring these sterically bulky
phosphine and NHC ligands were attributed to the presence of 12-electron, mono-
coordinated [Pd(0)L] intermediates.

Electronic factors have also played an important role in ligand design to
stabilize unsaturated Pd(0) complexes. For instance, the σ-donating property of NHC
and PR₃ ligands is accredited for strong metal-ligand binding in Pd(0) complexes, and
is thus considered to provide high thermal stability and catalyst longevity.²²,²³
However, metal-ligand π interactions are also proposed to impart stability within Pd(0)
complexes.³⁴,³⁵ This is exemplified by Buchwald’s dialkylphosphanylbiaryl complex
SPhos-Pd(dba).¹⁹-²¹ While the SPhos ligand provides sufficient sterical bulk to promote
[Pd(0)L] formation, structural studies reveal a stabilizing η¹-arene interaction between
Pd(0) and the ipso carbon on the distal ring (Figure 3.4). This π interaction presumably
contributes to the long catalyst lifetime exhibited by the complex.

![Figure 3.4. SPhos-Pd(dba) complex featuring a stabilizing π interaction with Cᵢᵖₛₒ. Adapted from references 19-21.](image)
It thus seems reasonable that π-acidic ligands could be used to effectively stabilize electron-rich, mono-coordinated [Pd(0)L] species. Surprisingly, there are only a few examples of π-acidic ligands in cross-coupling chemistry to date. Among these are alkene and phosphite ligands reported by Fairlamb\textsuperscript{36} and Bedford,\textsuperscript{37,38} respectively. While the π-acidic properties of these ligands are believed to promote catalyst longevity within cross-coupling reactions, additional studies on such catalytic systems are limited. Accordingly, we were prompted to pursue a detailed investigation of the catalytic competency of the zerovalent bis-isocyanide monomer Pd(CNAr\textsubscript{Dipp}2)\textsubscript{2} (2). As described in Chapter 2, Pd(CNAr\textsubscript{Dipp}2)\textsubscript{2} (2) mediated the Suzuki cross-coupling of aryl bromides with phenyl boronic acid under ambient conditions. Results from these preliminary unoptimized test screens also encouraged us to target catalyst precursors containing a 1:1 Pd/CNAr\textsubscript{Dipp}2 ratio. Indeed, DFT calculations on the proposed [Pd(0)(CNAr\textsubscript{Dipp}2)] species demonstrate stabilizing metal-ligand π-back bonding interactions (Figure 3.5). In contrast, such interactions are negligible in metal-NHC complexes, wherein σ-donation from the ligand to the metal dominates.\textsuperscript{39-41}

Herein we report kinetic, mechanistic and structural evidence for a monoligated [Pd(0)L] species within the Pd(CNAr\textsubscript{Dipp}2)\textsubscript{2}-based catalytic system. Synthetic strategies to obtain complexes with a 1:1 ligand to Pd ratio are also presented and culminate in the isolation and structural characterization of a catalytically competent Pd(0) mono-isocyanide species. The latter is a notable example of the steric and electronic stabilization of [Pd(0)L] using the strongly π-acidic and sterically encumbering \textit{m}-terphenyl isocyanide CNAr\textsubscript{Dipp}2.
3.2 Suzuki-Miyaura Cross-Coupling Mediated by Pd(CNA\textsubscript{r\textsubscript{Dipp\textsubscript{2}}})\textsubscript{2} (2)

In our initial experiments, 5 mol % of Pd(CNA\textsubscript{r\textsubscript{Dipp\textsubscript{2}}})\textsubscript{2} (2) catalyzed the Suzuki-Miyaura cross-coupling of aryl bromides with phenylboronic acid (PhB(OH)\textsubscript{2}) at room temperature within 8 h using K\textsubscript{3}PO\textsubscript{4} as base in THF.\textsuperscript{42} Since then, we discovered that cross-coupling reactions could be performed at mild temperatures (RT and 60 °C) using a lower catalyst loading of 1 mol % Pd(CNA\textsubscript{r\textsubscript{Dipp\textsubscript{2}}})\textsubscript{2} (2). The newly optimized reaction conditions also included the use of a strong base, NaO\textsuperscript{t}Bu, to better aid transmetalation,\textsuperscript{43,44} and \textsuperscript{t}PrOH as the solvent. As shown in Table 3.1, Pd(CNA\textsubscript{r\textsubscript{Dipp\textsubscript{2}}})\textsubscript{2} (2) promoted the cross-coupling of various unactivated aryl bromides and mono-ortho-substituted aryl boronic acids at room temperature within 8 h. Particularly, di-ortho-
substituted biaryls were produced under these conditions in moderate yields (Table 3.1, entries 13-14). Increasing the temperature to 60 °C enabled the coupling of more difficult substrates. For instance, a wider variety of hindered aryl bromides were coupled to furnish a larger number of di-ortho-substituted biaryls (Table 3.2, entries 5-8). Moreover, the electron deficient 2,4-difluorophenylboronic acid was successfully coupled under these conditions (Table 3.2, entries 9-10).

Table 3.1. Suzuki-Miyaura Cross-Coupling Reactions of Unactivated Aryl Bromides at Room Temperature

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<th>Boronic Acid</th>
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<sup>a</sup> GC yield (isolated yield) based upon an average of two runs.
Table 3.2. Suzuki-Miyaura Cross-Coupling Reactions of Hindered Aryl Bromides at 60 °C

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<td>6</td>
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<td><img src="image17" alt="Image" /></td>
<td><img src="image18" alt="Image" /></td>
<td>93 (76)</td>
</tr>
<tr>
<td>7</td>
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<td><img src="image20" alt="Image" /></td>
<td><img src="image21" alt="Image" /></td>
<td>87 (66)</td>
</tr>
<tr>
<td>8</td>
<td><img src="image22" alt="Image" /></td>
<td><img src="image23" alt="Image" /></td>
<td><img src="image24" alt="Image" /></td>
<td>94 (74)</td>
</tr>
<tr>
<td>9</td>
<td><img src="image25" alt="Image" /></td>
<td><img src="image26" alt="Image" /></td>
<td><img src="image27" alt="Image" /></td>
<td>99 (77)</td>
</tr>
<tr>
<td>10</td>
<td><img src="image28" alt="Image" /></td>
<td><img src="image29" alt="Image" /></td>
<td><img src="image30" alt="Image" /></td>
<td>99 (77)</td>
</tr>
</tbody>
</table>

<sup>a</sup> GC yield (isolated yield) based upon an average of two runs.

It is worth noting that the reactions listed in entries 2, 5, and 6 of Table 3.1 and entry 2 of Table 3.2 did not result in homocoupling of aryl boronic acids. These reactions are highlighted specifically because their cross-coupled products are isomers of the homocoupled biaryls, 2,2’-dimethylbiphenyl and 4,4’-dimethylibiphenyl. Accordingly, 2,2’-dimethylbiphenyl and 4,4’-dimethylibiphenyl were independently prepared from homocoupling reactions of o-tolyl and p-tolyl boronic acid, respectively. Their corresponding GC-MS traces are shown in Figures 3.6 and 3.7. In comparison, the GC-MS traces of the cross-coupled biphenyls 2,4’-dimethylibiphenyl (Tables 3.1 and 3.2, entry 2), 3,4’-dimethylibiphenyl (Table 3.1, entry 5), and 2,3’-dimethylibiphenyl (Table 3.1, entry 6) (Figures 3.8-3.10) differ distinctly from those of the homocoupled products. 3,4’-dimethylibiphenyl and 4,4’-dimethylibiphenyl were analyzed as a mixture to demonstrate that they can be distinguished separately despite their very similar retention times (Figure 3.9).
Figure 3.6. GC-MS trace of 2,2'-dimethylbiphenyl.
Figure 3.7. GC-MS trace of 4,4'-dimethylbiphenyl.

Figure 3.8. GC-MS trace of 2,4'-dimethylbiphenyl.
This catalytic system is the first example in which the cross-coupling of unactivated and hindered substrates is mediated by a homoleptic Pd(0) bis-isocyanide complex under mild conditions. While several divalent Pd complexes supported by isocyanide ligands have previously been reported to catalyze Suzuki-Miyaura cross-coupling reactions, their catalytic systems either featured mixed isocyanide-carbene ligand platforms\textsuperscript{46-48} or required more forcing reaction conditions (ca. 100 °C, 18 h).\textsuperscript{49}
Despite these advances, Pd(CNArDipp2)2 (2) did not effect the coupling of unactivated aryl chlorides. The π-acidity of the CNArDipp2 ligands likely attenuates the electron-rich nature of the Pd(0) center, thus rendering it less reactive towards aryl chlorides. Although Pd complexes supported by π-acidic phosphite ligands have been shown to couple aryl chlorides,⁵⁷,⁵⁸ the oxidative addition of these substrates is reputedly more difficult across Pd(0) centers with less electron-rich supporting groups.⁵⁰ An additional limitation of this system is its inability to produce tri-ortho and tetra-ortho substituted biaryls. While the reactions of hindered aryl bromides proceeded at increased temperature, the coupling of 2,6-disubstituted boronic acids was not observed. This steric inhibition likely stems from an excess equivalent of
CNAr$^{\text{Dipp}2}$ in the Pd(CNAr$^{\text{Dipp}2}$)$_2$ (2) system, which could hamper the formation of a catalytically active mono-coordinated [Pd(0)L] species.

### 3.3 Kinetics of Oxidative Addition

The proposed role of [Pd(0)L] in the Suzuki-Miyaura cross-coupling reaction within this system is illustrated in Scheme 3.2. Reversible ligand dissociation from Pd(0)L$_2$ initiates the cycle to form monoligated [Pd(0)L], which then oxidatively adds aryl halide (Path A, Scheme 3.2). Base-mediated transmetalation between the resulting Pd(II)ArX complex and boronic acid, followed by reductive elimination, produces cross-coupled biaryl with concomitant regeneration of [Pd(0)L]. While oxidative addition can alternatively proceed through an associative pathway$^{51,52}$ (Path B, Scheme 3.2), theoretical$^{53,54}$ and experimental$^{55-58}$ studies have demonstrated that a dissociative mechanism more appropriately describes systems possessing sterically demanding ligands. For example, Hartwig and co-workers discovered that monomeric$^{59,60}$ and dimeric$^{2,61}$ [LPd(II)ArBr] products were generated from oxidative addition reactions between aryl bromides and Pd(0)L$_2$ complexes containing bulky trialkylphosphine ligands. These observations suggested the intermediacy of monoligated [Pd(0)L] species prior to oxidative addition, thereby contributing to the proposals for a dissociative mechanism.
As previously demonstrated, treatment of Pd(CNArDipp2)2 (2) with MesBr in Et2O produced trans-PdBr(Mes)(CNArDipp2)2 (8, Scheme 3.3).42 The oxidative addition reaction producing trans-PdBr(Mes)(CNArDipp2)2 (8) may proceed through one of two pathways: 1) a dissociative pathway involving sequential ligand dissociation, oxidative addition, and ligand reassociation (Path A, Scheme 3.2), or 2) an associative pathway in which oxidative addition to a 14-electron Pd(0)L2 complex is followed by cis-trans isomerization (Path B, Scheme 3.2). Kinetic data on the reaction between Pd(CNArDipp2)2 (2) and aryl bromide would help deduce which of these pathways is more pertinent to the current system. Accordingly, the rate law for a dissociative mechanism can be expressed as:

$$\text{rate} = \frac{-d[PdL_2]}{dt} = \frac{k_1k_2[PdL_2][ArX]}{k_{-1}[L] + k_2[ArX]}$$
Meanwhile, an associative mechanism can be modeled as a bimolecular reaction, giving:

$$\text{rate} = -\frac{d[PdL_2]}{dt} = k_3[PdL_2][ArX]$$  \hspace{1cm} (2)

Using a large excess of aryl halide would allow the reactions to become pseudo first-order in $[PdL_2]$, simplifying both rate laws to give:

$$\text{rate} = -\frac{d[PdL_2]}{dt} = k_{obs}[PdL_2]$$  \hspace{1cm} (3)

Based on these models, the rate of oxidative addition following a dissociative pathway will decrease with the addition of free ligand to the reaction mixture.

Scheme 3.3. Synthesis of trans-PdBr(Mes)(CNAr^{Dipp}_2) \text{(8)} and trans-PdBr(m-Xyl)(CNAr^{Dipp}_2) \text{(14)}.

The reaction between Pd(CNAr^{Dipp}_2) \text{(2)} and MesBr (10 equiv) in C_6D_6 at 25 °C was monitored by ^1H NMR spectroscopy, with ferrocene as the internal standard. Complete consumption of Pd(CNAr^{Dipp}_2) \text{(2)} occurred within 1 h. In accord with pseudo-first order conditions, the plot of ln[Pd(CNAr^{Dipp}_2)] over time was linear past three half-lives (Figure 3.11). The slope of this line was then used to determine the
observed rate constant for this reaction ($k_{\text{obs}} = 1.47(2) \times 10^{-3} \text{ s}^{-1}$) (Table 3.3, entry 1). Reactions containing added ligand (0.1, 0.25, 0.5, and 1 equiv) were likewise assayed (Figure 3.11) and exhibited lower values of $k_{\text{obs}}$ compared to the reaction without added ligand (Table 3.3, entries 2-5). For instance, oxidative addition proceeded more slowly in the presence of 0.1 equiv of ligand (3 h), whereas 1 equiv of ligand drastically prolonged the reaction to 60 h (Table 3.3). The plot of $k_{\text{obs}}$ over the concentration of additional CNAr$_2^{Dipp2}$ depicts a nonlinear inverse dependence, which reaches a saturation point near 0.5 equiv (Figure 3.12).

![Figure 3.11. Effect of added CNAr$_2^{Dipp2}$ ligand (■ 0 equiv, ● 0.10 equiv, ▲ 0.25 equiv, ♦ 0.50 equiv, x 1.0 equiv) on the rate of oxidative addition of MesBr to Pd(CNAr$_2^{Dipp2}$)$_2$ (2) plotted in first-order coordinates.](image)

Table 3.3. Observed Rate Constants of Oxidative Addition Reactions With Added CNAr$_2^{Dipp2}$

<table>
<thead>
<tr>
<th>Equiv CNAr$_2^{Dipp2}$</th>
<th>$k_{\text{obs}}$ (s$^{-1}$)</th>
<th>Avg rxn time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$1.47(2) \times 10^{-3}$</td>
<td>1</td>
</tr>
<tr>
<td>0.1</td>
<td>$5.59(4) \times 10^{-4}$</td>
<td>3</td>
</tr>
<tr>
<td>0.25</td>
<td>$7.24(5) \times 10^{-5}$</td>
<td>10</td>
</tr>
<tr>
<td>0.50</td>
<td>$2.49(4) \times 10^{-5}$</td>
<td>&gt;12</td>
</tr>
<tr>
<td>1.0</td>
<td>$2.52(2) \times 10^{-5}$</td>
<td>&gt;12</td>
</tr>
</tbody>
</table>
Figure 3.12. Nonlinear inverse dependence of $k_{obs}$ on CNAr$^{Dipp2}$ concentration.

This observed rate inhibition in the presence of excess ligand is consistent with a dissociative mechanism, rather than the formation of a less reactive tris-isocyanide complex, Pd(CNAr$^{Dipp2}$)$_3$. To further illustrate this point, the reaction between Pd(CNAr$^{Dipp2}$)$_2$ (2) and MesBr (10 equiv) in the presence of CNAr$^{Dipp2}$ (1 equiv) in C$_6$D$_6$ at 25 °C was monitored hourly by $^1$H NMR spectroscopy (Figure 3.13). Initial broadening of the signals at 2.641 ppm (not pictured) and 1.239 ppm is consistent with ligand exchange between Pd(CNAr$^{Dipp2}$)$_2$ (2) and CNAr$^{Dipp2}$, as previously reported. Decoalescence of these signals with the consumption of Pd(CNAr$^{Dipp2}$)$_2$ (2) gradually gave rise to the signals corresponding to CNAr$^{Dipp2}$, with distinct doublets at $\delta = 1.284$ and 1.093 ppm.

We were additionally interested to determine if the steric properties of the aryl bromide have a significant effect on the rate of oxidative addition. For this purpose, the less sterically congested derivative, trans-PdBr($m$-Xyl)(CNAr$^{Dipp2}$)$_2$ ($m$-Xyl = C$_6$H$_3$-3,5-Me$_2$) (14, Scheme 3.2 and Figure 3.14), was prepared by addition of
Figure 3.13. $^1$H NMR (400 MHz, C$_6$D$_6$, 25 °C) stacked array monitoring the oxidative addition of MesBr to Pd(CNAr$^{Dipp_2}$)$_2$ (2) in the presence of 1.0 equiv CNAr$^{Dipp_2}$.

Figure 3.14. Molecular structure of trans-PdBr($m$-Xyl)(CNAr$^{Dipp_2}$)$_2$ (14). Selected bond distances (Å) and angles (°): Pd1–C1 = 1.966(3); Pd1–C2 = 1.962(3); Pd1–C63 = 2.024(3); Pd1–Br1 = 2.5016(5); C1–Pd1–C2 = 173.98(11); C63–Pd1–Br1 = 176.88(8).
(m-Xyl)Br to Pd(CNAr\textsuperscript{Dipp\textsubscript{2}}\textsubscript{2}) (2) in Et\textsubscript{2}O. In similarly monitored \textsuperscript{1}H NMR experiments, reactions between Pd(CNAr\textsuperscript{Dipp\textsubscript{2}}\textsubscript{2}) (2) and m-XylBr (10 equiv) in C\textsubscript{6}D\textsubscript{6} at 25 °C reached completion within 30 min. Kinetic analysis revealed a fairly small increase in the average observed rate constant for the reaction with m-XylBr ($k_{\text{obs}} = 2.46(3) \times 10^{-3}$ s\textsuperscript{-1}) relative to that with MesBr (Figure 3.15). In context, such a difference is negligible and suggests that the oxidative addition of aryl bromide poses little steric influence on the overall catalytic inhibition. So far, results from these experiments indicate the likelihood of a monoligated Pd(0)L intermediate for oxidative addition within this system.

**Figure 3.15.** Steric influence of aryl bromide on oxidative addition to Pd(CNAr\textsuperscript{Dipp\textsubscript{2}}\textsubscript{2}) (2) (▲ (m-XylBr), ■ MesBr).
3.4 Transmetalation Pathways

The inability of the Pd(CNAr\textsubscript{Dipp}\textsuperscript{2})\textsubscript{2}-based system to couple more hindered aryl boronic acids indicates additional steric inhibition within the transmetalation step. Similar observations reported in a previous study by Smith and co-workers were also attributed to steric factors pertaining to transmetalation.\textsuperscript{62} Accordingly, we sought to compare the rates of biaryl formation from both \textit{trans}-PdBr(\textit{Mes})(CNAr\textsubscript{Dipp}\textsuperscript{2})\textsubscript{2} (8) and \textit{trans}-PdBr(\textit{m}-Xyl)(CNAr\textsubscript{Dipp}\textsuperscript{2})\textsubscript{2} (14). To simplify the reaction conditions, we avoided the use of external base by employing aryltrifluoroborate salts [ArBF\textsubscript{3}]\textsuperscript{+} in lieu of aryl boronic acids. Organotrifluoroborate salts have served as arylating agents for cross-coupling reactions in the absence of base,\textsuperscript{63,64} and have additionally proven to be versatile reagents in Suzuki-Miyaura cross-coupling reactions.\textsuperscript{65,66} Their reactivity presumably stems from their similarity to anionic boronate compounds, which have traditionally been regarded as the active transmetalation species.\textsuperscript{43,44}

Surprisingly, treatment of both \textit{trans}-PdBr(\textit{Mes})(CNAr\textsubscript{Dipp}\textsuperscript{2})\textsubscript{2} (8) and \textit{trans}-PdBr(\textit{m}-Xyl)(CNAr\textsubscript{Dipp}\textsuperscript{2})\textsubscript{2} (14) with excess K[PhBF\textsubscript{3}] (10 equiv) did not effect biaryl formation, even after prolonged heating at 60 °C (Scheme 3.4). To overcome solubility limitations, the organic derivative (\textit{n}-Bu)\textsubscript{4}N[PhBF\textsubscript{3}] was prepared and utilized. Still, neither (\textit{n}-Bu)\textsubscript{4}N[PhBF\textsubscript{3}], nor water as a cosolvent, which has been shown to improve yields of cross-coupling reactions with trifluoroborate salts,\textsuperscript{67} induced the desired reaction. Moreover, cross-coupling between \textit{m}-XylBr and K[PhBF\textsubscript{3}] in the presence of Pd(CNAr\textsubscript{Dipp}\textsuperscript{2})\textsubscript{2} (2) (1 mol %) was not observed (Scheme
Addition of excess base to this reaction mixture instead prompted homocoupling of K[PhBF₃] to produce biphenyl.

**Scheme 3.4.** Attempted transmetalation (top) and cross-coupling (bottom) reactions with K[PhBF₃].

It is thus unlikely that boronate species promote transmetalation with Pd(II)ArX complexes in this system, as shown in Scheme 3.5 (Path A). This traditionally accepted transmetalation mechanism describes the formation of boronate anions from addition of base to boronic acid. In our system, however, the base may play a different role. For example, base may react directly with the aryl halide species Pd(II)ArX to generate an alkoxo Pd(II)Ar(OR) complex (Path B, Scheme 3.5). This alkoxo Pd(II)Ar(OR) species may then serve as the transmetalating agent in the presence of boronic acid (Path B, Scheme 3.5). Indeed, transmetalation reactions between alkoxo Pd(II)(OR) complexes and boronic acids have been observed in the absence of base. Kinetic studies by Hartwig and Amatore and Jutand also described preferences for this mechanism.
Accordingly, the aryl halide complexes \( \text{trans-PdBr(Mes)(CNAr}^{\text{Dipp2}})_{2} \) (8) and \( \text{trans-PdBr(m-Xyl)(CNAr}^{\text{Dipp2}})_{2} \) (14) were treated with NaOPr. Preliminary \(^1\)H NMR experiments provided evidence for the formation of new Pd species in these reactions. Additional studies on these products are forthcoming to elucidate whether alkoxo Pd(II)Ar(OR) species are indeed generated within the Pd(CNAr\(^{\text{Dipp2}}\))\(_{2}\)-based catalytic system. Such information would also offer further insight into the elusive transmetalation step and the steric factors associated with this process.

### 3.5 Synthesis of Monomeric and Dimeric Pd Mono-Isocyanide Complexes

Evidence acquired thus far implies that an unnecessary equivalent of CNAr\(^{\text{Dipp2}}\) in this catalytic system inhibits optimum activity. To overcome steric impediments due to excess ligand, we targeted complexes with a 1:1 Pd/CNAr\(^{\text{Dipp2}}\)
ratio. An equimolar mixture of PdCl₂ and trans-PdCl₂(CNAr\textsuperscript{Dipp}₂) \textsuperscript{2} (1) in EtOH/THF was stirred for 2 d to generate dimeric [(CNAr\textsuperscript{Dipp}₂)PdCl]₂(μ-Cl)₂ (15, Scheme 3.6).

The molecular structure of [(CNAr\textsuperscript{Dipp}₂)PdCl]₂(μ-Cl)₂ (15) features a dinuclear Pd complex in which each metal center is coordinated to one CNAr\textsuperscript{Dipp} ligand (Figure 3.15). [(CNAr\textsuperscript{Dipp}₂)PdCl]₂(μ-Cl)₂ (15) is reminiscent of the NHC-Pd halide dimers [(NHC)PdX₂] prepared by Shi and Qian\textsuperscript{76} and Nolan,\textsuperscript{28,77} which displayed exceptional catalytic activity in cross-coupling reactions. Likewise, [(CNAr\textsuperscript{Dipp}₂)PdCl]₂(μ-Cl)₂ (15) (1 mol % Pd) was found to cross-couple \textit{m}-XylBr and PhB(OH)₂ at room temperature. GC-MS analysis of these reactions revealed 82 % yield of biaryl product within 8 h (Table 3.4, entry 1).
Figure 3.16. Molecular structure of \([(\text{CNAr}^{\text{Dipp}2})\text{PdCl}]_2(\mu-\text{Cl})_2\) (15). Positional disorder on the Pd and Cl atoms is omitted for clarity.

Table 3.4. Cross-Coupling Screens of Pd Mono-Isocyanide Complexes

<table>
<thead>
<tr>
<th>Pd Mono-Isocyanide Complex</th>
<th>GC Yield</th>
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<tbody>
<tr>
<td>([(\text{CNAr}^{\text{Dipp}2})\text{PdCl}]_2(\mu-\text{Cl})_2) (15)</td>
<td>82 %</td>
</tr>
<tr>
<td>(\text{Pd}(\text{CNAr}^{\text{Dipp}2})(\eta^3-\text{allyl})\text{Cl}) (16)</td>
<td>6 %</td>
</tr>
<tr>
<td>([(\text{CNAr}^{\text{Dipp}2})\text{Pd}]_2(\mu-\eta^3-\text{allyl})(\mu-\text{O}^\text{Pr})) (17)</td>
<td>26 %</td>
</tr>
<tr>
<td>([\text{Pd}(\eta^3-\text{Dipp}-\mu-\text{CNAr}^{\text{Dipp}})]_3) (22)</td>
<td>83 %</td>
</tr>
</tbody>
</table>

Initial success with \([(\text{CNAr}^{\text{Dipp}2})\text{PdCl}]_2(\mu-\text{Cl})_2\) (15) prompted us to pursue additional Pd mono-isocyanide complexes. Accordingly, \([\text{Pd}(\text{allyl})\text{Cl}]_2\) was treated with 2 equiv of \text{CNAr}^{\text{Dipp}2} in THF to afford \(\text{Pd}(\text{CNAr}^{\text{Dipp}2})(\eta^3-\text{allyl})\text{Cl}\) (16, Scheme 3.7). The molecular structure of \(\text{Pd}(\text{CNAr}^{\text{Dipp}2})(\eta^3-\text{allyl})\text{Cl}\) (16) exhibits a distorted square-planar coordination geometry about Pd with the allyl moiety bound as a trihapto ligand (Figure 3.17). NHC analogues of \(\text{Pd}(\text{CNAr}^{\text{Dipp}2})(\eta^3-\text{allyl})\text{Cl}\) (16) have been reported by Nolan\textsuperscript{77,80} to effect cross-coupling reactions under activating
conditions involving alkoxide base and iPrOH. The standard conditions employed in our catalytic system were thus similarly applied here.

Scheme 3.7. Syntheses of monomeric and dimeric Pd mono-isocyanide complexes.

Reactions between (m-Xyl)Br and PhB(OH)₂ in the presence of 1 mol % of Pd(CNArDipp₂)(η³-allyl)Cl (16) resulted in only 6% GC yield to cross-coupled biaryl product within 8 h (Table 3.4, entry 2). Within this same time duration, reactions mediated by Pd(CNArDipp₂)₂ (2) achieved complete conversion. Such a decrease in catalytic performance prompted an investigation regarding the transformation of Pd(CNArDipp₂)(η³-allyl)Cl (16) under activating conditions. Thus, an equimolar mixture of Pd(CNArDipp₂)(η³-allyl)Cl (16) and NaO{Bu was stirred in iPrOH for 2 h to afford a beige solution from which a yellow solid was isolated. X-ray structural
determination revealed the formation of a dimeric \([(\text{CNAr}^{\text{Dipp}2})\text{Pd}]\) complex, yet crystallographic disorder about the bridging allyl and isopropoxide moieties precluded complete crystallographic characterization. Reduction from a divalent Pd center was implicated by $\nu_{\text{CN}}$ stretches (2116 and 2011 cm$^{-1}$, KBr) that are significantly lower in energy than that in Pd(\text{CNAr}^{\text{Dipp}2})(\eta^3\text{-allyl})\text{Cl} (16) ($\nu_{\text{CN}} = 2172$ cm$^{-1}$, KBr). The purity of the complex was confirmed by $^1$H NMR and elemental analysis, and consequently support a formulation of \([(\text{CNAr}^{\text{Dipp}2})\text{Pd}]_2(\mu-\eta^3\text{-allyl})(\mu-O'\text{Pr}) (17, Scheme 3.7). Two sets of signals corresponding to two chemically inequivalent flanking Dipp rings on the CNAr$^{\text{Dipp}2}$ ligands were observed in the $^1$H NMR spectrum, indicative of an asymmetric environment about the isocyanide ligand frameworks. Meanwhile, the instability of the product in solution over time at room temperature obviated the acquisition of $^{13}$C NMR data.

Figure 3.17. Molecular structure of one crystallographically independent molecule of Pd(\text{CNAr}^{\text{Dipp}2})(\eta^3\text{-allyl})\text{Cl} (16). Position disorder on the allyl group is omitted for clarity. Selected bond distances (Å) and angles (°): Pd1–C1 = 1.986(3); Pd1–Cl1 = 2.3478(11); C1–Pd1–Cl1 = 96.92(10).

Synthetic avenues to corroborate the connectivity of \([(\text{CNAr}^{\text{Dipp}2})\text{Pd}]_2(\mu-\eta^3\text{-allyl})(\mu-O'\text{Pr}) (17) led to the creation of other dimeric Pd(I) mono-isocyanide
complexes (Scheme 3.7). Treatment of \([{(CNArDipp^2)Pd}_2(\mu-\eta^3\text{-allyl})(\mu-O^iPr)} (17) with LDA resulted in clean substitution of the bridging isopropoxide fragment to afford \([{(CNArDipp^2)Pd}_2(\mu-\eta^3\text{-allyl})(\mu-N^i(Pr)_2)} (18, Scheme 3.7). Such behavior is noteworthy since isocyanide ligands in transition metal complexes are typically prone to nucleophilic attack by amines to form carbene complexes.81,82 Crystallographic characterization of \([{(CNArDipp^2)Pd}_2(\mu-\eta^3\text{-allyl})(\mu-N^i(Pr)_2)} (18) displays retention of the L–Pd–Pd–L(\mu-\eta^3\text{-allyl}) bonded framework (Figure 3.18). The Pd–Pd bond distance in \([{(CNArDipp^2)Pd}_2(\mu-\eta^3\text{-allyl})(\mu-N^i(Pr)_2)} (18) (2.5447(4) Å) is within the range found for dipalladium(I) complexes.83 Molecular asymmetry about the CNArDipp^2 frameworks is imposed by the nearly orthogonal orientation of the allyl plane with respect to the Pd coordination plane. This accounts for the two chemically inequivalent flanking Dipp groups on each isocyanide ligand observed in the ^1H NMR spectra of both dimers \([{(CNArDipp^2)Pd}_2(\mu-\eta^3\text{-allyl})(\mu-O^iPr)} (17) and \([{(CNArDipp^2)Pd}_2(\mu-\eta^3\text{-allyl})(\mu-N^i(Pr)_2)} (18). The stability of \([{(CNArDipp^2)Pd}_2(\mu-\eta^3\text{-allyl})(\mu-N^i(Pr)_2)} (18) is notable given that terminal alkylamido ligands are known to undergo β-hydride elimination to generate metal hydrides.84-87

To provide further evidence for a bridging isopropoxide moiety in \([{(CNArDipp^2)Pd}_2(\mu-\eta^3\text{-allyl})(\mu-O^iPr)} (17), the chloride complex \([{(CNArDipp^2)Pd}_2(\mu-\eta^3\text{-allyl})(\mu-Cl)} (19) was independently prepared from a comproportionation reaction between Pd(CNArDipp^2)_2 and 0.5 equiv of [Pd(allyl)Cl]_2 in Et_2O (19, Scheme 3.7). The molecular structure of \([{(CNArDipp^2)Pd}_2(\mu-\eta^3\text{-allyl})(\mu-Cl)} (19) reveals a dihedral angle of 69.44° between the allyl plane and the Pd–Pd–Cl plane (Figure 3.19). This decrease in the dihedral angle from 90° has been observed in other allyl-bridged dinuclear Pd(I)
complexes\textsuperscript{88-90} and purportedly results from increased overlap between the p-orbital of the central allyl carbon and the metal dσ-dσ and dπ-dπ orbitals.\textsuperscript{83,91,92}

Figure 3.18. Molecular structure of \([\text{CNAr}^{\text{Dipp}2}\text{Pd}]_2(\mu-\eta^3\text{-allyl})(\mu-\text{N}('\text{iPr})_2)\) (18). Positional disorder on the allyl group is omitted for clarity. Selected bond distances (Å) and angles (°): Pd1–Pd2 = 2.5447(4); Pd1–C1 = 1.922(4); Pd1–N1 = 2.125(3); Pd2–C2 = 1.921(4); Pd2–N1 = 2.130(3); C1–Pd1–Pd2 = 168.85(11); C2–Pd2–Pd1 = 164.99(11); Pd1–N1–Pd2 = 73.45(10).

Figure 3.19. Molecular structure of \([\text{CNAr}^{\text{Dipp}2}\text{Pd}]_2(\mu-\eta^3\text{-allyl})(\mu-\text{Cl})\) (19). Selected bond distances (Å) and angles (°): Pd1–Pd1’ = 2.5760(7); Pd1–C1 = 1.932(3); Pd1–C2 = 2.111(5); Pd1–C3 = 2.425(14); Pd1–Cl1 = 2.387(3); Pd1’–C3 = 2.341(15); Pd1’–C4 = 2.105(5); Pd1’–Cl1 = 2.395(3); C1–Pd1–Pd1’ = 176.72(9); C1–Pd1–C2 = 91.44(17); C1–Pd1–Cl1 = 123.55(11); C1’–Pd1’–C4 = 89.96(18); C1’–Pd1’–Cl1 = 121.53(11); Pd1–Cl1–Pd1’ = 65.18(8); C2–C3–C4 = 135.3(8).
Nucleophilic displacement of the chloride ligand in \([\text{CNAr}^\text{Dipp2}\text{Pd}]_2(\mu-\eta^3\text{-allyl})(\mu-\text{Cl})\) (19) was readily observed. Treatment of \([\text{CNAr}^\text{Dipp2}\text{Pd}]_2(\mu-\eta^3\text{-allyl})(\mu-\text{Cl})\) (19) with Na\text{O}^\text{iPr} and LDA independently generated \([\text{CNAr}^\text{Dipp2}\text{Pd}]_2(\mu-\eta^3\text{-allyl})(\mu-\text{O}^\text{iPr})\) (17) and \([\text{CNAr}^\text{Dipp2}\text{Pd}]_2(\mu-\eta^3\text{-allyl})(\mu-\text{N}(\text{iPr})_2)\) (18), respectively (Scheme 3.7). Likewise, addition of Na\text{O}^\text{tBu} afforded the corresponding tert-butoxide complex \([\text{CNAr}^\text{Dipp2}\text{Pd}]_2(\mu-\eta^3\text{-allyl})(\mu-\text{O}^\text{tBu})\) (20, Scheme 3.7). X-ray structural determination of \([\text{CNAr}^\text{Dipp2}\text{Pd}]_2(\mu-\eta^3\text{-allyl})(\mu-\text{O}^\text{tBu})\) (20) was achieved despite crystallographic disorder on the bridging groups (Figure 3.20). Distinct spectroscopic differences between \([\text{CNAr}^\text{Dipp2}\text{Pd}]_2(\mu-\eta^3\text{-allyl})(\mu-\text{O}^\text{iPr})\) (17) and \([\text{CNAr}^\text{Dipp2}\text{Pd}]_2(\mu-\eta^3\text{-allyl})(\mu-\text{O}^\text{tBu})\) (20) (\(\nu_{\text{CN}} = 2097\) and 2010 cm\(^{-1}\), KBr) are observed, thereby eliminating \([\text{CNAr}^\text{Dipp2}\text{Pd}]_2(\mu-\eta^3\text{-allyl})(\mu-\text{O}^\text{tBu})\) (20) as a byproduct of Pd(CNAr\text{Dipp2})(\eta^3\text{-allyl})Cl (16) activation. This implies that nucleophilic attack by isopropoxide, rather than the more basic tert-butoxide anion, is the predominant mechanism in the activation of Pd(CNAr\text{Dipp2})(\eta^3\text{-allyl})Cl (16).

**Figure 3.20.** Molecular structure of \([\text{CNAr}^\text{Dipp2}\text{Pd}]_2(\mu-\eta^3\text{-allyl})(\mu-\text{O}^\text{tBu})\) (20). Positional disorder on the Pd atoms, \(C_{\text{iso}}\) atoms, allyl and tert-butoxide groups is not shown.
3.6 Proposed Mechanism for Monoligated [Pd(0)L] Formation

The reaction between Pd(CNArDipp2)(η^3-allyl)Cl (16) and NaO/iPr in iPrOH is reminiscent of Nolan’s studies on the KO/iPr reduction of Pd(NHC)(η^3-allyl)Cl complexes to generate and trap [Pd(0)(NHC)] species in situ.77-80 [(CNArDipp2)Pd]2(μ-η^3-allyl)(μ-O/iPr) (17) is presumably generated via a similar mechanism involving a monoligated intermediate [Pd(0)(CNArDipp2)] (Scheme 3.8). First, NaO/iPr deprotonates iPrOH to generate isopropoxide anion. Nucleophilic displacement of Cl^- on Pd(CNArDipp2)(η^3-allyl)Cl (16) then produces the corresponding Pd-isopropoxide intermediate (i, Scheme 3.8). Subsequent β-hydride elimination generates acetone and the corresponding Pd-hydride species (ii, Scheme 3.8). Reductive elimination of propene from Pd-hydride (ii) affords the monoligated species [Pd(0)(CNArDipp2)] (Path A, Scheme 3.8). Alternatively, reductive elimination of allyl isopropyl ether from the Pd-isopropoxide intermediate (i) can also produce [Pd(0)(CNArDipp2)] (Path B, Scheme 3.8). Direct nucleophilic attack of the allyl moiety93-96 followed by reductive elimination provides a third route to [Pd(0)(CNArDipp2)]. The monoligated intermediate [Pd(0)(CNArDipp2)] can form the final product by two pathways: 1) interception by Pd-isopropoxide (i) to directly afford [(CNArDipp2)Pd]2(μ-η^3-allyl)(μ-O/iPr) (17), or 2) interception by unreacted Pd(CNArDipp2)(η^3-allyl)Cl (16) to first obtain [(CNArDipp2)Pd]2(μ-η^3-allyl)(μ-Cl) (19), which then yields [(CNArDipp2)Pd]2(μ-η^3-allyl)(μ-O/iPr) (17) in the presence of isopropoxide anion (Scheme 3.8).

To gain more insight into this mechanism, the reaction between Pd(CNArDipp2)(η^3-allyl)Cl (16) and NaO/iPr in C_6D_6 was monitored by ^1H NMR
spectroscopy. A mixture of \([\text{CNAr}^{Dipp2}\text{Pd}]_{2}(\mu-\eta^{3}\text{-allyl})(\mu-\text{O}^i\text{Pr})\) (17) and \([\text{CNAr}^{Dipp2}\text{Pd}]_{2}(\mu-\eta^{3}\text{-allyl})(\mu-\text{Cl})\) (19) was initially observed, with gradual conversion of the latter to generate additional \([\text{CNAr}^{Dipp2}\text{Pd}]_{2}(\mu-\eta^{3}\text{-allyl})(\mu-\text{O}^i\text{Pr})\) (17). Persistence of \([\text{CNAr}^{Dipp2}\text{Pd}]_{2}(\mu-\eta^{3}\text{-allyl})(\mu-\text{Cl})\) (19) in solution indicates slow nucleophilic displacement of the chloride moiety compared to \(\beta\)-hydride elimination, reductive elimination, and \([\text{Pd}(0)(\text{CNAr}^{Dipp2})]\) interception. Furthermore, acetone and propene were detected in the crude reaction mixture by \(^1\text{H}\) NMR and GC-MS analyses. Meanwhile, allyl isopropyl ether was not observed. These observations are consistent with the formation of monoligated \([\text{Pd}(0)(\text{CNAr}^{Dipp2})]\) via Path A rather than Path B (Scheme 3.8).

Scheme 3.8. Proposed mechanism for \([\text{CNAr}^{Dipp2}\text{Pd}]_{2}(\mu-\eta^{3}\text{-allyl})(\mu-\text{O}^i\text{Pr})\) (17) formation via a monoligated \([\text{Pd}(0)L]\) intermediate.
3.7 Reactivity of \([\text{CNAr}^{\text{Dipp2}}\text{Pd}]_2(\mu-\eta^3\text{-allyl})(\mu-\text{O}^\prime\text{Pr})\) (17)

As a product of Pd(\text{CNAr}^{\text{Dipp2}})(\eta^3\text{-allyl})\text{Cl} (16) activation, \([\text{CNAr}^{\text{Dipp2}}\text{Pd}]_2(\mu-\eta^3\text{-allyl})(\mu-\text{O}^\prime\text{Pr})\) (17) is expected to exhibit higher catalytic activity relative to its monomeric precursor. Indeed, reactions between \((m\text{-Xyl})\text{Br}\) and PhB(OH)\(_2\) in the presence of \([\text{CNAr}^{\text{Dipp2}}\text{Pd}]_2(\mu-\eta^3\text{-allyl})(\mu-\text{O}^\prime\text{Pr})\) (17) (1 mol % Pd) generated cross-coupled biaryl product in 26 % GC yield within 8 h at RT (Table 3.4, entry 3). Nevertheless, \([\text{CNAr}^{\text{Dipp2}}\text{Pd}]_2(\mu-\eta^3\text{-allyl})(\mu-\text{O}^\prime\text{Pr})\) (17) still served as a less effective catalyst precursor compared to Pd(\text{CNAr}^{\text{Dipp2}})_2 (2). This inferior reactivity could be a result of catalytic deactivation. To shed light on this matter, \([\text{CNAr}^{\text{Dipp2}}\text{Pd}]_2(\mu-\eta^3\text{-allyl})(\mu-\text{O}^\prime\text{Pr})\) (17) was treated with excess \((m\text{-Xyl})\text{Br}\) (5 equiv) in THF. Crystallographic characterization revealed one of the products in this mixture as the dimer \([\text{CNAr}^{\text{Dipp2}}\text{Pd}]_2(\mu-\eta^3\text{-allyl})(\mu-\text{Br})\) (21) (Figure 3.21, Scheme 3.7). Based on this result, it appears that oxidative addition of aryl bromide inhibits the reactivity of \([\text{CNAr}^{\text{Dipp2}}\text{Pd}]_2(\mu-\eta^3\text{-allyl})(\mu-\text{O}^\prime\text{Pr})\) (17) by producing a less catalytically active complex.

Formation of \([\text{CNAr}^{\text{Dipp2}}\text{Pd}]_2(\mu-\eta^3\text{-allyl})(\mu-\text{Br})\) (21) from this reaction initially implied the concomitant production of \(m\text{-xylyl isopropyl ether}\) as the other species. Interestingly, mass peaks corresponding to \(m\text{-xylyl isopropyl ether}\) were not observed by GC-MS analysis. Further, the \(^1\text{H}\) NMR chemical shifts corresponding to this unidentified product are identical to those belonging to the product generated from the reaction between \textit{trans-Pd(\text{Br})(m-Xyl)(\text{CNAr}^{\text{Dipp2}})_2} (14) and NaO\(^{\prime}\)Pr. Additional studies to uncover the identity of this shared product are underway.
When left in solution at room temperature, gradual decomposition of \([\text{CNAr}^\text{Dipp}^\text{a}_2\text{Pd}]_2(\mu-\eta^3-\text{allyl})(\mu-\text{Br})\) (21) is observed. This is not surprising, given the tendency of transition metal alkoxide complexes to undergo \(\beta\)-hydride elimination.\(^{84,87,97}\) Accordingly, a solution of \([\text{CNAr}^\text{Dipp}^\text{a}_2\text{Pd}]_2(\mu-\eta^3-\text{allyl})(\mu-\text{O}^\text{Pr})\) (17) in toluene-\(d_8\) was monitored by \(^1\text{H}\) NMR spectroscopy. The conversion of \([\text{CNAr}^\text{Dipp}^\text{a}_2\text{Pd}]_2(\mu-\eta^3-\text{allyl})(\mu-\text{O}^\text{Pr})\) (17) completed within 12 h at room temperature to generate a new compound along with acetone and propene. The formation of acetone and propene was also observed by GC-MS. Kinetic analysis revealed that this conversion is first-order in \([\text{CNAr}^\text{Dipp}^\text{a}_2\text{Pd}]_2(\mu-\eta^3-\text{C}_3\text{H}_5)(\mu-\text{O}^\text{Pr})\) (17). Plots of \(\ln[\text{Pd}]\) over time are linear past three half-lives, and the decomposition rate is fairly independent of the concentration of \([\text{CNAr}^\text{Dipp}^\text{a}_2\text{Pd}]_2(\mu-\eta^3-\text{C}_3\text{H}_5)(\mu-\text{O}^\text{Pr})\) (17) (Figure 3.22). X-ray diffraction revealed the new compound as a homoleptic Pd-isocyanide
trimer, $[\text{Pd}(\eta^2\text{-Dipp-}\mu\text{-CNAr}^{\text{Dipp}})]_3$ (22, Figure 3.23). The molecular structure of $[\text{Pd}(\eta^2\text{-Dipp-}\mu\text{-CNAr}^{\text{Dipp}})]_3$ (22) features a triangulo-Pd$_3$ core ($\text{Pd-Pd} = 2.6349(5) \text{ Å}$) wherein the metal centers are coordinated to bridging isocyanides ($\nu_{\text{CN}} = 1768 \text{ cm}^{-1}$, KBr) and flanking Dipp rings via $\eta^2$-interactions. Broken aromaticity$^{98,99}$ in the $\eta^2$-coordinated Dipp rings is evident from the molecular structure and reflects additional $\pi$ back-donation to the ligands (Figure 3.23). The presence of highly reduced Pd centers is evident by the low energy $\nu_{\text{CN}}$ stretch of the bound isocyanides compared to free CNAr$^{\text{Dipp}}_2$ ($2124 \text{ cm}^{-1}$). The $\eta^2$-interactions thus impart further electronic stabilization to the reduced metal centers. The $^1\text{H NMR}$ spectrum of $[\text{Pd}(\eta^2\text{-Dipp-}\mu\text{-CNAr}^{\text{Dipp}})]_3$ (22) in C$_6$D$_6$ at room temperature indicates that these $\eta^2$-interactions are fluxional in solution.

Figure 3.22. First-order plots of the decomposition of $[(\text{CNAr}^{\text{Dipp}}_2)\text{Pd}]_2(\mu-\eta^3\text{-allyl})(\mu-\text{O}^{\text{iPr}})$ (17) at varying concentrations (♦ 7 mM, ● 14 mM).
Figure 3.23. Molecular structure of \([\text{Pd}(\eta^2\text{-Dipp-}\mu\text{-CNArDipp})]_3\) (22). Selected bond distances (Å) and angles (°): Pd1–Pd1’ = 2.6348(4); Pd1–Pd1” = 2.6349(4); Pd1–C1 = 2.102(4); Pd1–C15 = 2.478(3); Pd1–C16 = 2.316(3); Pd1–C1’ = 2.109(4); C14–C15 = 1.421(5); C15–C16 = 1.411(5); C16–C17 = 1.415(6); C17–C18 = 1.378(6); C18–C19 = 1.408(5); C14–C19 = 1.386(5); Pd1–Pd1’–Pd1” = 60.001(1); C1–N1–C2 = 144.2(3).

3.8 Trimeric Stabilization of Monoligated \([\text{Pd(0)(CNAr}^{\text{Dipp}^2}]\) 

A proposed mechanism for the conversion of \([(\text{CNAr}^{\text{Dipp}^2})\text{Pd}]_2(\mu-\eta^3 \text{-allyl})(\mu-\text{O}^{i}\text{Pr})\) (17) to \([\text{Pd}(\eta^2\text{-Dipp-}\mu\text{-CNArDipp})]_3\) (22) is depicted in Scheme 3.9. First, dinuclear \(\beta\)-hydride elimination from \([(\text{CNAr}^{\text{Dipp}^2})\text{Pd}]_2(\mu-\eta^3 \text{-C}_3\text{H}_5)(\mu-\text{O}^{i}\text{Pr})\) (17) generates a dipalladium hydride intermediate and acetone. Subsequent dinuclear reductive elimination of propene then produces 2 units of \([\text{Pd(0)(CNAr}^{\text{Dipp}^2}]\), which subsequently trimerize to afford \([\text{Pd}(\eta^2\text{-Dipp-}\mu\text{-CNArDipp})]_3\) (22). This transformation is unique to \([(\text{CNAr}^{\text{Dipp}^2})\text{Pd}]_2(\mu-\eta^3 \text{-C}_3\text{H}_5)(\mu-\text{O}^{i}\text{Pr})\) (17) and is not observed among the
other allylPd(I)-isocyanide dimers (18-20). Such a process is remarkable since unimolecular conversion of a lower nuclearity complex to a Pd cluster is unprecedented.

Scheme 3.9. Proposed mechanism for the conversion of [(CNArDipp2)Pd]2(μ-η3-C3H5)(μ-OiPr) (17) to [Pd(η2-Dipp-μ-CNArDipp)]3 (22) via trimerization of monoligated Pd(0)L.

Unlike other 42-electron triangulo-Pd3 clusters, [Pd(η2-Dipp-μ-CNArDipp)]3 (22) is structurally unique in that the bridging and terminal moieties of each metal center are supplied by the same molecule. More notably, [Pd(η2-Dipp-μ-CNArDipp)]3 (22) is a direct trinuclear aggregate of the reactive monoligated [Pd(0)(CNArDipp2)] intermediate. This complex is noteworthy for it substantiates the presence of [Pd(0)(CNArDipp2)] in this system. Indeed, the isolation of such a species is rare and exemplifies the necessity for stabilizing π interactions between the ligands
and metal centers. To our knowledge, the only other structurally characterized homoleptic Pd complex possessing a 1:1 Pd/L formulation is Barder’s dialkylbiaryl phosphine Pd(I) dimer, which is stabilized by Pd-arene interactions on a ring of each biaryl ligand. Thus, \([\text{Pd}(\eta^2\text{-Dipp-}\mu\text{-CNAr}^{\text{Dipp}})]_3\) (22) lends further credence to the electronic and steric stabilization provided by the \(\pi\)-acidic, sterically encumbering \(m\)-terphenyl isocyanide platform.

### 3.9 Catalytic Competency of \([\text{Pd}(\eta^2\text{-Dipp-}\mu\text{-CNAr}^{\text{Dipp}})]_3\) (22)

\([\text{Pd}(\eta^2\text{-Dipp-}\mu\text{-CNAr}^{\text{Dipp}})]_3\) (22) proved to be an effective catalyst for Suzuki cross-coupling. Under our standard catalytic conditions, \([\text{Pd}(\eta^2\text{-Dipp-}\mu\text{-CNAr}^{\text{Dipp}})]_3\) (22) mediated the cross-coupling between \((m\text{-Xyl})\text{Br}\) and \(\text{PhB(OH)}_2\) to generate biaryl product in 83 % GC yield (Table 3.4, entry 4). Its improved performance relative to its monomeric and dimeric precursors demonstrates that monoligated \([\text{Pd}(0)(\text{CNAr}^{\text{Dipp}_2})]\) is indeed a catalytically active species. It is worth noting, however, that \([\text{Pd}(\eta^2\text{-Dipp-}\mu\text{-CNAr}^{\text{Dipp}})]_3\) (22) fully decomposes in solution at room temperature within one week to \(\text{Pd(CNAr}^{\text{Dipp}_2})\) (2). This does not present a detriment to the catalytic activity of \([\text{Pd}(\eta^2\text{-Dipp-}\mu\text{-CNAr}^{\text{Dipp}})]_3\) (22), since cluster fragmentation occurs too slowly to have an impact within the time frame of the cross-coupling reactions. Because of this decomposition, a trace amount of \(\text{Pd(CNAr}^{\text{Dipp}_2})\) (0.01 mol %) was continually present in samples of \([\text{Pd}(\eta^2\text{-Dipp-}\mu\text{-CNAr}^{\text{Dipp}})]_3\) (22) and could not be completely eliminated despite numerous recrystallizations. ESI-MS of \([\text{Pd}(\eta^2\text{-Dipp-}\mu\text{-CNAr}^{\text{Dipp}})]_3\) (22) \((m/z = 1589)\) samples indeed detected \(\text{Pd(CNAr}^{\text{Dipp}_2})\)
(2) \((m/z = 953)\) (Figure 3.24). A molecular ion peak at \(m/z = 1166\) was also observed, corresponding to the fragmentation of one \(\text{CNAr}^{\text{Dipp}}\) molecule from \([\text{Pd}(\eta^2\text{-Dipp}-\mu\text{-}\text{CNAr}^{\text{Dipp}})]_3\) (22). Control experiments were conducted to demonstrate that the trace amount of \(\text{Pd(CNAr}^{\text{Dipp}}\text{)}_2\) (2) has a negligible effect in cross-coupling mediated by \([\text{Pd}(\eta^2\text{-Dipp}-\mu\text{-CNAr}^{\text{Dipp}})]_3\) (22). At lower catalyst loadings of 0.1 and 0.01 mol %, the catalytic performance of \(\text{Pd(CNAr}^{\text{Dipp}}\text{)}_2\) (2) decreased drastically, resulting in GC yields of 13 % and 1%, respectively. This confirmed that \([\text{Pd}(\eta^2\text{-Dipp}-\mu\text{-CNAr}^{\text{Dipp}})]_3\) (22) is indeed catalytically competent.
3.10 Conclusions

The presumed role of monoligated [Pd(0)L] species as catalytically active intermediates in cross-coupling chemistry is widely accepted. Numerous studies have accordingly provided evidence for the likelihood of such intermediates, yet reports structurally verifying their existence and formation are rare. Given the highly electron-rich nature of these monoligated [Pd(0)L] species, we reasoned that the strongly π-acidic isocyanide CNAr$_{\text{Dipp2}}$ could provide sufficient electronic, as well as steric, stabilization. Surprisingly, π-acidic ligands are uncommon in cross-coupling chemistry, wherein σ-donating phosphine and NHC ligands prevail.

Our studies commenced with catalytic studies on the zerovalent, homoleptic bis-isocyanide monomer Pd(CNAr$_{\text{Dipp2}}$)$_2$ (2). Under mild conditions and fairly low catalyst loading (1 mol %), Pd(CNAr$_{\text{Dipp2}}$)$_2$ (2) mediated the Suzuki cross-coupling of various unactivated aryl bromides and aryl boronic acids. Yet, the activity of Pd(CNAr$_{\text{Dipp2}}$)$_2$ (2) does not competitively rival that of its phosphine and NHC counterparts, which have been shown to catalyze the cross-coupling of more hindered substrates to produce tri- and tetra-ortho-substituted biaryls. Steric inhibition due to the presence of an unnecessary equivalent of ligand in the Pd(CNAr$_{\text{Dipp2}}$)$_2$-based system seemed likely. Accordingly, kinetic experiments on the oxidative addition step yielded results consistent with a dissociative mechanism. That is, the rate of oxidative addition to Pd(CNAr$_{\text{Dipp2}}$)$_2$ (2) decreased significantly in the presence of additional ligand. This outcome implicated a monoligated Pd(0)L species as the active catalytic intermediate in this system.
Synthetic attempts at Pd mono-isocyanide complexes procured further evidence for monoligated [Pd(0)L]. For instance, activation of Pd(CNAr\textsubscript{Dipp}\textsuperscript{2})(\eta\textsuperscript{3}-allyl)Cl (16) by NaO\textsuperscript{t}Bu in \textsuperscript{t}PrOH generated the dimer [(CNAr\textsubscript{Dipp}\textsuperscript{2})Pd\textsubscript{2}(\mu-\eta\textsuperscript{3}-allyl)(\mu-O\textsuperscript{t}Pr)] (17). The proposed mechanism for this reaction featured the formation of [Pd(0)(CNAr\textsubscript{Dipp}\textsuperscript{2})] via β-hydride elimination and reductive elimination processes. More notably, [(CNAr\textsubscript{Dipp}\textsuperscript{2})Pd\textsubscript{2}(\mu-\eta\textsuperscript{3}-allyl)(\mu-O\textsuperscript{t}Pr)] (17) decomposed in solution via a similarly proposed mechanism to form the homoleptic Pd-isocyanide trimer [Pd(\eta\textsuperscript{2}-Dipp-\mu-CNAr\textsubscript{Dipp})\textsubscript{3}] (22). Structural characterization revealed that this complex is indeed the monoligated [Pd(0)(CNAr\textsubscript{Dipp}\textsuperscript{2})] intermediate in a stabilized trimeric form. As a testament to its reactivity, [Pd(\eta\textsuperscript{2}-Dipp-\mu-CNAr\textsubscript{Dipp})\textsubscript{3}] (22) was catalytically competent in Suzuki cross-coupling test reactions. Thus, [Pd(\eta\textsuperscript{2}-Dipp-\mu-CNAr\textsubscript{Dipp})\textsubscript{3}] (22) is a unique example of an isolable monoligated [Pd(0)(CNAr\textsubscript{Dipp}\textsuperscript{2})] species stabilized by π-acidic ligands.

3.11 Synthetic Procedures

**General considerations.** All manipulations were carried out under an atmosphere of dinitrogen using standard Schlenk and glovebox techniques. Solvents were dried and deoxygenated according to standard procedures. Benzene-\textit{d}\textsubscript{6} and toluene-\textit{d}\textsubscript{8} (Cambridge Isotope Laboratories) were degassed and stored over 4 Å molecular sieves for 2 d prior to use. CNAr\textsubscript{Dipp}\textsuperscript{2}, \textsuperscript{104} PdCNAr\textsubscript{Dipp}\textsuperscript{2} and \textit{trans}-PdBr(3,5-dimethylphenyl)(CNAr\textsubscript{Dipp}\textsuperscript{2})\textsubscript{42} were prepared by previously reported methods. (\textit{n}-Bu\textsubscript{4})\textsubscript{4}N[PhBF\textsubscript{3}] was produced through counterion exchange between K[PhBF\textsubscript{3}] and (\textit{n}-
Bu₄NCl in acetone. Lithium diisopropylamide (LDA) was prepared from diisopropylamine and n-BuLi in n-hexane. Celite 405 (Fisher Scientific) was dried under vacuum (24 h) at a temperature above 250 °C and stored in the glovebox prior to use. KBr (FTIR grade from Aldrich) was stirred overnight in anhydrous THF, filtered and dried under vacuum (24 h) at a temperature above 250 °C and stored in the glovebox prior to use. All other reagents were purchased from commercial sources and used as received.

Solution ¹H and ¹³C{¹H} NMR spectra were recorded on Varian Mercury 300 and 400 spectrometers and a Varian X-Sens500 spectrometer. ¹H and ¹³C{¹H} chemical shifts are reported in ppm relative to SiMe₄ (¹H and ¹³C δ = 0.0 ppm) with reference to residual solvent resonances of 7.26 ppm (¹H) and 77.16 ppm (¹³C) for CDCl₃, 7.16 ppm (¹H) and 128.06 ppm (¹³C) for C₆D₆, 5.32 ppm (¹H) for CD₂Cl₂, 2.08 ppm (¹H) for toluene-d₈. FTIR spectra were recorded on a Thermo-Nicolet iS10 FTIR spectrometer. Samples were prepared as KBr pellets. Combustion analyses were performed by Robertson Microlit Laboratories of Madison, NJ (USA). Electrospray ionization mass spectrometry (ESI-MS) was performed on a Thermo LCQdeca mass spectrometer. Samples were prepared as acetone solutions and diluted to concentrations on the order of 10⁻⁶ to 10⁻⁵ M. The following settings were used during data acquisition: temp = 180 °C; infusion flow rate = 100 μL min⁻¹; source voltage = 4 kV.

Synthesis of trans-PdBr(m-Xyl)(CNArDipp₂)₂ (14). To a solution of Pd(CNArDipp₂)₂ (2) (0.150 g, 0.157 mmol) in Et₂O (10 mL) was added 1-bromo-3,5-
dimethylbenzene (22.8 μL, 0.165 mmol, 1.05 equiv). The reaction mixture was stirred for 24 h, during which the orange color darkened slightly. All volatile materials were removed under reduced pressure to afford a pale orange residue. The material was dissolved in Et₂O (2 mL), filtered and stored at -35 °C overnight to produce white crystals suitable for X-ray analysis, which were collected, washed with n-pentane and dried *in vacuo*. Yield: 0.067 g, 0.059 mmol, 38%. ¹H NMR (400.1 MHz, C₆D₆, 20 °C): δ = 7.33 (t, 4H, J = 8 Hz, p-Dipp), 7.18 (d, 8H, J = 8 Hz, m-Dipp), 6.85 (m, 6H, m-Ph and p-Ph), 6.41 (s, 1H, o-aryl), 5.92 (s, 2H, o-aryl), 2.50 (septet, 8H, CH(CH₃)₂), 2.21 (s, 6H, m-C₃H₃), 1.19 (d, 24H, J = 8 Hz, CH(CH₃)₂), 1.03 (d, 24H, J = 8 Hz, CH(CH₃)₂) ppm. ¹³C{¹H} NMR (100.6 MHz, C₆D₆, 20 °C): δ = 146.4, 139.7, 138.3, 135.6, 134.6, 133.7, 129.9, 129.7, 129.2, 126.8, 125.7, 123.5, 31.4 (CH(CH₃)₂), 24.9 (CH(CH₃)₂), 24.0 (CH(CH₃)₂), 21.7 (m-C₃H₃) ppm (extended scanning (12h) failed to locate the Ciso ¹³C resonance for this complex). FTIR (KBr pellet): (νCN) 2178 cm⁻¹ also 3059, 3020, 2960, 2925, 2866, 1591, 1582, 1460, 1363, 1113, 1056, 802, 753 cm⁻¹. Anal. calcd. for C₇₀H₈₃BrN₂Pd: C, 73.83; H, 7.35; N, 2.46. Found: C, 73.60; H, 7.61; N, 2.38.

**Synthesis of \([(\text{CNAr}^{\text{Dipp}^2})\text{PdCl}]_2(\mu-\text{Cl})_2\) (15).** To a 1:1 EtOH/THF suspension of PdCl₂ (0.029 g, 0.161 mmol, 10 mL total) was added *trans*-PdCl₂(CNAr^{Dipp2})₂ (1) (0.165 g, 0.161 mmol, 1.0 equiv). The reaction mixture was stirred for 48 h, during which the color gradually turned yellow. The solvents were removed *in vacuo* and the resulting residue was washed with pentane (5 mL). The material was dissolved in THF (2 mL), filtered through a plug of Celite, and stored at -35 °C overnight to produce
orange crystals, which were isolated by filtration, washed with pentane and dried \textit{in vacuo}. Yield: 0.059 g, 0.049 mmol, 30%. $^1$H NMR (400.1 MHz, C$_6$D$_6$, 20 °C): $\delta$ = 7.32 (t, $J = 8$ Hz, 2H, $p$-Dipp), 7.15 (d, $J = 8$ Hz, 4H, $m$-Dipp), 6.81 (m, 3H, $m$-Ph and $p$-Ph), 2.43 (septet, $J = 7$ Hz, 4H, CH(CH$_3$)$_2$), 1.25 (d, $J = 7$ Hz, 12H, CH(CH$_3$)$_2$), 0.99 (d, $J = 7$ Hz, 12H, CH(CH$_3$)$_2$) ppm. $^{13}$C{$^1$H} NMR (100.6 MHz, C$_6$D$_6$, 20 °C): $\delta$ = 146.2, 140.8, 132.8, 130.5, 130.4, 129.9, 127.9, 123.9, 31.5 (CH(CH$_3$)$_2$), 24.7 (CH(CH$_3$)$_2$), 24.1 (CH(CH$_3$)$_2$) ppm (extended scanning (12h) failed to locate the C$_{iso}$ $^{13}$C resonance for this complex). FTIR (KBr pellet): (ν$_{CN}$) 2216 cm$^{-1}$ also 3062, 3023, 2962, 2926, 2868, 1593, 1574, 1462, 1413, 1385, 1364, 1056, 804, 793, 756 cm$^{-1}$. Anal. calcd. for C$_{62}$H$_{74}$Cl$_4$N$_2$Pd$_2$: C, 61.96; H, 6.21; N, 2.33. Found: C, 61.69; H, 6.17; N, 2.31.

**Synthesis of Pd(CNAr$^{Dipp2}$($\eta^3$-allyl))Cl (16).** To a solution of [Pd(allyl)Cl]$_2$ (0.086 g, 0.235 mmol) in THF (10 mL) was added CNAr$^{Dipp2}$ (0.199 g, 0.470 mmol, 2.0 equiv). The reaction mixture was stirred for 2 h, during which the color turned pale yellow. The mixture was then concentrated under reduced pressure to 2 mL and filtered through a plug of Celite. The resulting solution was layered with pentane (1 mL) and stored at −35 °C for 2 d to produce white crystals suitable for X-ray analysis. The crystals were collected, washed with n-pentane (2 x 2 mL) and dried \textit{in vacuo}. Yield: 0.108 g, 0.178 mmol, 38%. $^1$H NMR (300.1 MHz, C$_6$D$_6$, 20 °C): $\delta$ = 7.30 (t, 2H, $J = 7$ Hz, $p$-Dipp), 7.20 (d, 4H, $J = 7$ Hz, $m$-Dipp), 6.94 (s, 3H, $m$-Ph and $p$-Ph), 4.25 (m, 1H, CH allyl), 3.87 (d, 1H, $J = 7$ Hz, CH$_2$ allyl), 3.01 (d, 1H, $J = 6$ Hz, CH$_2$ allyl), 2.64 (septet, 4H, $J = 7$ Hz, CH(CH$_3$)$_2$), 2.61 (d, 1H, $J = 13$ Hz, CH$_2$ allyl), 1.83
(d, 1H, J = 12 Hz, CH$_2$ allyl), 1.39 (d, 12H, J = 7 Hz, CH(CH$_3$)$_2$), 1.08 (d, 12H, J = 7 Hz, CH(CH$_3$)$_2$) ppm. $^{13}$C{$^{1}$H} NMR (100.6 MHz, C$_6$D$_6$, 20 °C); δ = 151.5 (C≡N), 146.7, 140.0, 134.0, 130.0, 129.9, 129.6, 127.9, 123.6, 116.4 (CH allyl), 73.7 (CH$_2$ allyl), 56.8 (CH$_2$ allyl), 31.6 (CH(CH$_3$)$_2$), 24.6 (CH(CH$_3$)$_2$), 24.4 (CH(CH$_3$)$_2$) ppm. FTIR (KBr pellet): (ν$_{CN}$) 2172 cm$^{-1}$ also 3061, 3018, 2963, 2926, 2867, 1595, 1578, 1458, 1382, 1363, 1056, 753 cm$^{-1}$. Anal. calcd. for C$_{34}$H$_{42}$ClNPd: C, 67.32; H, 6.98; N, 2.31. Found: C, 67.07; H, 7.00; N, 2.52.

Synthesis of [(CNAr$^{Dipp}$Pd)$_2$(μ-η$^3$-allyl)(μ-O′Pr) (17). Method 1. To a suspension of Pd(CNAr$^{Dipp}$)(η$^3$-allyl)Cl (16) (0.100 g, 0.165 mmol) in $^t$PrOH (5 mL) was added a solution of NaO′Bu (0.017 g, 0.173 mmol, 1.05 equiv) in $^t$PrOH (5 mL). The reaction mixture was stirred for 2 h, during which the color gradually turned cloudy beige. All volatile materials were removed under reduced pressure and the resulting residue was washed with cold (−35 °C) n-pentane (3 x 2 mL) to remove any dark brown material. The resulting yellow solid was dissolved in THF (2 mL), filtered, and stored at −35 °C for one week to produce yellow crystals, which were collected and dried in vacuo. Yield: 0.006 g, 0.005 mmol, 6%.

Method 2. To a solution of [(CNAr$^{Dipp}$Pd)$_2$(μ-η$^3$-allyl)(μ-Cl) (19) (0.100 g, 0.088 mmol) in Et$_2$O (2 mL) was added a suspension of sodium isopropoxide (0.014 g, 0.176 mmol, 2.0 equiv) in n-pentane (5 mL). The reaction mixture was stirred for 30 min, during which the color gradually turned cloudy beige. All volatile materials were removed under reduced pressure and the resulting residue was washed with cold (−35 °C) n-pentane (3 x 2 mL) to remove any dark brown residue. The resulting yellow
solid was dried *in vacuo*, dissolved in THF (4 mL), filtered, and stored at −35 °C overnight to produce yellow crystals which were collected and dried *in vacuo*. Yield: 0.024 g, 0.021 mmol, 24%. ¹H NMR (400.1 MHz, C₆D₆, 20 °C): δ = 7.31 (t, 4H, J = 8 Hz, p-Dipp), 7.16 (d, 8H, J = 8 Hz, m-Dipp), 6.93 (m, 6H, m-Ph and p-Ph), 4.27 (m, 1H, CH allyl), 2.71 (septet, 4H, J = 8 Hz, CH(CH₃)₂), 2.70 (septet, 4H, J = 8 Hz, CH(CH₃)₂), 2.33 (d, 2H, CH₂ allyl), 1.99 (m, 1H, OCH(CH₃)₂), 1.26 (d, 12H, J = 8 Hz, CH(CH₃)₂), 1.25 (d, 12H, J = 8 Hz, CH(CH₃)₂), 1.08 (d, 30H, J = 8 Hz, CH(CH₃)₂ and OCH(CH₃)₂), 0.68 (d, 2H, J = 12 Hz, CH₂ allyl) ppm. FTIR (KBr pellet): (νCN) 2116 and 2011 cm⁻¹ also 3064, 3027, 2962, 2927, 2868, 1462, 1416, 1384, 1363, 1127, 1055, 1047, 803, 792, 755 cm⁻¹. Anal. calcd. for C₆₈H₈₆N₂OPd₂: C, 70.39; H, 7.47; N, 2.41. Found: C, 71.02; H, 7.42; N, 2.21.

**Synthesis of [(CNAr Dipp²)Pd]₂(μ-η³-allyl)(μ-N(-iPr)₂) (18). Method 1.** To a frozen solution of [(CNAr Dipp²)Pd]₂(μ-η³-allyl)(μ-OiPr) (17) (0.150 g, 0.129 mmol) in THF (5 mL) was added a thawed solution of LDA (0.015 g, 0.142 mmol, 1.1 equiv) in THF (5 mL). The reaction mixture was slowly warmed to room temperature and stirred overnight, during which the color turned golden brown. The solvent was removed under reduced pressure and the residue was dissolved in n-pentane (2 mL), filtered, and stored at −35 °C overnight to produce yellow crystals which were collected and dried *in vacuo*. Yield: 0.043 g, 0.036 mmol, 28%.

**Method 2.** To a frozen solution of [(CNAr Dipp²)Pd]₂(μ-η³-allyl)(μ-OiPr) (17) (0.150 g, 0.129 mmol) in THF (5 mL) was added a thawed solution of LDA (0.015 g, 0.142 mmol, 1.1 equiv) in THF (5 mL). The reaction mixture was slowly warmed to
room temperature and stirred overnight, during which the color turned golden brown and a gray precipitate formed. The resulting solution was filtered and the solvent was removed under reduced pressure. The resulting residue was washed with cold (-35 °C) n-pentane (5 mL) to afford a yellow solid, which was dissolved in Et₂O (2 mL), filtered, layered with n-pentane (4 mL), and stored at −35 °C overnight to produce yellow crystals which were collected and dried in vacuo. Yield: 0.066 g, 0.055 mmol, 63%. Crystals suitable for X-ray analysis were obtained by vapor diffusion of n-pentane into a saturated solution of \([(\text{CNAr}^{\text{Dipp}2})\text{Pd}]_2(\mu-\eta^3\text{-allyl})(\mu-\text{N}^{2}(\text{Pr})_2)\) (18) in Et₂O at -35 °C for 3 d. ¹H NMR (400.1 MHz, C₆D₆, 20 °C): δ = 7.32 (t, 4H, J = 8 Hz, p-Dipp), 7.17 (d, 8H, J = 8 Hz, m-Dipp), 6.95 (m, 6H, m-Ph and p-Ph), 3.27 (septet, 1H, J = 6 Hz, N(CH(CH₃)₂)₂), 3.18 (septet, 1H, J = 6 Hz, N(CH(CH₃)₂)₂), 2.75 (septet, 4H, J = 8 Hz, CH(CH₃)₂ Dipp), 2.74 (septet, 4H, J = 8 Hz, CH(CH₃)₂ Dipp), 2.46 (m, 2H, CH₂ allyl), 2.43 (m, 1H, CH allyl), 1.28 (d, 12H, J = 8 Hz, CH(CH₃)₂ Dipp), 1.26 (d, 12H, J = 8 Hz, CH(CH₃)₂ Dipp), 1.10 (d, 24H, J = 8 Hz, CH(CH₃)₂ Dipp), 0.94 (d, 6H, J = 6 Hz, NCH(CH₃)₂), 0.88 (d, 6H, J = 6 Hz, NCH(CH₃)₂), 0.67 (d, 2H, J = 12 Hz, CH₂ allyl) ppm. ¹³C{¹H} NMR (100.6 MHz, C₆D₆, 20 °C): δ = 159.5 (C≡N), 146.7, 146.6, 139.3, 135.3, 129.7, 129.5, 123.4, 123.3, 80.0 (CH allyl), 55.2 (N(CH(CH₃)₂)₂), 55.1 (N(CH(CH₃)₂)₂), 31.5 (CH(CH₃)₂ Dipp), 27.6 (NCH(CH₃)₂), 27.3 (NCH(CH₃)₂), 26.9 (CH₂ allyl), 24.5 (CH(CH₃)₂ Dipp), 24.3 (CH(CH₃)₂ Dipp) ppm. FTIR (KBr pellet): (νCN) 2083 and 2013 cm⁻¹ also 3061, 3025, 2928, 2867, 1579, 1459, 1419, 1384, 1363, 1349, 1328, 1308, 1252, 1153, 1056, 803, 791, 756 cm⁻¹. Anal. calcd. for C₇₁H₉₃N₃Pd₂: C, 70.98; H, 7.80; N, 3.50. Found: C, 70.73; H, 7.88; N, 3.39.
Synthesis of [(CNArDipp²)Pd]₂(μ-η^3-allyl)(μ-Cl) (19). To a 1:1 pentane/Et₂O solution of Pd(CNArDipp²)₂ (2) (0.300 g, 0.315 mmol, 10 mL total) was added [Pd(allyl)Cl]₂ (0.058 g, 0.157 mmol, 0.5 equiv). The reaction mixture was stirred for 45 min, during which a pale yellow precipitate formed. The solvents were removed under reduced pressure, then the resulting yellow solid was dissolved in Et₂O (2 mL) and filtered through a plug of Celite. The resulting solution was layered with n-pentane (2 mL) and stored at −35 °C overnight to produce yellow crystals. The crystals were collected, washed with n-pentane (5 mL) and dried in vacuo. Yield: 0.318 g, 0.280 mmol, 89%. Crystals suitable for X-ray analysis were obtained by slow evaporation of a solution of [(CNArDipp²)Pd]₂(μ-η^3-allyl)(μ-Cl) (19) in Et₂O at −35 °C for 3 d. \(^1\)H NMR (400.1 MHz, C₆D₆, 20 °C): δ = 7.26 (t, 4H, J = 8 Hz, p-Dipp), 7.15 (d, 8H, J = 8 Hz, m-Dipp), 6.94 (m, 6H, m-Ph and p-Ph), 2.76 (d, 2H, J = 8 Hz, CH₂ allyl), 2.69 (septet, 8H, J = 7 Hz, CH(CH₃)₂), 1.74 (m, 1H, CH allyl), 1.30 (d, 24H, J = 8 Hz, CH(CH₃)₂), 1.08 (d, 24H, J = 7 Hz, CH(CH₃)₂), 0.75 (d, 2H, J = 12 Hz, CH₂ allyl) ppm. \(^13\)C{¹H} NMR (100.6 MHz, C₆D₆, 20 °C): δ = 154.5 (C≡N), 146.7, 139.4, 134.6, 129.7, 129.6, 128.7, 123.5, 123.4, 68.8 (CH allyl), 33.4 (CH₂ allyl), 31.5 (CH(CH₃)₂), 24.6 (CH(CH₃)₂), 24.3 (CH(CH₃)₂) ppm. FTIR (KBr pellet): (νCN) 2121 and 2010 cm⁻¹ also 3073, 3051, 3017, 2960, 2926, 2867, 1596, 1577, 1460, 1418, 1383, 1362, 1055, 803, 790, 755 cm⁻¹. Anal. calcd. for C₆₅H₇₉ClN₂Pd₂: C, 68.69; H, 7.01; N, 2.46. Found: C, 68.39; H, 7.19; N, 2.40.

Synthesis of [(CNArDipp²)Pd]₂(μ-η^3-allyl)(μ-O'Bu) (20). To a solution of [(CNArDipp²)Pd]₂(μ-η^3-allyl)(μ-Cl) (19) (0.100 g, 0.088 mmol) in Et₂O (5 mL) was
added a solution of NaO\textsuperscript{t}Bu (0.025 g, 0.264 mmol, 3.0 equiv) in Et\textsubscript{2}O (5 mL). The reaction mixture turned cloudy bright orange in color and was stirred overnight, during which the color turned cloudy beige. The solvent was then removed under reduced pressure and the resulting residue was washed with \(n\)-pentane (5 mL) to afford a yellow solid. The material was dissolved in THF (4 mL), filtered through a plug of Celite, and stored at \(-35\) °C overnight to produce yellow crystals which were collected, washed with \(n\)-pentane (5 mL), and dried \textit{in vacuo}. Yield: 0.053 g, 0.045 mmol, 51%. Crystals suitable for X-ray analysis were obtained by vapor diffusion of Et\textsubscript{2}O into a saturated solution of \([(CNAr^Dipp^2)Pd]_2(\mu-\eta^3\text{-allyl})(\mu-\text{OtBu})\) (20) in fluorobenzene at \(-35\) °C for 5 d. \(\textsuperscript{1}H\) NMR (400.1 MHz, C\textsubscript{6}D\textsubscript{6}, 20 °C): \(\delta = 7.33\) (t, 4H, \(J = 8\) Hz, \(p\)-Dipp), 7.17 (d, 8H, \(J = 8\) Hz, \(m\)-Dipp), 6.92 (s, 6H, \(m\)-Ph and \(p\)-Ph), 2.72 (septet, 4H, \(J = 8\) Hz, \(CH(CH_3)_2\)), 2.70 (septet, 4H, \(J = 8\) Hz, \(CH(CH_3)_2\)), 2.25 (d, 2H, \(CH_2\) allyl), 2.04 (m, 1H, \(CH\) allyl), 1.26 (d, 12H, \(J = 8\) Hz, \(CH(CH_3)_2\)), 1.23 (d, 12H, \(J = 8\) Hz, \(CH(CH_3)_2\)), 2.72 (d, 2H, \(CH_2\) allyl) ppm. \(\textsuperscript{13}C\{\textsuperscript{1}H\}\) NMR (100.6 MHz, C\textsubscript{6}D\textsubscript{6}, 20 °C): \(\delta = 155.9\) (C≡N), 146.7, 146.6, 139.6, 135.0, 129.8, 129.6, 129.2, 123.5, 123.4, 70.1 (CH allyl), 37.2 (OC(CH\textsubscript{3})\textsubscript{3}), 31.5 (CH(CH\textsubscript{3})\textsubscript{2}), 26.7 (CH\textsubscript{2} allyl), 24.6 (CH(CH\textsubscript{3})\textsubscript{2}), 24.4 (CH(CH\textsubscript{3})\textsubscript{2}) ppm. FTIR (KBr pellet): (\nu\textsubscript{CN}) 2097 and 2010 cm\textsuperscript{-1} also 3062, 3026, 2961, 2927, 2868, 1580, 1462, 1417, 1384, 1363, 1348, 1180, 1056, 945, 803, 792, 755 cm\textsuperscript{-1}. Anal. calcd. for C\textsubscript{69}H\textsubscript{88}N\textsubscript{2}OPd\textsubscript{2}: C, 70.57; H, 7.55; N, 2.39. Found: C, 70.29; H, 7.51; N, 2.32.
Synthesis of \([\text{Pd}(\mu-\text{CNAr}^{\text{Dipp}^2}-\eta^2-\text{Dipp})_3]\) (22). To a solution of \([\text{CNAr}^{\text{Dipp}^2}\text{Pd}]_2(\mu-\eta^3\text{-allyl})(\mu-\text{Cl})\) (19) (0.100 g, 0.088 mmol) in THF (5 mL) was added a solution of sodium isopropoxide (0.029 g, 0.350 mmol, 4.0 equiv) in THF (5 mL). The reaction mixture was stirred for 1 h, during which the color turned dark red. All volatile materials were removed under reduced pressure to afford an oily dark red residue from which the product was extracted with \(n\)-pentane (10 mL), filtered, and dried under reduced pressure. Dissolution of the resulting red residue in THF (2 mL) and storage at \(-35^\circ\text{C}\) for 3 d produced red crystals suitable for X-ray analysis, which were collected and dried in vacuo. Yield: 0.049 g, 0.031 mmol, 53%. \(^1\text{H}\) NMR (400.1 MHz, \(\text{C}_6\text{D}_6\), 20 °C): \(\delta = 7.13\) (m, 2H, \(p\)-Dipp), 7.01 (m, 7H, \(m\)-Dipp, \(m\)-Ph, and \(p\)-Ph), 2.90 (septet, 4H, \(J = 7\) Hz, \(\text{CH(CH}_3)_2\)), 1.22 (d, 12H, \(J = 7\) Hz, \(\text{CH(CH}_3)_2\)), 1.10 (d, 12H, \(J = 7\) Hz, \(\text{CH(CH}_3)_2\)) ppm. \(^{13}\text{C}\{^1\text{H}\}\) NMR (100.6 MHz, \(\text{C}_6\text{D}_6\), 20 °C): \(\delta = 220.8\) (\(\equiv\text{N}\)), 141.9, 141.7, 137.8, 137.4, 135.0, 130.3, 125.6, 118.7, 31.7 (\(\text{CH(CH}_3)_2\)), 24.6 (\(\text{CH(CH}_3)_2\)), 24.4 (\(\text{CH(CH}_3)_2\)) ppm. FTIR (KBr pellet): \((\nu_{\text{CN}}) 1768\) cm\(^{-1}\) also 2963, 2931, 2868, 1458, 1383, 1363, 1177, 1047, 906, 804, 792, 758 cm\(^{-1}\). ESI-MS (\(m/z\)) caled. for \(\text{C}_{93}\text{H}_{111}\text{N}_3\text{Pd}_3\): 1588.596 [\(\text{M}\)]\(^+\). Found: 1589.25 [\(\text{M}\)]\(^+\), 1166.35 [\(\text{M} - \text{CNAr}^{\text{Dipp}^2}\)]\(^+\). Combustion analysis was not obtained due to the presence of a trace amount of \(\text{Pd(CNAr}^{\text{Dipp}^2})_2\).
3.12 Suzuki-Miyaura Cross-Coupling Procedures

General considerations. Aryl boronic acids were purchased from Sigma-Aldrich and recrystallized from a 1:1 H₂O/EtOH solution prior to use. iPrOH was degassed over 3 freeze-pump-thaw cycles and then vacuum distilled into an Airfree® storage vessel containing 4 Å molecular sieves, over which the solvent was stored for 2 days prior to use. All other reagents were purchased from commercial sources and used as received. GC-MS analyses were performed on a Hewlett-Packard 5890 Series II chromatograph equipped with an automatic liquid sampler and HP-5 column (30 m x 0.25 mm i.d., 0.25 μm film thickness). The following GC oven conditions were employed: inlet temp. = 220 °C; detector temp. = 280 °C; initial temp. = 60 °C with an initial hold time of 2 min, followed by a 30 °C min⁻¹ ramp to 260 °C, and then a hold at 260 °C for 4 min.

General Procedure A: Cross-Coupling Reactions at Room Temperature

Using Pd(CNArDipp₂)₂ (2). A 25 mL Airfree® storage vessel was charged under argon with aryl bromide (0.522 mmol, 1.0 equiv), aryl boronic acid (1.04 mmol, 2.0 equiv), Pd(CNArDipp₂)₂ (0.005 g, 0.005 mmol, 1.0 mol %), NaO'Bu (0.150 g, 1.57 mmol, 3.0 equiv), and iPrOH (2.0 mL). The vessel was sealed and the reaction mixture was magnetically stirred for 8 h. Conversion of aryl bromide to product was determined by GC-MS analysis. The solvent was then removed from the reaction mixture under reduced pressure to give a residue that was dissolved in water (6 mL) and extracted with hexanes (3 x 4 mL). The organic layers were combined and concentrated under
reduced pressure to give crude biaryl product that was purified by column chromatography on silica gel, eluting with hexanes.

4-methylbiphenyl\textsuperscript{105} (Table 3.1, entry 1). General procedure A was followed using 4-bromotoluene (64 μL) and phenylboronic acid (0.127 g). Yield: 0.066 g, 0.392 mmol, 75%. MS (EI) \textit{m/z}: 168 [M\textsuperscript{+}]. The \textsuperscript{1}H NMR spectrum is shown in Figure 3.25.

\textbf{Figure 3.25.} \textsuperscript{1}H NMR spectrum of 4-methylbiphenyl (400.1 MHz, CD\textsubscript{2}Cl\textsubscript{2}, 20 °C).
2,4’-dimethylbiphenyl\textsuperscript{106} (Table 3.1, entry 2). General procedure A was followed using 4-bromotoluene (64 μL) and o-tolylboronic acid (0.142 g). Yield: 0.073 g, 0.400 mmol, 77%. MS (EI) m/z: 182 [M\textsuperscript{+}]. The \textsuperscript{1}H NMR spectrum is shown in Figure 3.26.

**Figure 3.26.** \textsuperscript{1}H NMR spectrum of 2,4’-dimethylbiphenyl (400.1 MHz, CD\textsubscript{2}Cl\textsubscript{2}, 20 °C).
4-methyl-(1,1’,2’,1’’)-terphenyl\textsuperscript{107} (Table 3.1, entry 3). General procedure A was followed using 4-bromotoluene (64 μL) and 2-biphenylboronic acid (0.207 g). Yield: 0.092 g, 0.378 mmol, 73%. MS (EI) $m/z$: 244 [M$^+$]. The $^1$H NMR spectrum is shown in Figure 3.27.

**Figure 3.27.** $^1$H NMR spectrum of 4-methyl-(1,1’,2’,1’’)-terphenyl (400.1 MHz, CDCl$_3$, 20 °C).
3-methylbiphenyl (Table 3.1, entry 4). General procedure A was followed using 3-bromotoluene (63 μL) and phenylboronic acid (0.127 g). Yield: 0.065 g, 0.386 mmol, 74%. MS (EI) m/z: 168 [M⁺]. The 1H NMR spectrum is shown in Figure 3.28.

![Figure 3.28. 1H NMR spectrum of 3-methylbiphenyl (400.1 MHz, CD₂Cl₂, 20 °C).](image-url)
3,4'-dimethylbiphenyl\textsuperscript{109} (Table 3.1, entry 5). General procedure A was followed using 3-bromotoluene (63 μL) and p-tolylboronic acid (0.142 g). Yield: 0.081 g, 0.442 mmol, 85%. MS (EI) \textit{m/z}: 182 [M\textsuperscript+]. The \textsuperscript{1}H NMR spectrum is shown in Figure 3.29.

\textbf{Figure 3.29.} \textsuperscript{1}H NMR spectrum of 3,4'-dimethylbiphenyl (400.1 MHz, CD\textsubscript{2}Cl\textsubscript{2}, 20 °C).
2,3’-dimethylbiphenyl\textsuperscript{110} (Table 3.1, entry 6). General procedure A was followed using 3-bromotoluene (63 μL) and \textit{o}-tolylboronic acid (0.142 g). Yield: 0.069 g, 0.380 mmol, 73\%. MS (EI) \textit{m/z}: 182 [M\textsuperscript{+}]. The \textsuperscript{1}H NMR spectrum is shown in Figure 3.30.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.30.png}
\caption{\textsuperscript{1}H NMR spectrum of 2,3’-dimethylbiphenyl (400.1 MHz, CDCl\textsubscript{3}, 20 °C).}
\end{figure}
3,5-dimethylbiphenyl \(^{105}\) (Table 3.1, entry 7). General procedure A was followed using 1-bromo-3,5-dimethylbenzene (71 μL) and phenylboronic acid (0.127 g). Yield: 0.074 g, 0.404 mmol, 77%. MS (EI) \(m/z\): 182 [M\(^+\)]. The \(^1\)H NMR spectrum is shown in Figure 3.31.

![Figure 3.31. \(^1\)H NMR spectrum of 3,5-dimethylbiphenyl (400.1 MHz, CD\(_2\)Cl\(_2\), 20 °C).](image)
3,4',5-trimethylbiphenyl\textsuperscript{111} (Table 3.1, entry 8). General procedure A was followed using 1-bromo-3,5-dimethylbenzene (71 \, \mu\text{L}) and p-tolylboronic acid (0.142 g). Yield: 0.079 g, 0.401 mmol, 77\%. MS (EI) \textit{m/z}: 196 [M\textsuperscript{+}]. The \textsuperscript{1}H NMR spectrum is shown in Figure 3.32.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{nmrスペクトル.jpg}
\caption{\textsuperscript{1}H NMR spectrum of 3,4',5-trimethylbiphenyl (400.1 MHz, CD\textsubscript{2}Cl\textsubscript{2}, 20 °C).}
\end{figure}
2’,3,5-trimethylbiphenyl\textsuperscript{112} (Table 3.1, entry 9). General procedure A was followed using 1-bromo-3,5-dimethylbenzene (71 μL) and o-tolylboronic acid (0.142 g). Yield: 0.078 g, 0.395 mmol, 76%. MS (EI) \textit{m/z}: 196 [M\textsuperscript{+}]. The \textsuperscript{1}H NMR spectrum is shown in Figure 3.33.

**Figure 3.33.** \textsuperscript{1}H NMR spectrum of 2’,3,5-trimethylbiphenyl (400.1 MHz, CD\textsubscript{2}Cl\textsubscript{2}, 20 °C).
3,5-dimethyl-(1,1’,2’,1’”)-terphenyl (Table 3.1, entry 10). General procedure A was followed using 1-bromo-3,5-dimethylbenzene (71 μL) and 2-biphenylboronic acid (0.207 g). The product was isolated as a colorless oil. Yield: 0.092 g, 0.358 mmol, 69%. $^1$H NMR (400.1 MHz, CDCl$_3$, 20 °C): $\delta = 7.47$-7.35 (m, 5H, $H_{\text{arom}}$), 7.23-7.13 (m, 5H, $H_{\text{arom}}$), 6.83 (s, 1H, $H_{\text{arom}}$), 6.75 (s, 2H, $H_{\text{arom}}$), 2.19 (s, 6H) ppm. $^{13}$C{$^1$H} NMR (CDCl$_3$, 100.6 MHz) $\delta = 141.8$, 141.5, 140.9, 140.7, 137.3, 130.6, 130.0, 128.9, 128.2, 128.0, 127.9, 127.5, 127.4, 126.5, 21.4 ppm. HRMS (EI) $m/z$: 258 [M$^+$]. NMR spectra and HRMS traces are shown in Figures 3.34–3.36.

![Figure 3.34](image)

**Figure 3.34.** $^1$H NMR spectrum of 3,5-dimethyl-(1,1’,2’,1’”)-terphenyl (400.1 MHz, CDCl$_3$, 20 °C).
Figure 3.35. $^{13}$C NMR spectrum of 3,5-dimethyl-(1,1',2',1'')-terphenyl (100.6 MHz, CDCl$_3$, 20 °C).

Figure 3.36. HRMS of 3,5-dimethyl-(1,1',2',1'')-terphenyl.
1-phenylnaphthalene\textsuperscript{108} (Table 3.1, entry 11). General procedure A was followed using 1-bromonaphthalene (73 μL) and phenylboronic acid (0.127 g). Yield: 0.078 g, 0.384 mmol, 74%. MS (EI) $m/z$: 204 [M$^+$]. The $^1$H NMR spectrum is shown in Figure 3.37.

\textbf{Figure 3.37.} $^1$H NMR spectrum of 1-phenylnaphthalene (400.1 MHz, CDCl$_3$, 20 °C).
1-(4-methylphenyl)-naphthalene (Table 3.1, entry 12). General procedure A was followed using 1-bromonaphthalene (73 μL) and \( p \)-tolylboronic acid (0.142 g). Yield: 0.084 g, 0.385 mmol, 74\%. MS (EI) \( m/z \): 218 [M\(^+\)]. The \(^1\)H NMR spectrum is shown in Figure 3.38.

**Figure 3.38.** NMR spectrum of 1-(4-methylphenyl)-naphthalene (400.1 MHz, CDCl\(_3\), 20 °C).
1-(2-methylphenyl)-naphthalene\textsuperscript{114} (Table 3.1, entry 13). General procedure A was followed using 1-bromonaphthalene (73 μL) and o-tolylboronic acid (0.142 g). Yield: 0.087 g, 0.397 mmol, 74%. MS (EI) \( m/z \): 218 [M\(^+\)]. The \(^1\)H NMR spectrum is shown in Figure 3.39.

\textbf{Figure 3.39.} \(^1\)H NMR spectrum of 1-(2-methylphenyl)-naphthalene (400.1 MHz, CDCl\(_3\), 20 °C).
1,1’-biphenyl[naphthalene\textsuperscript{115} (Table 3.1, entry 14). General procedure A was followed using 1-bromonaphthalene (73 μL) and 2-biphenylboronic acid (0.207 g). Yield: 0.104 g, 0.371 mmol, 71\%. MS (EI) \textit{m/z}: 280 [M\textsuperscript{+}]. The \textsuperscript{1}H NMR spectrum is shown in Figure 3.40.

![1H NMR spectrum of 1,1’-biphenyl[naphthalene](400.1 MHz, CDCl\textsubscript{3}, 20 °C).](image)

\textbf{General Procedure B: Cross-Coupling Reactions at 60 °C Using Pd(CNAr\textsubscript{Dipp}\textsuperscript{2})\textsubscript{2} (2).} A 25 mL Airfree\textsuperscript{®} storage vessel was charged under argon with aryl bromide (0.522 mmol, 1.0 equiv), aryl boronic acid (1.04 mmol, 2.0 equiv), Pd(CNAr\textsubscript{Dipp}\textsuperscript{2})\textsubscript{2} (0.005 g, 0.005 mmol, 1.0 mol %), NaO\textsuperscript{t}Bu (0.150 g, 1.57 mmol, 3.0 equiv), and \textsuperscript{t}PrOH (2.0 mL). The vessel was sealed and the reaction mixture was magnetically stirred at 60 °C for 8 h. Conversion of aryl bromide to product was
determined by GC-MS analysis. The reaction mixture was allowed to cool to room temperature and then the solvent was removed from the reaction mixture under reduced pressure. The resulting residue was dissolved in water (6 mL) and extracted with hexanes (3 x 4 mL). The organic layers were combined and concentrated under reduced pressure to give crude biaryl product that was purified by column chromatography on silica gel, eluting with hexanes.

2-methylbiphenyl\(^{105}\) (Table 3.2, entry 1). General procedure B was followed using 2-bromotoluene (63 μL) and phenylboronic acid (0.127 g). Yield: 0.065 g, 0.388 mmol, 74%. MS (EI) \(m/z\): 168 [M\(^+\)]. The \(^1\)H NMR spectrum is shown in Figure 3.41.

![Figure 3.41. \(^1\)H NMR spectrum of 2-methylbiphenyl (400.1 MHz, CD\(_2\)Cl\(_2\), 20 °C).](image)
2,4’-dimethylbiphenyl\textsuperscript{106} (Table 3.2, entry 2). General procedure B was followed using 2-bromotoluene (63 μL) and p-tolylboronic acid (0.142 g). Yield: 0.074 g, 0.405 mmol, 78%. MS (EI) \textit{m/z}: 182 [M\textsuperscript{+}]. The \textsuperscript{1}H NMR spectrum is identical to that shown in Figure 3.26.

2,4-dimethylbiphenyl\textsuperscript{116} (Table 3.2, entry 3). General procedure B was followed using 1-bromo-2,4-dimethylbenzene (71 μL) and phenylboronic acid (0.127 g). Yield: 0.075 g, 0.409 mmol, 78%. MS (EI) \textit{m/z}: 182 [M\textsuperscript{+}]. The \textsuperscript{1}H NMR spectrum is identical to that shown in Figure 3.42.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3_42.png}
\caption{\textsuperscript{1}H NMR spectrum of 2,4-dimethylbiphenyl (400.1 MHz, CD\textsubscript{2}Cl\textsubscript{2}, 20 °C).}
\end{figure}
2,4,4’-trimethylbiphenyl$^{117}$ (Table 3.2, entry 4). General procedure B was followed using 1-bromo-2,4-dimethylbenzene (71 μL) and p-tolylboronic acid (0.142 g). Yield: 0.078 g, 0.398 mmol, 76%. MS (EI) $m/z$: 196 [M$^+$]. The $^1$H NMR spectrum is identical to that shown in Figure 3.43.

![Figure 3.43. $^1$H NMR spectrum of 2,4,4’-trimethylbiphenyl (400.1 MHz, CDCl$_3$, 20 °C).]
2’,2,4-trimethylbiphenyl\textsuperscript{118} (Table 3.2, entry 5). General procedure B was followed using 1-bromo-2,4-dimethylbenzene (71 μL) and o-tolyboronic acid (0.142 g). Yield: 0.076 g, 0.386 mmol, 74%. MS (EI) \( m/z \): 196 [M\textsuperscript{+}]. The \(^1\text{H}\) NMR spectrum is identical to that shown in Figure 3.44.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{nmr_spectrum}
\caption{\(^1\text{H}\) NMR spectrum of 2’,2,4-trimethylbiphenyl (400.1 MHz, CD\textsubscript{2}Cl\textsubscript{2}, 20 °C).}
\end{figure}
2,4-dimethyl-(1,1',2',1")-terphenyl (Table 3.2, entry 6). General procedure B was followed using 1-bromo-2,4-dimethylbenzene (71 μL) and 2-biphenylboronic acid (0.207 g). Yield: 0.102 g, 0.395 mmol, 76%. MS (EI) \( m/z \): 258 [M⁺]. The \(^1\)H NMR spectrum is identical to that shown in Figure 3.45.

**Figure 3.45.** \(^1\)H NMR spectrum of 2,4-dimethyl-(1,1',2',1")-terphenyl (400.1 MHz, CDCl₃, 20 °C).
2,6-dimethylbiphenyl\textsuperscript{119} (Table 3.2, entry 7). General procedure B was followed using 2-bromo-1,3-dimethylbenzene (70 μL) and phenylboronic acid (0.127 g). Yield: 0.063 g, 0.343 mmol, 66%. MS (EI) \( m/z \): 182 [M\(^+\)]. The \(^1\)H NMR spectrum is identical to that shown in Figure 3.46.

![Figure 3.46](image-url)  

**Figure 3.46.** \(^1\)H NMR spectrum of 2,6-dimethylbiphenyl (400.1 MHz, CD\(_2\)Cl\(_2\), 20 °C).
2,4',6-trimethylbiphenyl\textsuperscript{120} (Table 3.2, entry 8). General procedure B was followed using 2-bromo-1,3-dimethylbenzene (70 μL) and p-tolyllboronic acid (0.142 g). Yield: 0.076 g, 0.385 mmol, 74%. MS (EI) \textit{m/z}: 196 [M\textsuperscript{+}]. The \textsuperscript{1}H NMR spectrum is identical to that shown in Figure 3.47.

\textbf{Figure 3.47.} \textsuperscript{1}H NMR spectrum of 2,4',6-trimethylbiphenyl (400.1 MHz, CD\textsubscript{2}Cl\textsubscript{2}, 20 °C).
2',4'-difluoro-4-methylbiphenyl (Table 3.2, entry 9). General procedure B was followed using 4-bromotoluene (64 μL) and 2,4-difluorophenylboronic acid (0.165 g). The product was isolated as a white solid. Yield: 0.082 g, 0.402 mmol, 77%. $^1$H NMR (400.1 MHz, CDCl$_3$, 20 °C): $\delta = 7.43$–7.37 (m, 3H, $H_{\text{arom}}$), 7.28–7.27 (m, 2H, $H_{\text{arom}}$), 6.97–6.88 (m, 2H, $H_{\text{arom}}$), 2.42 (s, 3H) ppm. $^{13}$C{$^1$H} NMR (100.6 MHz, CDCl$_3$, 20 °C) $\delta = 163.5$, 161.0, 137.7, 132.2, 131.4, 129.4, 128.9, 128.9, 111.6, 104.4, 21.3 ppm. $^{19}$F{$^1$H} NMR (282.3 MHz, CDCl$_3$, 20 °C) $\delta = -110.6$, -112.2 ppm. HRMS (EI) m/z: 204 [M$^+$]. NMR spectra and HRMS traces are shown in Figures 3.48–3.51.

Figure 3.48. $^1$H NMR spectrum of 2',4'-difluoro-4-methylbiphenyl (400.1 MHz, CDCl$_3$, 20 °C).
Figure 3.49. $^{13}$C NMR spectrum of 2',4'-difluoro-4-methylbiphenyl (100.6 MHz, CDCl$_3$, 20 °C).

Figure 3.50. $^{19}$F NMR spectrum of 2',4'-difluoro-4-methylbiphenyl (282.3 MHz, CDCl$_3$, 20 °C).
2',4'-difluoro-3-methylbiphenyl (Table 3.2, entry 10). General procedure B was followed using 3-bromotoluene (63 μL) and 2,4-difluorophenylboronic acid (0.165 g). The product was isolated as a colorless oil. Yield: 0.082 g, 0.403 mmol, 77%. $^1$H NMR (400.1 MHz, CDCl$_3$, 20 °C): $\delta = 7.42$–$7.31$ (m, 4H, $H_{arom}$), 7.20–7.18 (m, 1H, $H_{arom}$), 6.97–6.88 (m, 2H, $H_{arom}$), 2.41 (s, 3H) ppm. $^{13}$C{$^1$H} NMR (100.6 MHz, CDCl$_3$, 20 °C) $\delta =$ 162.3 (dd, $^1J_{C-F} = 252$ Hz, $^3J_{C-F} = 12$ Hz, o-C-F), 159.9 (dd $^1J_{C-F} = 245$ Hz, $^3J_{C-F} = 12$ Hz, p-C-F), 138.3, 135.1, 131.6, 129.8, 129.8, 128.6, 128.55, 126.1, 111.6, 104.4, 21.6 ppm. $^{19}$F{$^1$H} NMR (282.3 MHz, CDCl$_3$, 20 °C) $\delta =$ $-112.5$, $-114.2$ ppm. MS (EI) $m/z$: 204 [M$^-$]. NMR spectra and HRMS traces are shown in Figures 3.52–3.55.
Figure 3.52. $^1$H NMR spectrum of 2’,4’-difluoro-3-methylbiphenyl (400.1 MHz, CDCl$_3$, 20 °C).

Figure 3.53. $^{13}$C NMR spectrum of 2’,4’-difluoro-3-methylbiphenyl (100.6 MHz, CDCl$_3$, 20 °C).
Figure 3.54. $^{19}$F NMR spectrum of 2',4'-difluoro-3-methylbiphenyl (282.3 MHz, CDCl$_3$, 20 °C).

Figure 3.55. HRMS of 2',4'-difluoro-3-methylbiphenyl.
General Procedure C: Cross-Coupling Screens of Pd Mono-Isocyanide Complexes. A 25 mL Airfree® storage vessel was charged under argon with the corresponding Pd mono-isocyanide complex (1 mol % Pd), 1-bromo-3,5-dimethylbenzene (69 µL, 0.50 mmol, 1.0 equiv), phenylboronic acid (0.122 g, 1.00 mmol, 2.0 equiv), NaO'Bu (0.144 g, 1.50 mmol, 3.0 equiv), and iPrOH (2.0 mL). The vessel was sealed and the reaction mixture was magnetically stirred for 8 h. An aliquot was taken from the reaction mixture, quenched by dilution in hexane, and analyzed by GC-MS.

Cross-Coupling Screens With [(CNArDipp2)PdCl]2(μ-Cl)2 (15). General procedure C was followed using [(CNArDipp2)PdCl]2(μ-Cl)2 (15) (0.003 g, 2.5 μmol). The observed GC yield (82 %) is an average of 5 independent runs (Table 3.5).

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</table>

Cross-Coupling Screens With Pd(CNArDipp2)(η^3-allyl)Cl (16). General procedure C was followed using Pd(CNArDipp2)(η^3-allyl)Cl (16) (0.003 g, 5 μmol). The observed GC yield (6 %) is an average of 5 independent runs (Table 3.6).
Table 3.6. GC Yields of Cross-Coupling Screens With Pd(CNArDipp2)(η3-allyl)Cl (16)

<table>
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<td>5</td>
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</tbody>
</table>

Cross-Coupling Screens With [(CNArDipp2)Pd]2(μ-η3-allyl)(μ-O’Pr) (17).

General procedure C was followed using [(CNArDipp2)Pd]2(μ-η3-allyl)(μ-O’Pr) (17) (0.003 g, 2.5 μmol). The observed GC yield (26 %) is an average of 5 independent runs (Table 3.7).

Table 3.7. GC Yields of Cross-Coupling Screens With [(CNArDipp2)Pd]2(μ-η3-allyl)(μ-O’Pr) (17)

<table>
<thead>
<tr>
<th>Run</th>
<th>GC Yield (%)</th>
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<tr>
<td>Average</td>
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</tbody>
</table>

Cross-Coupling Screens With [Pd(μ-CNArDipp2-η2-Dipp)]3 (22). General procedure C was followed using [Pd(μ-CNArDipp2-η2-Dipp)]3 (22) (0.003 g, 1.7 μmol). The observed GC yield (83 %) is an average of 5 independent runs (Table 3.8).
Table 3.8. GC Yields of Cross-Coupling Screens With [Pd(μ-CNArDipp2-η2-Dipp)]3 (22)

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<td>5</td>
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</table>

**General Procedure D: Cross-Coupling Screens at Low Pd(CNArDipp2)2 Catalyst Loading.** A 0.26 mM stock solution of Pd(CNArDipp2)2 (0.005 g, 5 µmol) in Et2O (20 mL) was prepared in the glovebox and the appropriate amount was added to a 25 mL Airfree® storage vessel. Et2O was removed under reduced pressure and the vessel was sealed and taken out of the glovebox. Under positive argon pressure, the vessel was charged with 1-bromo-3,5-dimethylbenzene (69 µL, 0.50 mmol, 1.0 equiv), phenylboronic acid (0.122 g, 1.00 mmol, 2.0 equiv), NaO'Bu (0.144 g, 1.50 mmol, 3.0 equiv), and iPrOH (2.0 mL). The sealed reaction mixture was magnetically stirred at room temperature for 8 h. An aliquot was taken from the reaction mixture, quenched by dilution in hexane, and analyzed by GC-MS.

**Cross-Coupling Screens With 0.1 mol % Pd(CNArDipp2)2 Catalyst Loading.** General procedure D was followed using 1.9 mL of the 0.26 mM stock solution of Pd(CNArDipp2)2. The observed GC yield (13.18 %) is an average of 5 independent runs (Table 3.9).
Table 3.9. GC Yields of Cross-Coupling Screens With 0.1 mol % Pd(CNAr\textsuperscript{Dipp\textsuperscript{2}})\textsubscript{2} (2)

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</tr>
<tr>
<td>Average</td>
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</tr>
</tbody>
</table>

Cross-Coupling Screens With 0.01 mol % Pd(CNAr\textsuperscript{Dipp\textsuperscript{2}})\textsubscript{2} Catalyst Loading. General procedure D was followed using 190 µL of the 0.26 mM stock solution of Pd(CNAr\textsuperscript{Dipp\textsuperscript{2}})\textsubscript{2}. The observed GC yield (1.41 %) is an average of 5 independent runs (Table 3.10).

Table 3.10. GC Yields of Cross-Coupling Screens With 0.1 mol % Pd(CNAr\textsuperscript{Dipp\textsuperscript{2}})\textsubscript{2} (2)

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3.13 Kinetic Measurement Details

**General considerations.** All measurements were obtained by \(^1\text{H}\) NMR on a Varian Mercury 400 MHz spectrometer. Samples were prepared in the glovebox and loaded into a J Young tube as either C\(_6\)D\(_6\) or toluene-\(d_8\) solutions (0.6 mL total) which contained Cp\(_2\)Fe as an internal standard. The samples were placed in the spectrometer pre-warmed to the reaction temperature, then subjected to a 10 min equilibration period prior to initial data collection. The experiments were conducted with single pulse acquisitions. All data were processed with the MestReNova software. Oxidative addition reaction plots were generated from integration of the upfield isopropyl methyl doublet of Pd(CNAr\(^{Dipp^2}\))\(_2\) (2) (1.10 ppm in benzene-\(d_6\)). Plots for the decomposition of \([(\text{CNAr}^{Dipp^2}\text{Pd}\text{)}_2(\mu-\eta^3-C_3H_5)(\mu-O'\text{Pr})\text{)}\text{ (17)}\) were generated from integration of the isopropyl methine septet (2.65 ppm in toluene-\(d_8\)). All linear plots (ln[Pd] over time) include data past three half-lives. Slopes for these lines were calculated by linear regression to give the observed rate constants (\(k_{obs}\)). Standard errors were also obtained from linear regression.

**Oxidative Addition of MesBr to Pd(CNAr\(^{Dipp^2}\))\(_2\) (2).** A J Young NMR tube was charged with a solution of Pd(CNAr\(^{Dipp^2}\))\(_2\) (2) (0.010 g, 0.010 mmol) and Cp\(_2\)Fe (0.002 g, 0.011 mmol) in C\(_6\)D\(_6\) (0.3 mL). This solution was frozen and layered with MesBr (16 \(\mu\)L, 0.10 mmol, 10 equiv) in C\(_6\)D\(_6\) (0.3 mL). The entire solution was refrozen and the sealed J Young tube was removed from the glovebox. Once the solution thawed, the sample was quickly shaken and placed in the spectrometer. \(^1\text{H}\)
NMR spectra were acquired every 2 min at 25 °C until the reaction had reached completion (60 min).

Oxidative Addition of MesBr to Pd(CNArDipp2)2 (2) with 0.10 Equiv. Additional CNArDipp2 Ligand. A 50 mM stock solution of CNArDipp2 (0.005 g, 0.010 mmol) in C_6D_6 (0.2 mL) was prepared in the glovebox. 20 μL of this CNArDipp2 stock solution was added to a J Young NMR tube containing Pd(CNArDipp2)2 (2) (0.010 g, 0.010 mmol) and Cp_2Fe (0.002 g, 0.011 mmol) in C_6D_6 (0.3 mL). The entire solution was frozen and layered with MesBr (16 μL, 0.10 mmol, 10 equiv) in C_6D_6 (0.3 mL). The entire solution was refrozen and the sealed J Young tube was removed from the glovebox. Once the solution thawed, the sample was quickly shaken and placed in the spectrometer. ^1H NMR spectra were acquired every 3 min at 25 °C until the reaction had reached completion (180 min).

Oxidative Addition of MesBr to Pd(CNArDipp2)2 (2) with 0.25 Equiv. Additional CNArDipp2 Ligand. A J Young NMR tube was charged with a solution of Pd(CNArDipp2)2 (2) (0.010 g, 0.010 mmol), CNArDipp2 (0.001 g, 0.003 mmol, 0.25 equiv), and Cp_2Fe (0.002 g, 0.011 mmol) in C_6D_6 (0.3 mL). This solution was frozen and layered with MesBr (16 μL, 0.10 mmol, 10 equiv) in C_6D_6 (0.3 mL). The entire solution was refrozen and the sealed J Young tube was removed from the glovebox. Once the solution thawed, the sample was quickly shaken and placed in the spectrometer. ^1H NMR spectra were acquired every 10 min at 25 °C until the reaction had reached completion (600 min).
Oxidative Addition of MesBr to Pd(CNArDipp²)₂ (2) with 0.50 Equiv. Additional CNArDipp² Ligand. A J Young NMR tube was charged with a solution of Pd(CNArDipp²)₂ (2) (0.010 g, 0.010 mmol), CNArDipp² (0.002 g, 0.005 mmol, 0.50 equiv), and Cp₂Fe (0.002 g, 0.011 mmol) in C₆D₆ (0.3 mL). This solution was frozen and layered with MesBr (16 μL, 0.10 mmol, 10 equiv) in C₆D₆ (0.3 mL). The entire solution was refrozen and the sealed J Young tube was removed from the glovebox. Once the solution thawed, the sample was quickly shaken and placed in the spectrometer. ¹H NMR spectra were acquired every 1 h at 25 °C until the reaction had reached completion (20 h).

Oxidative Addition of MesBr to Pd(CNArDipp²)₂ (2) with 1.0 Equiv. Additional CNArDipp² Ligand. A J Young NMR tube was charged with a solution of Pd(CNArDipp²)₂ (2) (0.010 g, 0.010 mmol), CNArDipp² (0.005 g, 0.010 mmol, 1.0 equiv), and Cp₂Fe (0.002 g, 0.011 mmol) in C₆D₆ (0.3 mL). This solution was frozen and layered with MesBr (16 μL, 0.10 mmol, 10 equiv) in C₆D₆ (0.3 mL). The entire solution was refrozen and the sealed J Young tube was removed from the glovebox. Once the solution thawed, the sample was quickly shaken and placed in the spectrometer. ¹H NMR spectra were acquired every 1 h at 25 °C until the reaction had reached completion (60 h). Due to overlap between the upfield isopropyl methyl doublets of Pd(CNArDipp²)₂ (2) and CNArDipp², integration of the Pd(CNArDipp²)₂ resonance was obtained by the following equation:
\[ \text{[Area Pd(CNAr^{Dipp2})_2]}_t = \text{[Area doublet (1.10 ppm)]}_t - \text{[Area CNAr^{Dipp2} doublet (1.09 ppm)]}_{\text{final}} \]

where \( t \) indicates a discrete time point during the reaction and \([\text{Area CNAr^{Dipp2} (1.09 ppm)]}_{\text{final}}\) is the area corresponding to one of the CNAr^{Dipp2} doublets upon completion of the reaction.

**Oxidative Addition of \((m\text{-Xyl})\text{Br}\) to \(\text{Pd(CNAr^{Dipp2})_2}\).** A J Young NMR tube was charged with a solution of \(\text{Pd(CNAr^{Dipp2})_2 (2)} (0.010 \text{ g, 0.010 mmol)}\) and \(\text{Cp}_2\text{Fe (0.002 g, 0.011 mmol)}\) in C\(_6\)D\(_6\) (0.3 mL). This solution was frozen and layered with \((m\text{-Xyl})\text{Br (14 \mu L, 0.10 mmol, 10 equiv)}\) in C\(_6\)D\(_6\) (0.3 mL). The entire solution was refrozen and the sealed J Young tube was removed from the glovebox. Once the solution thawed, the sample was quickly shaken and placed in the spectrometer. \(^1\text{H NMR spectra were acquired every 1 min at 25 °C until the reaction had reached completion (30 min).}"

**Decomposition of \([\text{(CNAr^{Dipp2})Pd}]_2(\mu-\eta^3\text{-allyl})(\mu-\text{O}^\prime\text{Pr}) (17)\) in a 7 mM Solution.** A J Young NMR tube was charged with a solution of \([\text{(CNAr^{Dipp2})Pd}]_2(\mu-\eta^3\text{-allyl})(\mu-\text{O}^\prime\text{Pr}) (17) (0.005 \text{ g, 0.004 mmol, 7 mM)}\) and \(\text{Cp}_2\text{Fe (0.002 g, 0.011 mmol)}\) in toluene-\(d_8\) (0.6 mL). The sample was placed in the spectrometer and \(^1\text{H NMR spectra were acquired every 5 min at 45 °C until } \text{[CNAr^{Dipp2}Pd]}_2(\mu-\eta^3\text{-C}_3\text{H}_5)(\mu-\text{O}^\prime\text{Pr}) (17) \text{ was completely consumed (150 min).}"


Decomposition of $[(\text{CNAr}^{\text{Dipp}})_2\text{Pd}]_2(\mu-\eta^3\text{-allyl})(\mu-\text{O}^\prime\text{Pr})$ (17) in a 14 mM Solution. A J Young NMR tube was charged with a solution of $[(\text{CNAr}^{\text{Dipp}})_2\text{Pd}]_2(\mu-\eta^3\text{-allyl})(\mu-\text{O}^\prime\text{Pr})$ (17) (0.010 g, 0.008 mmol, 14 mM) and Cp$_2$Fe (0.002 g, 0.011 mmol) in toluene-$d_8$ (0.6 mL). The sample was placed in the spectrometer and $^1$H NMR spectra were acquired every 5 min at 45 °C until $[(\text{CNAr}^{\text{Dipp}})_2\text{Pd}]_2(\mu-\eta^3\text{-C}_3\text{H}_5)(\mu-\text{O}^\prime\text{Pr})$ (17) was completely consumed (150 min).

3.14 Crystallographic Structure Determinations

General considerations. Single crystal X-ray structure determinations were carried out at low temperature on a Bruker P4, Platform, or Kappa Diffractometer equipped with a Bruker APEX detector. All structures were solved by direct methods with SIR 2004$^{121}$ and refined by full-matrix least-squares procedures utilizing SHELXL-97$^{122}$. Crystallographic data collection and refinement information are listed in Tables 3.11–3.13. The crystallographic routine SQUEEZE$^{123}$ was performed on disordered Et$_2$O molecules of co-crystallization in the structure of $\text{trans-PdBr}(m\text{-Xyl})(\text{CNAr}^{\text{Dipp}})_2$ (14). SQUEEZE was also performed on disordered THF molecules of co-crystallization in the structures of $[(\text{CNAr}^{\text{Dipp}})_2\text{PdCl}]_2(\mu-\text{Cl})_2$ (15) and $[\text{Pd}(\mu-\text{CNAr}^{\text{Dipp}}-\eta^2\text{-Dipp})_3$ (22). The crystal structure of $[(\text{CNAr}^{\text{Dipp}})_2\text{PdCl}]_2(\mu-\text{Cl})_2$ (15) contains positional disorder on the Pd and Cl atoms, with additional two-site positional disorder created by crystallographic symmetry. These atoms were modeled and refined with a 33 % site occupation factor (sof). The crystal structures of $\text{Pd}(\text{CNAr}^{\text{Dipp}})(\eta^3\text{-allyl})\text{Cl}$ (16) and $[(\text{CNAr}^{\text{Dipp}})_2\text{Pd}]_2(\mu-\eta^3\text{-allyl})(\mu-\text{N}^\prime\text{Pr})_2$ (18)
contain allyl-group positional disorder, which was modeled and refined. The crystal structure of \( [(\text{CNAr}^{\text{Dipp2}})\text{Pd}]_2(\mu-\eta^3\text{-allyl})(\mu-N(\text{iPr})_2) \) (18) contains additional isopropyl-group positional disorder, which was modeled and refined. The crystal structure of \( [(\text{CNAr}^{\text{Dipp2}})\text{Pd}]_2(\mu-\eta^3\text{-allyl})(\mu-O^t\text{Bu}) \) (20) contains positional disorder on the isocyanide carbon and Pd atoms, and the bridging allyl and tert-butoxide ligands. Crystallographic symmetry creates additional two-site positional disorder on these moieties and the \( \text{C}_6\text{H}_5\text{F} \) molecule of co-crystallization. All disorder was accounted for in the modeling and refinement of these components. Lastly, crystallographic symmetry on the structures of \( [(\text{CNAr}^{\text{Dipp2}})\text{Pd}]_2(\mu-\eta^3\text{-allyl})(\mu-\text{Cl}) \) (19) and \( [(\text{CNAr}^{\text{Dipp2}})\text{Pd}]_2(\mu-\eta^3\text{-allyl})(\mu-\text{Br}) \) (21) creates two-site positional disorder on the bridging allyl and halide ligands, which were modeled and refined with a 50% sof.

### Table 3.11. Crystallographic Data Collection and Refinement Information for trans-PdBr(\(m\)-Xyl)\((\text{CNAr}^{\text{Dipp2}})\)\(_2\)\(\cdot\)0.5\(\text{Et}_2\text{O}\), \( [(\text{CNAr}^{\text{Dipp2}})\text{PdCl}]_2(\mu-\text{Cl})_2\)\(\cdot\)3.5\(\text{THF}\), and Pd(\(\text{CNAr}^{\text{Dipp2}}\))(\(\mu-\eta^3\text{-allyl}\))\(\text{Cl}\)\(\cdot\)0.5\(\text{THF}\).

<table>
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<th>( [(\text{CNAr}^{\text{Dipp2}})\text{PdCl}]_2(\mu-\text{Cl})_2)(\cdot)3.5(\text{THF}) (15)</th>
<th>Pd((\text{CNAr}^{\text{Dipp2}}))((\mu-\eta^3\text{-allyl}))(\text{Cl})(\cdot)0.5(\text{THF}) (16)</th>
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<td><strong>Formula</strong></td>
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<td>( \text{C}<em>{76}\text{H}</em>{102}\text{Cl}_4\text{N}_2\text{O}_3\text{Pd}_2 )</td>
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<td>( \text{I}4/m )</td>
<td>( \text{P}_{2_1}/c )</td>
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<td>22.184(6)</td>
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<td>( c ), Å</td>
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<td>Mo-(\text{K}_{\alpha}), 0.71073</td>
<td>Mo-(\text{K}_{\alpha}), 0.71073</td>
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Table 3.12. Crystallographic Data Collection and Refinement Information for [(CNArDipp\(^{2}\))Pd\(_{2}\)](μ-η\(^{-3}\)-allyl)(μ-N(Pr))\(_{2}\), [(CNAr\(^{\text{Dipp}}\))Pd\(_{2}\)](μ-η\(^{-3}\)-allyl)(μ-Cl), and [(CNAr\(^{\text{Dipp}}\))Pd\(_{2}\)](μ-η\(^{-3}\)-allyl)(μ-Ο-Bu)•C\(_{6}H\(_{5}\)F.

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<th>(b), Å</th>
<th>(c), Å</th>
<th>(α), deg</th>
<th>(β), deg</th>
<th>(γ), deg</th>
<th>V, Å(^3)</th>
<th>Z</th>
<th>(\rho) (calcd.), g/cm(^3)</th>
<th>(\mu), mm(^{-1})</th>
<th>(\lambda), Å</th>
<th>Temp, K</th>
<th>(θ) max, deg</th>
<th>R/1</th>
<th>(wR)(_2)</th>
<th>GOF</th>
</tr>
</thead>
<tbody>
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<td>16.9767(11)</td>
<td>19.6154(13)</td>
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<td>P-1</td>
<td>8.534(3)</td>
<td>11.030(4)</td>
<td>16.148(5)</td>
<td>75.637(4)</td>
<td>84.351(5)</td>
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<td>P-1</td>
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Table 3.13. Crystallographic Data Collection and Refinement Information for [(CNAr\(^{\text{Dipp}}\))Pd\(_{2}\)](μ-η\(^{-3}\)-allyl)(μ-Br) and [Pd(μ-CNAr\(^{\text{Dipp}}\)-η\(^{-2}\)-Dipp)]\(_{2}\)•13.25THF.

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<th>(γ), deg</th>
<th>V, Å(^3)</th>
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<th>(\rho) (calcd.), g/cm(^3)</th>
<th>(\mu), mm(^{-1})</th>
<th>(\lambda), Å</th>
<th>Temp, K</th>
<th>(θ) max, deg</th>
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<th>(wR)(_2)</th>
<th>GOF</th>
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</thead>
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<td>90</td>
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3.15 References


(82) Scrivanti, A.; Carturan, G.; Crociani, B. Organometallics 1983, 2, 1612-1617.


### 3.16 Acknowledgments

Chapter 3 is currently being prepared for publication by Labios, L. A.; Stauber, J. M.; Moore, C. E.; Rheingold, A. L.; and Figueroa, J. S. The dissertation author is the primary author of this paper.
Chapter 4

Preparation and Electronic Modulation of Novel Palladium-Isocyanide Complexes Containing Redox Non-Innocent Nitrosoarene Ligands

4.1 Introduction

Redox-active ligands offer unique strategies to modulate the electronic structure and reactivity of transition metal complexes. As opposed to traditional spectator ligands, which remain unaffected in redox transformations, redox-active ligands, otherwise termed “non-innocent” ligands, are directly involved in redox reactions of coordination complexes and can thereby adopt multiple oxidation states.\textsuperscript{1,2} Some classically recognized examples are the NO\textsuperscript{+}/NO\textsuperscript{-}/NO\textsuperscript{-},\textsuperscript{3-5} O\textsubscript{2}/O\textsubscript{2}•\textsuperscript{-}/O\textsubscript{2}\textsuperscript{2-}\textsuperscript{,6,7} and o-quinone/o-semiquinone/catecholate\textsuperscript{8-11} redox series, which have found significance in biochemical processes.\textsuperscript{12} The synergistic behavior of these ligands with transition metals in redox reactions arises from the energy match between the metal and ligand frontier orbitals. Such electronic variability has made “non-innocent” ligands, such as α-diimines,\textsuperscript{13-16} catecholates,\textsuperscript{8-11} 2,6-diiminopyridines,\textsuperscript{17} and α-dithiolenes,\textsuperscript{18,19}
increasingly useful in metal-catalyzed transformations.\textsuperscript{20,21} For example, the groups of Chirik\textsuperscript{22} and Heyduk\textsuperscript{23} have exploited 2,6-diiminopyridine and bis(amidophenolate) ligands as electron reservoirs that store and release electron equivalents in reactions mediated by Fe(II) and Zr(IV) complexes, respectively.

*C*-organonitroso (RNO) moieties have also been shown to exhibit “noninnocent” behavior in transition metal complexes.\textsuperscript{24} Previous reports have indicated the formation of metal nitroxide species, \(\text{M}(\text{RNO})^{1-}\), from the one-electron reduction of free RNO,\textsuperscript{25-31} and from the use of RNO compounds as spin traps for organometallic radicals.\textsuperscript{32} While the latter studies suggest the presence of (RNO)\textsuperscript{1-} as an \(\eta^1\)-N-bound ligand, structural data for the existence of these species is lacking. Due to their transient nature, metal nitroxides have primarily been observed in EPR spectroscopic studies. Thus far, the only examples of structurally characterized transition metal complexes containing the \((\text{PhNO})^{1-}\) radical monoanion are the bimetallic compounds \([\{\text{Cp}^*\text{M}(\mu-S^\prime \text{Pr})\} _2(\mu-1\kappa^1N:2\kappa^1O-\text{PhNO})][\text{X}] (\text{M} = \text{Ru, Rh, Ir}; \text{X} = \text{OTf, BPh}_4)\).\textsuperscript{33}

Given the biological relevance of RNO compounds\textsuperscript{34,35} and their diverse coordination chemistry within transition metal complexes,\textsuperscript{36,37} it is surprising that the redox-activity of these ligands has received limited attention. This report constitutes the first study in which metal complexes of the full \((\text{PhNO})^0/(\text{PhNO})^{1-}/(\text{PhNO})^{2-}\) electron transfer series (Scheme 4.1) have been isolated and structurally characterized. Herein we also outline the structural, spectroscopic, and computational parameters that collectively elucidate the ground state electronic structure of these molecules. Indeed, recent developments in the chemistry of metal complexes with redox-active ligands
have emphasized the need for methods which can clearly distinguish between a closed-shell electronic configuration and a singlet diradical ground state containing antiferromagnetically coupled radical ligands.\(^{38}\) Moreover, we have also prepared and structurally characterized a range of novel palladium complexes containing substituted \(\eta^1-N-(\text{ArNO})^{\text{\textendash}1}\) ligands, and describe some interesting discrepancies between their solid state and solution state behaviors.

![Scheme 4.1. Top: (PhNO)\(^0\)/(PhNO)\(^1\)\(-1\)//(PhNO)\(^2\)\(-2\) electron transfer series. Bottom: Resonance structures of (PhNO)\(^1\)\(-1\).](image)

### 4.2 Electronic Reduction of Nitrosoarene Ligands by Pd(CNAr\text{Dipp}\textsuperscript{2})\textsubscript{2} (2)

The reactivity of Pd(CNAr\text{Dipp}\textsuperscript{2})\textsubscript{2} (2) towards electronically unsaturated substrates such as PhNO was described in Chapter 2. The mono-nitrosoarene complex Pd(\(\eta^2-O,N\)-PhNO)(CNAr\text{Dipp}\textsuperscript{2})\textsubscript{2} (12) was isolated from the reaction between Pd(CNAr\text{Dipp}\textsuperscript{2})\textsubscript{2} (2) and 1 equiv of PhNO. Bond reduction of the nitroso moiety is evident from the N–O bond distance of 1.349(3) Å, which is significantly longer than the N–O distance observed in free PhNO (\(d(\text{N–O}) = 1.268(4)\) Å).\(^{37}\) N–O bond reduction is further supported by the square planar environment about the Pd center and the \(\nu_{\text{CN}}\) stretches at 2149 and 2105 cm\(^{-1}\), which are higher in energy than in
Pd(CNArDipp\(^2\))\(_2\) (2). The \(o\)-TolNO derivative, Pd(\(\eta^2\)-\(O,N\)-\(o\)-TolNO)(CNArDipp\(^2\))\(_2\) (23) was analogously obtained by treatment of Pd(CNArDipp\(^2\))\(_2\) (2) with 1 equiv of \(o\)-TolNO. Similar to its PhNO analogue, Pd(\(\eta^2\)-\(O,N\)-\(o\)-TolNO)(CNArDipp\(^2\))\(_2\) (23) gives rise to fairly high energy \(\nu_{CN}\) stretches at 2141 and 2112 cm\(^{-1}\), and its molecular structure displays a lengthened N–O bond distance of 1.364(4) Å (Figure 4.1). The ArNO ligands in Pd(\(\eta^2\)-\(O,N\)-PhNO)(CNArDipp\(^2\))\(_2\) (12) and Pd(\(\eta^2\)-\(O,N\)-\(o\)-TolNO)(CNArDipp\(^2\))\(_2\) (23) can thus be regarded as doubly-\(N,O\)-deprotonated derivatives of \(N\)-arylhydroxylamine.\(^{39}\) There are several examples of structurally characterized mononuclear “metallooxaziridine” complexes, which contain \(\eta^2\)-coordinated nitrosoarene ligands exhibiting N–O bond distances between 1.385 and 1.431 Å.\(^{40-44}\) The first of these complexes was [Mo\(\text{V}^{\text{II}}\)(pic)(HMPA)(\(\eta^2\)-PhNO\(^2\))], reported by Sharpless and co-workers, for which the N–O bond distance of 1.416(7) Å implied reduction to an N–O single bond.\(^{40}\) The complex Pt(\(\eta^2\)-PhNO)(PPh\(_3\))\(_2\) displayed a similar N–O bond distance of 1.410(7) Å, and is the first monomeric group 10 “metallooxaziridine” to be structurally characterized.\(^{41}\) While \(\eta^2\)-coordination of PhNO ligands has been proposed for other group 10 metal complexes,\(^{45-49}\) structural data for these compounds have not been reported.

An interesting result was observed in the reaction between Pd(CNArDipp\(^2\))\(_2\) (2) and 2 equiv of PhNO. The product is the square planar complex Pd(\(\kappa^1\)-\(N\)-PhNO)\(_2\)(CNArDipp\(^2\))\(_2\) (13) with two \(\eta^1\)-N-PhNO ligands trans to each other. As mentioned in Chapter 2, the square planar coordination geometry in Pd(\(\kappa^1\)-\(N\)-PhNO)\(_2\)(CNArDipp\(^2\))\(_2\) (13) is consistent with the presence of a divalent Pd center.
Figure 4.1. Molecular structure of one crystallographically independent molecule of Pd($\eta^2$-$O,N$-$o$-TolNO)(CNAr$^{Dipp2}$)$_2$ (23). Selected bond distances (Å) and angles (°): Pd1–C1 = 1.971(4); Pd1–C2 = 2.010(4); Pd1–N1 = 2.079(3); Pd1–O1 = 2.021(3); N1–O1 = 1.364(4); C1–Pd1–C2 = 104.68(1); C1–Pd1–N1 = 114.37(1); C2–Pd1–O1 = 102.16(1); C1–N2–C3 = 173.77(3); C2–N3–C33 = 164.01(3).

Additionally, several structural and spectral properties demonstrate decreased π-back donation to the isocyanide ligands. These include ν_{CN} stretches at 2188, 2146, and 2111 cm$^{-1}$, which are higher in energy relative to those of zerovalent Pd(CNAr$^{Dipp2}$)$_2$, a lengthened Pd–C$_{iso}$ bond distance of 2.004(2) Å, and lack of bending in the isocyanide ligands (∠(C$_{iso}$–N2–C$_{ipso}$) = 174.6(2°)). A particularly noteworthy feature is the N–O bond distance of 1.291(2) Å in Pd(κ$^1$-$N$-PhNO)$_2$(CNAr$^{Dipp2}$)$_2$ (13). This is considerably longer than the N–O bond distance of 1.209(3) Å in Balch’s complex, PdCl$_2$(κ$^1$-$N$-PhNO)$_2$,50,51 which contains two neutral $\eta^1$-$N$-PhNO ligands, (Figure 4.2). In addition, the N–O bond distance in Pd(κ$^1$-$N$-PhNO)$_2$(CNAr$^{Dipp2}$)$_2$ (13) is shorter than that in Pd($\eta^2$-$O,N$-PhNO)(CNAr$^{Dipp2}$)$_2$ (12), which contains a dianionic (PhNO)$_2^-$ ligand (Figure 4.2).
From these parameters, it is reasonable to postulate a one-electron reduction of each PhNO unit by Pd in Pd(κ₁-N-PhNO)₂(CNArDipp₂)₂ (13) (Figure 4.2). Consequently, two electronic descriptions for this divalent Pd complex were previously proposed in Chapter 2. One was a closed-shell representation consisting of a (σ)⁴(π)⁴(π*)² singlet ground state with two nondegenerate π*orbitals (a₉ and a₁ in Cᵥ symmetry), wherein the HOMO is the lower energy ligand-based a₁ orbital (Figure 2.22). An alternative description was a singlet diradical description containing two antiferromagnetically coupled (PhNO)⁺⁻ radical monoanions. Spin-restricted DFT calculations had previously been shown to agree with the closed-shell description. To distinguish between these two electronic descriptions, additional experimental and computational studies were accordingly pursued.
4.3 (PhNO)_{0-1/2} Redox Series Featuring a Singlet Diradical Complex

The relative oxidation states of the Pd centers in these nitrosoarene complexes were determined via Pd K-edge X-ray absorption spectroscopy (XAS) (Figure 4.3, Table 4.1). In K-edge XAS experiments conducted on a series of compounds, an increase in the K-edge energy by 1 – 2 eV typically corresponds to an increase in the oxidation state by one unit. While 1s → 3d pre-edge features are typically used to compare oxidation states within a series of complexes, the position of the rising Pd K-edge is less sensitive to the coordination number about the metal center and provides a more direct comparison between two-coordinate Pd(CNArDipp)_{2} (2) and the four-coordinate Pd-nitrosoarene complexes. As shown in Figure 4.3 and Table 4.1, the rising edge energies corresponding to the nitrosoarene complexes are 2.4 – 4.0 eV higher in energy than that of zerovalent Pd(CNArDipp)_{2} (2). This provides direct evidence for divalent Pd centers in Pd(κ_{1}-N-PhNO)_{2}(CNArDipp)_{2} (13) and Pd(η^{2}-O,N-o-TolNO)(CNArDipp)_{2} (23) (Pd K-edge XAS data for Pd(η^{2}-O,N-PhNO)(CNArDipp)_{2} (12) has not yet been obtained). For comparison, data for the dichloride trans-PdCl_{2}(CNArDipp)_{2} (1) is included and is consistent with the presence of a Pd(II) atom.

Experimental evidence for a singlet diradical electronic structure was obtained from magnetic susceptibility measurements on a solid sample of Pd(κ_{1}-N-PhNO)_{2}(CNArDipp)_{2} (13). SQUID magnetometry data in Figure 4.4 reveal that Pd(κ_{1}-N-PhNO)_{2}(CNArDipp)_{2} (13) is paramagnetic at room temperature, with a temperature-dependent magnetic moment of ~1.9 μ_{B} at 300 K that gradually decreases to ~0.3 μ_{B} at 4 K. Data above 300 K are not included due to decomposition of the complex at higher
temperatures. The observed coupling constant $J$ is $-115(2)$ cm$^{-1}$ ($H = -2J \cdot S_1 \cdot S_2$, $S_1 = S_2 = 1/2$, $g = 2.0$) and agrees well with the calculated coupling constant of $-114$ cm$^{-1}$.

These data demonstrate the diradical character of Pd($\kappa^1$-N-PhNO)$_2$(CNArDipp$_2$)$_2$ (13), which is comprised of an $S = 0$ ground state and a low-lying $S = 1$ excited state, featuring two antiferromagnetically coupled (PhNO)$^{1-}$ radical monoanions. While a variety of $N,O$ binding modes have been observed among nitroso complexes of the transition metals, this is the first isolable and structurally characterized example of a metal complex containing $\eta^1$-N-(PhNO)$^{1-}$ ligands.

![Figure 4.3. Pd K-edge XAS data of Pd(CNArDipp$_2$)$_2$ (2, black), Balch’s complex (orange), PdCl$_2$(CNArDipp$_2$)$_2$ (1) (pink), Pd($\kappa^1$-N-PhNO)$_2$(CNArDipp$_2$)$_2$ (13) (blue), and Pd($\eta^2$-O,N-o-TolNO)(CNArDipp$_2$)$_2$ (23) (green).]
Table 4.1. Pd Rising Edge Energies

| Complex | Energy of the Pd Rising Edge (eV) | |Δ|E| (eV)\(^a\) |
|---------|----------------------------------|---|---------------|
| Pd(CNAr\(^{Dipp2}\))\(_2\) (2) | 24343.2 | | 0 |
| PdCl\(_2\)(κ\(^1\)-N-PhNO)\(_2\) | 24345.6 | | 2.4 |
| PdCl\(_2\)(CNAr\(^{Dipp2}\))\(_2\) (1) | 24346.5 | | 3.3 |
| Pd[κ\(^1\)-N-PhNO]\(_2\)(CNAr\(^{Dipp2}\))\(_2\) (13) | 24347.2 | | 4.0 |
| Pd(η\(^2\)-O,N-o-TolNO)(CNAr\(^{Dipp2}\))\(_2\) (23) | 24346.3 | | 3.1 |

\(^a\) Energy difference between the Pd rising edge energy of 2 (Pd\(^{0}\)) and the other complexes given (Pd\(^{II}\)).

Figure 4.4. SQUID magnetometry data of Pd(κ\(^1\)-N-PhNO)\(_2\)(CNAr\(^{Dipp2}\))\(_2\) (13) (open circles) along with simulated data (red line). Fixed simulation parameters: Spin 1 = Spin 2 = 0.5; \(g_1 = g_2 = 2.000\); \(\chi_{dia} = -800.0 \times 10^{-6}\) emu. Fit variables: \(J_{12} = -115.1\) cm\(^{-1}\); paramagnetic impurity (\(S = 0.5\)) = 4.0%; temperature-independent paramagnetism (TIP) = 4.8 \times 10^{-6} emu.

Additional DFT calculations were performed on Pd(κ\(^1\)-N-PhNO)\(_2\)(CNAr\(^{Dipp2}\))\(_2\) (13) to further elucidate the singlet diradical electronic ground state. The experimentally determined and geometry-optimized structural parameters are listed in Table 4.2. Bachler and co-workers have reported a detailed outline of theoretical evidence for singlet diradical character,\(^{54}\) and the following observations are consistent with their criteria. First, a broken symmetry solution (BS(1,1), \(S = 0\)) was found to be
32 kcal mol\(^{-1}\) lower in energy than the spin-restricted closed-shell solution. Second, the magnetic orbitals corresponding to the \(\alpha\) spin electron and \(\beta\) spin electron are localized on different PhNO ligands in the complex and exhibit low overlap (\(S_{\alpha\beta} = 0.10\)) (Figure 4.5). This is reflective of weak antiferromagnetic coupling between the two spins. The calculated Mulliken spin density plot for Pd(\(\kappa^1\text{-N-PhNO})_2\text{CNAr}^{\text{Dipp}_2})_2\) (13) additionally shows the presence of two antiferromagnetically coupled (PhNO)^1− radical monoanions (Figure 4.6). In accord with the observed and calculated coupling constants, the computed energy gap between the singlet and triplet states is only 0.4 kcal mol\(^{-1}\). This thereby demonstrates a mixture of a singlet ground state with a low-lying triplet excited state in Pd(\(\kappa^1\text{-N-PhNO})_2\text{CNAr}^{\text{Dipp}_2})_2\) (13).

*Table 4.2.* Experimental and Calculated Structural Parameters for Pd(PhNO) Complexes

<table>
<thead>
<tr>
<th>Complexes</th>
<th>N‒O (Å)</th>
<th>av. Pd‒N (Å)</th>
<th>av. Pd‒C (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>exp.</td>
<td>calc.</td>
<td>exp.</td>
</tr>
<tr>
<td>Pd((\kappa^1\text{-N-PhNO})_2\text{CNAr}^{\text{Dipp}_2})_2) (13)</td>
<td>1.291(2)</td>
<td>1.278</td>
<td>2.011(2)</td>
</tr>
<tr>
<td>PdCl(_2)((\kappa^1\text{-N-PhNO})_2)</td>
<td>1.209(3)</td>
<td>1.221</td>
<td>1.994(2)</td>
</tr>
</tbody>
</table>

*Figure 4.5.* Magnetic orbitals of Pd(\(\kappa^1\text{-N-PhNO})_2\text{CNAr}^{\text{Dipp}_2})_2\) (13).
4.4. Molecular Orbital Descriptions of Pd(PhNO) Complexes

The effects of electronic reduction on the N–O bond length in PhNO can further be visualized on the Molecular Orbitals of (PhNO)$_{1-}$. The HOMO (a') and SOMO (a'') are shown in Figure 4.7. DFT calculations on the uncoordinated (PhNO)$_{1-}$ radical monoanion determined that the geometry optimized planar structure is 11.8 kcal mol$^{-1}$ lower in energy than the structure in which the O–N–C–C dihedral angle is constrained to 90° (the arene ring and the O–N–C plane are perpendicular to each other). The SOMO (a''), which is the LUMO in (PhNO)$^0$ and the HOMO in (PhNO)$^2-$, consists of $\pi$-anti-bonding character with respect to the N–O bond. Thus, one-electron oxidation to (PhNO)$^0$ should induce N–O bond shortening, whereas one-electron reduction to (PhNO)$^2-$ should induce N–O bond lengthening. This overall trend is indeed observed among Balch’s complex PdCl$_2$(κ$^1$-N-PhNO)$_2$, the singlet diradical Pd(κ$^1$-N-PhNO)$_2$(CNArDipp)$_2$ (13), and the palladium oxaziridines Pd($\eta^2$-
These complexes constitute an electron transfer series which illustrates the relationship between nitrosoarene ligand reduction and various structural parameters, including N–O bond distance and metal oxidation state.

DFT calculations on Balch’s complex PdCl₂(κ¹⁻N-PhNO)₂ confirmed its closed-shell electronic structure containing two neutral (PhNO)⁰ ligands. Unlike Pd(κ¹⁻N-PhNO)₂(CNArdipp²)₂ (13), no broken symmetry solution was found for this
complex. The calculated N‒O distance of 1.221 Å is consistent with N‒O double bonds, yet is slightly longer than the observed N‒O distance (Table 4.2). The short N‒O distance indicates that the planar PhNO ligands in Balch’s complex serve as σ-donors and weak π-acceptors. This demonstrates the weak π-basicity of the divalent Pd center, which is due to the low energy of the Pd(II)-d orbitals relative to the LUMO of PhNO. Consistent with the d8 electron count for the Pd(II) center, the following four occupied metal d orbitals were found: HOMO-6 (d_{yz}), HOMO-2 (d_{x^2}), HOMO-1 (d_{xy}), and HOMO (d_{xz}) (Figure 4.8). The LUMO exhibits no Pd-d character, as it results from the formal bonding combination of the two PhNO a”-π* orbitals (Figure 4.9). Meanwhile, the LUMO+1 consists of the anti-bonding combination of these orbitals, which has the appropriate symmetry to interact with the Pd-d_{xy} orbital (Figure 4.9). This interaction is weakly anti-bonding and results in a small energy gap (~ 7 kcal mol\(^{-1}\)) between the LUMO and the LUMO+1.

![Figure 4.8](Image). The four occupied Pd-d orbitals in Balch’s complex PdCl₂(κ¹-N-PhNO)₂.
To provide a further understanding of the singlet diradical ground state in Pd(κ¹⁻N-PhNO)₂(CNArDipp)₂ (13), a molecular orbital interaction diagram and corresponding state-interaction diagram are employed. For simplicity, a generic L₂Pd(η¹⁻N-PhNO)₂ structure with C₂ᵥ site-symmetry was used, in which the L–Pd–L fragment coincides with the z-axis. The molecular orbital interaction diagram is accordingly constructed from this PdL₂ fragment and a (PhNO)₂ set of degenerate ligand group orbitals (LGOs) arranged in C₂ᵥ symmetry (Figure 4.10). These LGOs (a_u[LGO] and b_g[LGO]) result from the bonding and anti-bonding combinations of the two PhNO a''⁻π* orbitals. The b_g[LGO] has the appropriate symmetry to interact with the Pd-dₓz orbital (b_g[PdL₂]), whereas the a_u[LGO] is nonbonding with respect to the
metal d orbitals. As mentioned earlier, the Pd(II)-d orbitals are relatively lower in energy than the LUMO of PhNO, thereby resulting in poor overlap between the Pd-d and PhNO $\pi^*$ orbitals. This poor overlap gives rise to a small HOMO–LUMO gap between the ligand-based $1a_u$ HOMO and the $2b_g$ LUMO ($b_g[\text{PdL}_2]$-$b_g[\text{LGO}]$). The composition of these frontier orbitals also describes the LUMO and LUMO+1 in Balch’s complex PdCl$_2$(κ$^1$-N-PhNO)$_2$, which are shown in Figure 4.7 to consist of the same orbital makeup as the HOMO and LUMO of Pd(κ$^1$-N-PhNO)$_2$(CNAr$^{Dipp^2}$)$_2$ (13). The closed-shell configuration for the latter complex arises from the presence of two electrons in the $1a_u$ HOMO (Figure 4.10).

This small HOMO–LUMO gap results in mixing of a symmetry appropriate excited state into the closed-shell electronic state to give rise to the singlet diradical ground state. As illustrated in the electronic state-interaction diagram in Figure 4.10, this involves mixing between the symmetry-matched $\Gamma_2(1A_g)$ and $\Gamma_3(1A_g)$ states, leaving the low-lying triplet excited state $\Gamma_1(3B_u)$ unchanged. This mixing represents

![Figure 4.10. Molecular orbital interaction diagram (left) and electronic state-interaction diagram (right) for an idealized version of Pd(κ$^1$-N-PhNO)$_2$(CNAr$^{Dipp^2}$)$_2$ (13).](image)
an antiferromagnetic coupling pathway in which the spins of two independent ligand-based radicals (a”) can couple to each other. Such a description accounts for the singlet ground state observed at low temperatures in the solid state.

4.5 Solution Behavior of Pd(ArNO) Complexes

The singlet diradical character of Pd(κ¹-N-PhNO)₂(CNArDipp²)₂ (13) is confirmed in the solid state, yet its accessibility in solution at room temperature is questionable. Upon closer inspection, Pd(κ¹-N-PhNO)₂(CNArDipp²)₂ (13) was found to exhibit the same solution properties as its mono-nitrosoarene counterpart Pd(η²-O,N-PhNO)(CNArDipp²)₂ (12). For instance, the IR spectra of both compounds differ from each other in the solid state by the presence of a third, higher energy νCN stretch at 2188 cm⁻¹ in the spectrum of Pd(κ¹-N-PhNO)₂(CNArDipp²)₂ (13) (Figure 4.11). Yet, the solution IR spectra of both compounds in C₆D₆ at room temperature exhibit two strong νCN stretches at similar energies (Figure 4.12). The ¹H NMR spectra corresponding to both compounds are also very similar in C₆D₆ at room temperature. These spectra differ mainly in the chemical shifts and patterns of the PhNO signals, which are broadened in Pd(κ¹-N-PhNO)₂(CNArDipp²)₂ (13) (Figure 4.13). Further, Pd(κ¹-N-PhNO)₂(CNArDipp²)₂ (13) exhibits no significant magnetic susceptibility in solution at room temperature, according to Evans method magnetic moment determination (C₆D₆/(Me₃Si)₂O, 20 °C). This is likewise observed for Pd(η²-O,N-PhNO)(CNArDipp²)₂ (12), as well as for trans-PdCl₂(CNArDipp²)₂ (1) and Pd(CNArDipp²)₂ (2), which are all expected to be diamagnetic.
Figure 4.11. FTIR (KBr) spectra of Pd(η²-O,N-PhNO)(CNAr\textsuperscript{Dipp}²)\textsubscript{2} (12) (top) and Pd(κ¹-N-PhNO)\textsubscript{2}(CNAr\textsuperscript{Dipp}²)\textsubscript{2} (13) (bottom).
Figure 4.12. FTIR spectra of Pd($\eta^2$-$O,N$-PhNO)(CNAr$^{Dipp_2}$)$_2$ (12) (top) and Pd($\kappa^1$-$N$-PhNO)$_2$(CNAr$^{Dipp_2}$)$_2$ (13) (bottom) in C$_6$D$_6$. 
Figure 4.13. $^1$H NMR (400 MHz, 20 °C) spectra of Pd(η$^2$-O,N-PhNO)(CNAr$^{Dipp}_2$)$_2$ (12) (top) and Pd(κ$^1$-N-PhNO)$_2$(CNAr$^{Dipp}_2$)$_2$ (13) (bottom) in C$_6$D$_6$. 
These data suggest an equilibrium between $\text{Pd}(\kappa^1-N\text{-PhNO})_2(\text{CNAr}^{\text{Dipp}^2})_2$ (13) and $\text{Pd}(\eta^2-O,N\text{-PhNO})(\text{CNAr}^{\text{Dipp}^2})_2$ (12) via PhNO dissociation in solution at room temperature. Accordingly, solutions of both compounds were treated with excess PhNO (4–5 equiv) to shift the equilibrium towards bis-PhNO complexation. Interestingly, $^1\text{H}$ NMR, FTIR, and GC-MS analyses revealed azoxybenzene$^{55,56}$ and the isocyanate $\text{OCNAr}^{\text{Dipp}^2}$ as the major products in these transformations. The latter was also confirmed by X-ray structural determination (Figure 4.14). The IR stretches observed for $\text{OCNAr}^{\text{Dipp}^2}$ (2280 and 2249 cm$^{-1}$, KBr) are consistent with those reported by Hillhouse and co-workers for $\text{OCNAr}^{\text{Mes}^2}$ (2283 and 2253 cm$^{-1}$).$^{57}$

![Figure 4.14. Molecular structure of $\text{OCNAr}^{\text{Dipp}^2}$. Selected bond distances (Å) and angles (°): O1–C1 = 1.1830(18); C1–N1 = 1.1913(19); O1–C1–N1 = 171.48(15); C1–N1–C2 = 140.52(13).](image)

A third product was additionally detected in the $^1\text{H}$ NMR spectra of these reaction mixtures. Isolation and crystallographic characterization of this product revealed a trinuclear complex $[\text{Pd}(\eta^2-O,N\text{-PhNO})(\text{CNAr}^{\text{Dipp}^2})]_3$ (24, Figure 4.15). The molecular structure can be viewed as an aggregation of three palladium-oxaziridine units through their Pd–N bonds, which constitute the sides of a six-membered ring.
The Pd and N atoms are coordinated to terminal isocyanide and phenyl groups, respectively, and are both bridged by O atoms. More importantly, the formation of $[\text{Pd}(\eta^2-O,N-\text{PhNO})(\text{CNAr}^{\text{Dipp}^2})]_3$ (24) indicates the presence of a Pd mono-isocyanide intermediate in the reaction. Such an intermediate was the focus of Chapter 3 and was stabilized in a trinuclear form to give $[\text{Pd}(\eta^2-\text{Dipp}-\mu-\text{CNAr}^{\text{Dipp}})]_3$ (22). Indeed, treatment of $[\text{Pd}(\eta^2-\text{Dipp}-\mu-\text{CNAr}^{\text{Dipp}})]_3$ (22) with 3 equiv of PhNO independently yielded $[\text{Pd}(\eta^2-O,N-\text{PhNO})(\text{CNAr}^{\text{Dipp}^2})]_3$ (24) (Scheme 4.2).

Figure 4.15. Molecular structure of $[\text{Pd}(\eta^2-O,N-\text{PhNO})(\text{CNAr}^{\text{Dipp}^2})]_3$ (24). Positional disorder on the Pd atoms, and on the N atoms and phenyl rings of the nitrosobenzene units is not shown.
Scheme 4.2. Synthesis of $[\text{Pd}(\eta^2-O,N-\text{PhNO})(\text{CNAr}^{\text{Dipp2}})]_3$ (24).

A proposed mechanism consistent with these observations is depicted in Scheme 4.3. Upon dissolution, $\text{Pd}(\kappa^1-N-\text{PhNO})_2(\text{CNAr}^{\text{Dipp2}})_2$ (13) releases one PhNO molecule to generate $\text{Pd}(\eta^2-O,N-\text{PhNO})(\text{CNAr}^{\text{Dipp2}})_2$ (12), which is the species more likely observed in solution at room temperature. The dianionic $(\text{PhNO})^2-$ moiety in $\text{Pd}(\eta^2-O,N-\text{PhNO})(\text{CNAr}^{\text{Dipp2}})_2$ (12) can presumably serve as a doubly-$N,O$-deprotonated $N$-phenylhydroxylamine, which is known to react with PhNO to produce azoxybenzene.\(^{58}\) As illustrated in Scheme 4.3, $\text{Pd}(\eta^2-O,N-\text{PhNO})(\text{CNAr}^{\text{Dipp2}})_2$ (12) reacts with uncoordinated PhNO to generate azoxybenzene and an oxopalladium intermediate. Subsequent oxygen atom transfer to a CNAr\(^{\text{Dipp2}}\) ligand generates the corresponding isocyanate and a monoligated $[\text{Pd}(0)(\text{CNAr}^{\text{Dipp2}})]$ species. The latter trimerizes to $[\text{Pd}(\eta^2-\text{Dipp-}\mu-N-\text{PhNO})]_3$ (22) and reacts with additional PhNO to produce $[\text{Pd}(\eta^2-O,N-\text{PhNO})(\text{CNAr}^{\text{Dipp2}})]_3$ (24). Similar transformations have been previously reported, in which arylamido transfer from molybdenum oxaziridines to unsaturated organic substrates resulted in molybdenum(oxo) complexes.\(^{40,59}\)
reaction between Pd(CNAr\textsuperscript{Dipp}\textsubscript{2})\textsubscript{2} (2) and dimethyldioxirane (DMDO) also generated isocyanate, thereby providing indirect evidence for an oxopalladium species as a transient intermediate in O atom transfer to a coordinated CNAr\textsuperscript{Dipp}\textsubscript{2} ligand.

Scheme 4.3. Proposed mechanism for the generation of azoxybenzene and OCNAr\textsuperscript{Dipp}\textsubscript{2}.

The question then arises whether or not Pd(κ\textsuperscript{1}-N-PhNO)\textsubscript{2}(CNAr\textsuperscript{Dipp}\textsubscript{2})\textsubscript{2} (13) can be observed in solution at all. So far, crystallographic data and elemental analysis support its formulation as a bis-nitrosoarene complex in the solid state. It is worth noting that Pd(κ\textsuperscript{1}-N-PhNO)\textsubscript{2}(CNAr\textsuperscript{Dipp}\textsubscript{2})\textsubscript{2} (13) has only been isolated via low temperature (−35 °C) crystallization. Moreover, Pd(κ\textsuperscript{1}-N-PhNO)\textsubscript{2}(CNAr\textsuperscript{Dipp}\textsubscript{2})\textsubscript{2} (13)
crystallizes from a solution of its mono-nitrosoarene counterpart Pd(η²-O,N-PhNO)(CNArDipp₂)₂ (12) at −35 °C. These observations so far imply that PhNO is a thermally labile ligand in solution and that binding of two PhNO ligands is induced at lower temperature.

Variable temperature ¹H NMR studies of Pd(κ¹⁻N-PhNO)₂(CNArDipp₂)₂ (13) in toluene-ᵈ₈ indicate the presence of paramagnetic ligand radicals at lower temperature. A broad PhNO signal is present at 20 °C (δ = 7.38 ppm), which continually broadens into the baseline as the temperature is lowered. A doublet located at 7.38 ppm begins to emerge at −40 °C, which moves downfield to 7.60 ppm as the temperature decreases to −80 °C (Figure 4.16). The remaining PhNO resonances are obscured by toluene and CNArDipp₂ ligand signals and cannot be clearly distinguished. The appearance of this temperature-dependent signal at −40 °C presumably indicates the formation of Pd(κ¹⁻N-PhNO)₂(CNArDipp₂)₂ (13), which is isolated crystallographically near this temperature. A plot of the chemical shifts of this doublet vs 1/T is linear, indicating Curie-Weiss behavior (Figure 4.17). Yet, the temperature-dependence of this PhNO signal may also indicate antiferromagnetic exchange between ligand radicals at low temperatures.⁶⁰

Variable temperature IR studies of Pd(κ¹⁻N-PhNO)₂(CNArDipp₂)₂ (13) in toluene were also conducted to discern its formation at lower temperatures (Figure 4.18). The IR stretches at 2143 and 2115 cm⁻¹ at 20 °C are consistent with those observed for Pd(η²-O,N-PhNO)(CNArDipp₂)₂ (12). As the temperature was lowered to −80 °C, these resonances were shifted slightly higher in energy to 2152 and 2117 cm⁻¹, and a resonance at 2197 cm⁻¹ grew more prominent. The rise of this third IR
stretch at $-80 \degree C$ is reminiscent of the $\nu_{CN}$ stretches observed for a solid sample of Pd($\kappa^1$-$N$-PhNO)$_2$(CNAr$^{Dipp^2}$)$_2$ (13) (Figure 4.11). These observations show promising signs of Pd($\kappa^1$-$N$-PhNO)$_2$(CNAr$^{Dipp^2}$)$_2$ (13) in solution at low temperatures, and additional investigations on this complex are underway.

**Figure 4.16.** VT-NMR stacked plot (aromatic region) for a solution of Pd($\kappa^1$-$N$-PhNO)$_2$(CNAr$^{Dipp^2}$)$_2$ (13) in toluene-$d_8$. 
Figure 4.17. Curie-Weiss plot of the temperature-dependent chemical shifts of Pd(κ¹-N-PhNO)$_2$(CNAr$^{Dipp2}$)$_2$ (13) in toluene-$d_8$.

Figure 4.18. VT-IR stacked spectra ($\nu_{CN}$ stretches) for a solution of Pd(κ¹-N-PhNO)$_2$(CNAr$^{Dipp2}$)$_2$ (13) in toluene. The $\nu_{CN}$ stretches at 2143 and 2115 cm$^{-1}$ (solid black line, 20 °C) are assigned to Pd($\eta^2$-O,N-PhNO)(CNAr$^{Dipp2}$)$_2$ (12). The rise of the $\nu_{CN}$ stretch from the baseline at 2197 cm$^{-1}$, and the presence of the $\nu_{CN}$ stretches at 2152 and 217 cm$^{-1}$, which have also increased in intensity (solid red line, −80 °C), are indicative of Pd(κ¹-N-PhNO)$_2$(CNAr$^{Dipp2}$)$_2$ (13).
4.6 Preparation of Palladium-Nitrosoarene Derivatives

Given the elusive nature of \( \text{Pd}(\kappa^1-N-\text{PhNO})_2(\text{CNAr}^{\text{Dipp}})_2 \) (13) in solution, we pursued substituted nitrosoarene derivatives to modulate the equilibrium to favor bis-nitrosoarene complexation for room temperature solution studies. Accordingly, our survey commenced with the \( \text{o-TolNO} \) derivative \( \text{Pd}(\eta^2-O,N-o-\text{TolNO})(\text{CNAr}^{\text{Dipp}})_2 \) (23). Unlike its PhNO counterpart, this complex crystallized as a mono-nitrosoarene at both room temperature and \(-35^\circ C\), and could not accommodate a second \( o-\text{TolNO} \) ligand. Treatment with excess \( o-\text{TolNO} \) and extended heating at 60 \(^\circ\)C produced the isocyanate \( \text{OCNAr}^{\text{Dipp}} \) and azoxytoluene. The inability of \( \text{Pd}(\eta^2-O,N-o-\text{TolNO})(\text{CNAr}^{\text{Dipp}})_2 \) (23) to bind another \( o-\text{TolNO} \) molecule is presumably due to steric pressure from the ortho-methyl substituent. A more proximal arrangement of the \( cis \)-isocyanide ligands is demonstrated by the decrease in the \( C_{\text{iso}}-\text{Pd}-C_{\text{iso}} \) angle from 108.61(9)\(^\circ\) in \( \text{Pd}(\eta^2-O,N-\text{PhNO})(\text{CNAr}^{\text{Dipp}})_2 \) (12) to 104.68(1)\(^\circ\) in \( \text{Pd}(\eta^2-O,N-o-\text{TolNO})(\text{CNAr}^{\text{Dipp}})_2 \) (23). In addition, the latter exhibits a relatively larger angle between the nitrosoarene ring and the \( \text{CNAr}^{\text{Dipp}} \) ligand \( cis \) to the coordinated N atom (\( \angle(C_{\text{iso}}-\text{Pd}-\text{NArNO}) = 114.37(1)\(^\circ\) for 23 vs 109.21(8)\(^\circ\) for 12).

Additional nitrosoarenes were prepared from either PhSeSePh-catalyzed oxidation of the substituted anilines using \( \text{H}_2\text{O}_2 \),\(^{61}\) or by nitrosation of substituted aryltrifluoroborates using \( \text{NOBF}_4 \).\(^{62}\) It is worth noting that synthetic attempts at nitrosoarenes containing strongly electron-withdrawing substituents were unsuccessful under the former procedure, which generated the corresponding azoarenes. Nitrosoarenes containing Me, Cl, and Br substituents at the \( meta \) and \( para \) positions
were found to exhibit similar reactivity as PhNO towards Pd(CNAr^{Dipp2})_2 (2). Reactions between Pd(CNAr^{Dipp2})_2 (2) and these ArNO compounds yielded the corresponding \( \eta^2 \)-coordinated mono-nitrosoarene complexes 25–30 and the \( \eta^1-N \)-bound bis-nitrosoarene complexes 31–36 at room temperature and \(-35 \, ^\circ C\), respectively (Scheme 4.4). The molecular structures of these complexes are displayed in Figures 4.19–4.20, and their structural parameters are listed in Tables 4.3–4.6.

**Scheme 4.4.** Synthesis of substituted mono-nitrosoarene and bis-nitrosoarene Pd complexes at room temperature and \(-35 \, ^\circ C\), respectively.
Figure 4.19. Molecular structures of Pd($\eta^2$\text{-}O\text{-}N\text{-}m\text{-}TolNO)(CNArDipp)\textsubscript{2} (25), Pd($\eta^2$\text{-}O\text{-}N\text{-}p\text{-}TolNO)(CNArDipp)\textsubscript{2} (26), Pd($\eta^2$\text{-}O\text{-}N\text{-}p\text{-}F\text{-}C\textsubscript{6}H\textsubscript{4}NO)(CNArDipp)\textsubscript{2} (27), Pd($\eta^2$\text{-}O\text{-}N\text{-}m\text{-}Cl\text{-}C\textsubscript{6}H\textsubscript{4}NO)(CNArDipp)\textsubscript{2} (28), Pd($\eta^2$\text{-}O\text{-}N\text{-}p\text{-}Cl\text{-}C\textsubscript{6}H\textsubscript{4}NO)(CNArDipp)\textsubscript{2} (29), and Pd($\eta^2$\text{-}O\text{-}N\text{-}m\text{-}Br\text{-}C\textsubscript{6}H\textsubscript{4}NO)(CNArDipp)\textsubscript{2} (30).
Figure 4.20. Molecular structures of $\text{Pd}(\kappa^1-N-p$-TolNO)$_2$(CNAr$^\text{Dipp}$)$_2$ (31), $\text{Pd}(\kappa^1-N-p$-F-C$_6$H$_4$NO)$_2$(CNAr$^\text{Dipp}$)$_2$ (32), $\text{Pd}(\kappa^1-N-m$-Cl-C$_6$H$_4$NO)$_2$(CNAr$^\text{Dipp}$)$_2$ (33), $\text{Pd}(\kappa^1-N-p$-Cl-C$_6$H$_4$NO)$_2$(CNAr$^\text{Dipp}$)$_2$ (34), $\text{Pd}(\kappa^1-N-m$-Br-C$_6$H$_4$NO)$_2$(CNAr$^\text{Dipp}$)$_2$ (35), and $\text{Pd}(\kappa^1-N-p$-Br-C$_6$H$_4$NO)$_2$(CNAr$^\text{Dipp}$)$_2$ (36).
Table 4.3. Selected Bond Distances (Å) for Pd(η²-ArNO)(CNArDipp₂)₂ Complexes

<table>
<thead>
<tr>
<th>ArNO</th>
<th>Pd₁–C₁</th>
<th>Pd₁–C₂</th>
<th>Pd₁–N₁</th>
<th>Pd₁–O₁</th>
<th>N₁–O₁</th>
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</thead>
<tbody>
<tr>
<td>PhNO (12)</td>
<td>1.985(2)</td>
<td>2.033(2)</td>
<td>2.072(2)</td>
<td>2.0369(17)</td>
<td>1.349(3)</td>
</tr>
<tr>
<td>o-TolNO (23)</td>
<td>1.971(4)</td>
<td>2.010(4)</td>
<td>2.079(3)</td>
<td>2.021(3)</td>
<td>1.364(4)</td>
</tr>
<tr>
<td>m-TolNO (25)</td>
<td>1.9876(19)</td>
<td>2.0211(19)</td>
<td>2.0516(15)</td>
<td>2.0332(13)</td>
<td>1.349(2)</td>
</tr>
<tr>
<td>p-TolNO (26)</td>
<td>1.976(4)</td>
<td>2.017(4)</td>
<td>2.061(4)</td>
<td>2.017(3)</td>
<td>1.353(5)</td>
</tr>
<tr>
<td>p-F-C₆H₅NO (27)</td>
<td>1.976(7)</td>
<td>2.015(7)</td>
<td>2.104(7)</td>
<td>2.017(6)</td>
<td>1.351(10)</td>
</tr>
<tr>
<td>m-Cl-C₆H₅NO (28)</td>
<td>1.975(3)</td>
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<td>2.031(2)</td>
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<tr>
<td>p-Cl-C₆H₅NO (29)</td>
<td>1.966(3)</td>
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<td>2.066(2)</td>
<td>2.0219(18)</td>
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<tr>
<td>m-Br-C₆H₅NO (30)</td>
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<td>2.020(3)</td>
<td>2.055(3)</td>
<td>2.031(2)</td>
<td>1.340(3)</td>
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Table 4.4. Selected Angles (°) for Pd(η²-ArNO)(CNArDipp₂)₂ Complexes

<table>
<thead>
<tr>
<th>ArNO</th>
<th>C₁–Pd₁–C₂</th>
<th>C₁–Pd₁–N₁</th>
<th>C₂–Pd₁–O₁</th>
<th>C₁–N₁–C₃</th>
<th>C₂–N₁–C₃3</th>
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<tr>
<td>PhNO (12)</td>
<td>108.61(9)</td>
<td>109.21(8)</td>
<td>103.56(8)</td>
<td>169.7(2)</td>
<td>177.6(2)</td>
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<tr>
<td>o-TolNO (23)</td>
<td>104.68(1)</td>
<td>114.37(1)</td>
<td>102.16(1)</td>
<td>173.77(3)</td>
<td>164.01(3)</td>
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<tr>
<td>m-TolNO (25)</td>
<td>109.66(7)</td>
<td>108.73(7)</td>
<td>103.19(7)</td>
<td>174.33(18)</td>
<td>165.9(4)</td>
</tr>
<tr>
<td>p-TolNO (26)</td>
<td>110.64(15)</td>
<td>109.95(15)</td>
<td>100.66(14)</td>
<td>174.9(4)</td>
<td>166.3(3)</td>
</tr>
<tr>
<td>p-F-C₆H₅NO (27)</td>
<td>107.6(3)</td>
<td>113.0(3)</td>
<td>101.3(3)</td>
<td>171.6(6)</td>
<td>165.8(6)</td>
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<tr>
<td>m-Cl-C₆H₅NO (28)</td>
<td>108.76(11)</td>
<td>108.71(10)</td>
<td>104.04(10)</td>
<td>170.3(3)</td>
<td>175.8(3)</td>
</tr>
<tr>
<td>p-Cl-C₆H₅NO (29)</td>
<td>103.24(10)</td>
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<td>106.25(9)</td>
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<td>m-Br-C₆H₅NO (30)</td>
<td>108.84(12)</td>
<td>107.96(12)</td>
<td>104.53(11)</td>
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<td>175.0(3)</td>
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Table 4.5. Selected Bond Distances (Å) for Pd(κ¹-N-ArNO)(CNArDipp₂)₂ Complexes

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<th>ArNO</th>
<th>Pd₁–C₁</th>
<th>Pd₁–N₁</th>
<th>N₁–O₁</th>
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<tr>
<td>p-TolNO (31)</td>
<td>2.005(3)</td>
<td>2.032(3)</td>
<td>1.267(3)</td>
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<tr>
<td>p-F-C₆H₅NO (32)</td>
<td>2.003(3)</td>
<td>2.011(2)</td>
<td>1.287(3)</td>
</tr>
<tr>
<td>m-Cl-C₆H₅NO (33)</td>
<td>2.002(4)</td>
<td>2.023(5)</td>
<td>1.267(6)</td>
</tr>
<tr>
<td>p-Cl-C₆H₅NO (34)</td>
<td>2.006(2)</td>
<td>2.0250(17)</td>
<td>1.279(2)</td>
</tr>
<tr>
<td>m-Br-C₆H₅NO (35)</td>
<td>1.995(5)</td>
<td>2.017(4)</td>
<td>1.280(5)</td>
</tr>
<tr>
<td>p-Br-C₆H₅NO (36)</td>
<td>2.002(3)</td>
<td>2.055(3)</td>
<td>1.256(3)</td>
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Table 4.6. Selected Angles (°) for Pd(κ¹-N-ArNO)(CNArDipp₂)₂ Complexes

<table>
<thead>
<tr>
<th>ArNO</th>
<th>C₁–Pd₁–C₁</th>
<th>N₁–Pd₁–N₁</th>
<th>C₁–Pd₁–N₁</th>
<th>C₁–Pd₁–N₁</th>
</tr>
</thead>
<tbody>
<tr>
<td>PhNO (13)</td>
<td>179.997(8)</td>
<td>179.966(1)</td>
<td>89.64(8)</td>
<td>90.35(8)</td>
</tr>
<tr>
<td>p-TolNO (31)</td>
<td>180.000(1)</td>
<td>180.00(1)</td>
<td>89.48(11)</td>
<td>90.52(11)</td>
</tr>
<tr>
<td>p-F-C₆H₅NO (32)</td>
<td>180.000(1)</td>
<td>180.00(1)</td>
<td>89.11(10)</td>
<td>90.89(10)</td>
</tr>
<tr>
<td>m-Cl-C₆H₅NO (33)</td>
<td>180.000(1)</td>
<td>180.00(1)</td>
<td>88.65(17)</td>
<td>91.35(17)</td>
</tr>
<tr>
<td>p-Cl-C₆H₅NO (34)</td>
<td>180.000(1)</td>
<td>180.00(7)</td>
<td>89.27(7)</td>
<td>90.73(7)</td>
</tr>
<tr>
<td>m-Br-C₆H₅NO (35)</td>
<td>180.002(8)</td>
<td>180.000(1)</td>
<td>89.91(16)</td>
<td>90.09(16)</td>
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<tr>
<td>p-Br-C₆H₅NO (36)</td>
<td>180.000(13)</td>
<td>180.000(1)</td>
<td>89.31(11)</td>
<td>90.69(11)</td>
</tr>
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</table>

The Pd(η²-ArNO) complexes 25–30 are structurally similar to Pd(η²-O,N-PhNO)(CNArDipp₂)₂ (12) and Pd(η²-O,N-o-TolNO)(CNArDipp₂)₂ (23). Collectively,
these complexes exhibit lengthened N–O bond distances between 1.334–1.364 Å, indicating the presence of dianionic (ArNO)\(^{2−}\) units. In addition, the Pd–C\(_{iso}\) bond \textit{trans} to the nitrosoarene N atom is consistently longer than the Pd–C\(_{iso}\) bond \textit{cis} to N in each complex (d(Pd1–C2) > d(Pd1–C1), Table 4.3). This is reflective of the greater \textit{trans} influence of the nitrosoarene N atom relative to the O atom.

The Pd bis-nitrosoarene derivatives 31–36 also display the same structural features as the parent complex, Pd(κ\(^1\)-N-PhNO)\(_2\)(CNAr\(^{Dipp2}\))\(_2\) (13) (Tables 4.5 and 4.6). These complexes all exhibit a square planar coordination geometry and the typical metrical parameters indicative of decreased π-back donation to the isocyanide ligands, such as long Pd–C\(_{iso}\) distances (1.995–2.006 Å) and nearly linear C\(_{iso}\)–N–C\(_{ipso}\) angles. The N–O bond distances (1.256–1.287 Å) are all consistent with reduction to (ArNO)\(^{1−}\). Further, the variances in these distances reflect differing degrees of N–O bond reduction (Table 4.5). When the \(η^1\)-N-ArNO units are listed in order of increasing N–O distance, the resulting trend demonstrates increased reduction from the metal center onto nitrosoarenes that are more deactivated at the C\(_{ipso}\) position: \(p\)-Br-C\(_6\)H\(_4\)NO < \(p\)-TolNO < \(m\)-Cl-C\(_6\)H\(_4\)NO < \(p\)-Cl-C\(_6\)H\(_4\)NO < \(m\)-Br-C\(_6\)H\(_4\)NO < \(p\)-F-C\(_6\)H\(_4\)NO < PhNO. While this trend is generally consistent with the relative electronegativities of the substituents, the degrees of N–O bond reduction in halide-substituted nitrosoarenes are less than that in PhNO since halides also serve as π-donors.

The \(η^2\)-mono-nitrosoarene complex generated from the reaction between Pd(CNAr\(^{Dipp2}\))\(_2\) (2) and \(p\)-Br-C\(_6\)H\(_4\)NO has not been isolated or structurally characterized thus far due to the C–Br oxidative addition process. \(^1\)H NMR
spectroscopy indicates that the reaction between $p$-Br-C$_6$H$_4$NO and Pd(CNAr$_{\text{Dipp}}^2$)$_2$ (2) kinetically forms an $\eta^2$-ArNO complex, Pd($\eta^2$-O,N-$p$-Br-C$_6$H$_4$NO)(CNAr$_{\text{Dipp}}^2$)$_2$, which subsequently converts to trans-PdBr(C$_6$H$_4$NO)(CNAr$_{\text{Dipp}}^2$)$_2$ (37, Scheme 4.5, Figure 4.21). These observations suggest that oxidative addition of $p$-Br-C$_6$H$_4$NO to Pd(CNAr$_{\text{Dipp}}^2$)$_2$ (2) is thermodynamically favored over nitroso binding. Reduction of the N–O fragment is also evident from lengthening of the N–O bond (1.229(3) Å) in trans-PdBr(C$_6$H$_4$NO)(CNAr$_{\text{Dipp}}^2$)$_2$ (37) relative to that in Balch’s complex. Although the extent of reduction to the N–O fragment is significantly less than that observed in the $\eta^2$-coordinated and $\eta^1$-N-bound nitrosoarenes, electron density from the metal center is apparently delocalized onto the N–O substituent.

Scheme 4.5. Synthesis of trans-PdBr(C$_6$H$_4$NO)(CNAr$_{\text{Dipp}}^2$)$_2$ (37).
Treatment of Pd(CNArDipp\textsuperscript{2})\textsubscript{2} (2) with \textit{p}-MeO-C\textsubscript{6}H\textsubscript{4}NO and \textit{p}-Me\textsubscript{2}N-C\textsubscript{6}H\textsubscript{4}NO did not result in nitrosoarene complexation. The dipolar resonance forms corresponding to these nitrosoarenes render the N–O fragments too electron-rich to react with Pd(CNArDipp\textsuperscript{2})\textsubscript{2} (2) (Scheme 4.6). On the contrary, remarkable reactivity is observed when a nitrosoarene containing an unsaturated functional group is employed. Addition of 2 equiv of \textit{p}-OCH-C\textsubscript{6}H\textsubscript{4}NO to Pd(CNArDipp\textsuperscript{2})\textsubscript{2} (2) in Et\textsubscript{2}O/THF generated the bis-nitrosoarene complex Pd(\kappa^{1-}\textit{N}	extit{-}p\textendash OCH-C\textsubscript{6}H\textsubscript{4}NO)\textsubscript{2}(CNArDipp\textsuperscript{2})\textsubscript{2} (38), which crystallized readily at room temperature. The structural parameters of this complex are analogous to those of its bis-nitrosoarene derivatives isolated at low temperature (Figure 4.22). Based on the trend described earlier, the N–O distance (1.276(4) Å) is shorter than what we would expect given the presence of the more deactivating \textit{para}-formyl substituent. However, this relatively short N–O distance may arise from delocalization of electron density to the \textit{para}-formyl group as a result of increased \pi-
conjugation. Crystallographic disorder on the formyl group obviates any measurement of C–O bond reduction, yet such delocalization was indicated earlier for trans-PdBr(C₆H₄NO)(CNArDipp₂)₂ (37).

![Scheme 4.6. Resonance forms of electron-rich nitrosoarenes.](image)

**Figure 4.22.** Molecular structure of Pd(κ¹-N-POCH₆H₄NO)₂(CNArDipp₂)₂ (38). Positional disorder on the p-formyl substituent is not shown. Selected bond distances (Å) and angles (°): Pd1–C1 = 2.005(4); Pd1–N1 = 2.023(3); N1–O1 = 1.276(4); C1–Pd1–C1' = 180.000(1); N1–Pd1–N1' = 180.00(1); C1–Pd1–N1 = 88.84(13); C1–Pd1–N1' = 91.16(13); C1–N2–C2 = 177.0(4).
The $^1$H NMR spectrum of $\text{Pd}(\kappa^1-N-p\text{-OCH}-C_6H_4\text{NO})_2(\text{CNAr}^{\text{Dipp2}})_2$ (38) in $C_6D_6$ at room temperature displays significant broadening indicative of paramagnetism. Evans method magnetic moment determination ($C_6D_6/(\text{Me}_3\text{Si})_2\text{O}$, 20 °C) resulted in a $\mu_{\text{eff}}$ value of 1.9(2) $\mu_B$, which is consistent with the paramagnetic behavior observed for $\text{Pd}(\kappa^1-N\text{-PhNO})_2(\text{CNAr}^{\text{Dipp2}})_2$ (13) at room temperature in the solid state (vide supra). Preliminary variable temperature $^1$H NMR studies in toluene-$d_8$ indicate the presence of paramagnetic ArNO ligand radicals. Two doublets in the aromatic region were observed to move downfield as the temperature decreased from 20 °C to −50 °C (Figure 4.23). Due to the poor solubility of $\text{Pd}(\kappa^1-N-p\text{-OCH}-C_6H_4\text{NO})_2(\text{CNAr}^{\text{Dipp2}})_2$ (38) in toluene-$d_8$, $^1$H NMR spectra could not be obtained at temperatures below −50 °C. Curie-Weiss plots of the chemical shifts of these doublets vs $1/T$ are fairly linear over the 20 °C to −50 °C temperature range (Figure 4.24). Thus far, these spectroscopic results indicate the presence of antiferromagnetically coupled ArNO ligand radicals in $\text{Pd}(\kappa^1-N-p\text{-OCH}-C_6H_4\text{NO})_2(\text{CNAr}^{\text{Dipp2}})_2$ (38) in solution at room temperature, and additional investigations on its electronic structure and solution chemistry are underway. The isolation of a bis-nitrosoarene complex using $p\text{-OCH}-C_6H_4\text{NO}$ additionally inspires future work on the chemistry accessible with other ArNO derivatives containing electronically unsaturated substituents.
**Figure 4.23.** VT-NMR stacked plot (aromatic region) for a solution of Pd(κ¹-N-p-OCH-C₆H₄NO)₂(CNArDipp)₂ (38) in toluene-\(d_8\).

**Figure 4.24.** Curie-Weiss plot of the temperature-dependent chemical shifts (♦, 20 °C to −40 °C; ■, 10 °C to −50 °C) of Pd(κ¹-N-p-OCH-C₆H₄NO)₂(CNArDipp)₂ (38) in toluene-\(d_8\).
4.7 Conclusions

The reactivity of Pd(CNAr\textsubscript{Dipp}\textsuperscript{2})\textsubscript{2} (2) has granted access to some remarkable chemistry involving redox non-innocent C-organonitroso compounds. This investigation featured the first structurally characterized transition metal complex containing η\textsuperscript{1}-N-coordinated (PhNO)\textsuperscript{1-} ligands, Pd(κ\textsuperscript{1}-N-PhNO)\textsubscript{2}(CNAr\textsubscript{Dipp}\textsuperscript{2})\textsubscript{2} (13). Pd(κ\textsuperscript{1}-N-PhNO)\textsubscript{2}(CNAr\textsubscript{Dipp}\textsuperscript{2})\textsubscript{2} (13) was studied in conjunction with Pd(η\textsuperscript{2}-O,N-PhNO)(CNAr\textsubscript{Dipp}\textsuperscript{2})\textsubscript{2} (12) and Balch’s complex PdCl\textsubscript{2}(κ\textsuperscript{1}-N-PhNO)\textsubscript{2} to present a complete redox series in which PhNO exists in three oxidation states: neutral (PhNO)\textsuperscript{0} (S = 0), the nitroxyl radical monanion (PhNO)\textsuperscript{1-} (S = 1/2), and dianionic (PhNO)\textsuperscript{2-} (S = 0). These assignments were based on various structural, spectroscopic, and electronic differences associated with the changes in PhNO redox states. Moreover, extensive experimental and computational studies on Pd(κ\textsuperscript{1}-N-PhNO)\textsubscript{2}(CNAr\textsubscript{Dipp}\textsuperscript{2})\textsubscript{2} (13) provided clear evidence for its singlet diradical electronic configuration in the solid state, which was shown to arise from the mixture of the singlet ground state with a low-energy triplet state.

On the contrary, solution studies indicated that Pd(κ\textsuperscript{1}-N-PhNO)\textsubscript{2}(CNAr\textsubscript{Dipp}\textsuperscript{2})\textsubscript{2} (13) cannot be observed at room temperature. Variable temperature \textsuperscript{1}H NMR and IR studies thus far implied the existence of Pd(κ\textsuperscript{1}-N-PhNO)\textsubscript{2}(CNAr\textsubscript{Dipp}\textsuperscript{2})\textsubscript{2} (13) primarily at low temperatures, while PhNO dissociation to give the mono-nitrosoarene complex Pd(η\textsuperscript{2}-O,N-PhNO)(CNAr\textsubscript{Dipp}\textsuperscript{2})\textsubscript{2} (12) is more likely at room temperature. Solution studies also revealed that this dissociation could not be overcome by employing an excess of PhNO. Instead, azoxybenzene and OCNAr\textsubscript{Dipp} were produced presumably
via an oxopalladium intermediate. Pd(κ1-N-PhNO)2(CNArDipp2)2 (13) further did not exhibit magnetic susceptibility in solution at room temperature. It is thus apparent that the behavior and formulation of Pd(κ1-N-PhNO)2(CNArDipp2)2 (13) in the solid state do not provide a reliable description of this complex in solution.

Meanwhile, various substituted ArNO derivatives of Pd(κ1-N-PhNO)2(CNArDipp2)2 (13) were prepared and structurally characterized. While the crystallographically determined N–O bond distance served as a useful parameter to help distinguish between the (PhNO)0/(PhNO)+/(PhNO)2− oxidation states, it was also used to evaluate nitrosoarene substituent effects on the extent of N–O bond reduction. Overall, greater N–O bond reduction from the metal center was observed in complexes containing more electron-poor N–O fragments. In addition, the slightly lengthened N–O bond in trans-PdBr(C6H4NO)(CNArDipp2)2 (37) compared to the N–O bond in Balch’s complex implied delocalization of electron density onto the N–O substituent. Such delocalization was also presumed for Pd(κ1-N-p-OCH-C6H4NO)2(CNArDipp2)2 (38), which contains an electronically unsaturated substituent at the para position of the ArNO ring. These observations could inspire future work on the electronics pertaining to other Pd(ArNO)(CNArDipp2)2 derivatives featuring increasingly conjugated nitrosoarene systems. More notably, Pd(κ1-N-p-OCH-C6H4NO)2(CNArDipp2)2 (38) was isolated as a bis-nitrosoarene complex from solution at room temperature and exhibits paramagnetic features based on 1H NMR studies. Accordingly, extensions of this work will include further elucidating the electronic nature and the reaction chemistry of Pd(κ1-N-p-OCH-C6H4NO)2(CNArDipp2)2 (38) under ambient conditions.
4.8 Synthetic Procedures

**General considerations.** All manipulations were carried out under an atmosphere of dinitrogen using standard Schlenk and glovebox techniques. Solvents were dried and deoxygenated according to standard procedures. Benzene-$d_6$ and toluene-$d_8$ (Cambridge Isotope Laboratories) were degassed and stored over 4 Å molecular sieves for 2 d prior to use. PdCNAr$_{Dipp}^2$ was prepared as previously reported. Celite 405 (Fisher Scientific) was dried under vacuum (24 h) at a temperature above 250 °C and stored in the glovebox prior to use. KBr (FTIR grade from Aldrich) was stirred overnight in anhydrous THF, filtered and dried under vacuum (24 h) at a temperature above 250 °C and stored in the glovebox prior to use. All other reagents were purchased from commercial sources and used as received.

Solution $^1$H, $^{13}$C{$^1$H} and $^{19}$F{$^1$H} NMR spectra were recorded on Varian Mercury 300 and 400 spectrometers and a Jeol ECA 500 spectrometer. $^1$H and $^{13}$C{$^1$H} chemical shifts are reported in ppm relative to SiMe$_4$ ($^1$H and $^{13}$C δ = 0.0 ppm) with reference to residual solvent resonances of 7.16 ppm ($^1$H) and 128.06 ppm ($^{13}$C) for C$_6$D$_6$. 2.08 ppm ($^1$H) for toluene-$d_8$. $^{19}$F{$^1$H} NMR spectra were referenced externally to neat trifluoroacetic acid, F$_3$CC(O)OH (δ = −78.5 ppm vs. CFCl$_3$ = 0.0 ppm). FTIR spectra were recorded on a Thermo-Nicolet iS10 FTIR spectrometer. Samples were prepared as either KBr pellets or as C$_6$D$_6$ solutions injected into a ThermoFisher solution cell equipped with NaCl windows. For solution FTIR spectra, solvent peaks were digitally subtracted from all spectra by comparison with an authentic spectrum obtained immediately prior to that of the sample. Combustion
analyses were performed by Robertson Microlit Laboratories of Madison, NJ (USA).
High-resolution mass spectrometry (HRMS) analyses were performed by the UCSD
Chemistry and Biochemistry Molecular MS Facility.

**Synthesis of Pd(η²-O,N-o-TolNO)(CNAr^Dipp₂)₂ (23).** To a solution of
Pd(CNAr^Dipp₂)₂ (0.100 g, 0.105 mmol) in Et₂O (2 mL) was added a solution of o-
TolNO (0.013 g, 0.105 mmol, 1.0 equiv) in Et₂O (2 mL). Upon addition, the reaction
mixture turned red in color. The reaction mixture was stirred for 15 min, and then the
solvent was removed under reduced pressure. To the resulting red residue was added
n-pentane (5 mL). Filtration and storage of this solution at room temperature for 1 h
produced dark red crystals suitable for X-ray analysis, which were collected and dried
in vacuo. Yield: 0.074 g, 0.069 mmol, 66 %. ¹H NMR (500.1 MHz, C₆D₆, 20 °C): δ =
7.32 (t, 4H, J = 8 Hz, p-Dipp), 7.18 (d, 8H, J = 8 Hz, m-Dipp), 7.05 (d, 1H, J = 5 Hz,
m-ArNO), 7.04 (d, 1H, J = 5 Hz, o-Tol), 6.93–6.87 (m, 8H, m-ArNO, p-ArNO, m-Ph
and p-Ph), 2.62 (septet, 8H, J = 8 Hz, CH(CH₃)₂), 2.40 (s, 3H, ON-Tol-CH₃), 1.20 (d
br, 24H, J = 8 Hz, CH(CH₃)₂), 1.09 (d, 24H, J = 8 Hz, CH(CH₃)₂) ppm. ¹³C{¹H} NMR
(125.7 MHz, C₆D₆, 20 °C): δ = 160.9 (ON-C₉H₈), 159.2 (C≡N), 146.4, 139.5, 134.4,
130.8, 130.1, 129.8, 128.4, 128.2, 128.0, 127.5, 125.9, 123.6, 121.6, 31.4 (CH(CH₃)₂),
24.7 (CH(CH₃)₂), 24.3 (CH(CH₃)₂), 18.6 (ON-Tol-CH₃) ppm. FTIR (KBr pellet):
(νCN) 2141 and 2112 cm⁻¹ also 3059, 2962, 2925, 2868, 1579, 1460, 1414, 1384, 1363,
1105, 1057, 805, 755 cm⁻¹. Anal. calcd. for C₆₉H₈₁N₃O:Pd: C, 77.10; H, 7.60; N, 3.91.
Found: C, 77.32; H, 7.73; N, 3.74.
Synthesis of OCNAr\textsuperscript{Dipp2}. To a solution of Pd(CNAr\textsuperscript{Dipp2})\textsubscript{2} (0.100 g, 0.105 mmol) in C\textsubscript{6}H\textsubscript{6} (2 mL) was added a solution of PhNO (0.056 g, 0.524 mmol, 5.0 equiv) in C\textsubscript{6}H\textsubscript{6} (2 mL). The reaction mixture was stirred for 24 h and then concentrated under reduced pressure. The resulting residue was extracted with acetonitrile and filtered, and then the solvent was removed under reduced pressure. The product was purified by column chromatography on silica gel, eluting with hexanes. Crystallization of the product from a saturated solution in methylene chloride at −35 °C produced colorless crystals suitable for X-ray analysis. Yield: 0.016 g, 0.036 mmol, 34 %. \textsuperscript{1}H NMR (400.1 MHz, C\textsubscript{6}D\textsubscript{6}, 20 °C): δ = 7.32 (t, J = 8 Hz, 2H, p-Dipp), 7.19 (d, 4H, J = 8 Hz, m-Dipp), 7.02–6.93 (m, 3H, m-Ph and p-Ph), 2.78 (septet, 4H, J = 7 Hz, CH(CH\textsubscript{3})\textsubscript{2}), 1.23 (d, 12H, J = 7 Hz, CH(CH\textsubscript{3})\textsubscript{2}), 1.10 (d, 12H, J = 7 Hz, CH(CH\textsubscript{3})\textsubscript{2}) ppm. \textsuperscript{13}C{\textsuperscript{1}H} NMR (100.6 MHz, C\textsubscript{6}D\textsubscript{6}, 20 °C): δ = 147.2, 137.0, 135.6, 133.6, 129.8, 129.6, 129.0, 123.5, 31.2 (CH(CH\textsubscript{3})\textsubscript{2}), 24.6 (CH(CH\textsubscript{3})\textsubscript{2}), 24.0 (CH(CH\textsubscript{3})\textsubscript{2}) ppm (extended scanning (12 h) failed to locate the O=C=N resonance for this complex). FTIR (KBr pellet): (ν\textsubscript{OC}) 2280 cm\textsuperscript{-1}, (ν\textsubscript{CN}) 2249 cm\textsuperscript{-1} also 2962, 2926, 2868, 1579, 1494, 1463, 1383, 1362, 1251, 1178, 1056, 936, 807, 791, 756 cm\textsuperscript{-1}. Anal. calcd. for C\textsubscript{31}H\textsubscript{37}NO: C, 84.69; N, 8.48; H, 3.19. Found: C, 85.11; N, 8.29; H, 3.16.

Synthesis of [Pd(η\textsuperscript{2}-O,N-PhNO)(CNAr\textsuperscript{Dipp2})\textsubscript{3}] (24). To a solution of [Pd(η\textsuperscript{2}-Dipp-μ-CNAr\textsuperscript{Dipp})\textsubscript{3}] (0.060 g, 0.038 mmol) in Et\textsubscript{2}O (2 mL) was added a solution of PhNO (0.012 g, 0.113 mmol, 3.0 equiv) in Et\textsubscript{2}O (2 mL). The reaction mixture was stirred for 10 min and then concentrated under reduced pressure. Addition of acetonitrile (10 mL) resulted in the formation of orange precipitate, which was then
isolated, washed with acetonitrile, and dried in vacuo. Yield: 0.048 g, 0.025 mmol, 66%.

Red-orange crystals suitable for X-ray analysis were obtained by slow evaporation of an n-pentane solution of \([\text{Pd}(\eta^2-O,N-\text{PhNO})(\text{CNAr}^{\text{Dipp}^2})_3]\) overnight at room temperature. $^1$H NMR (500.1 MHz, C$_6$D$_6$, 20 °C): $\delta =$ 7.36–7.32 (m, 4H, p-Dipp, p-Ph and PhNO), 7.17 (d, 1H, $J = 7$ Hz, m-Ph), 7.16 (d, 1H, $J = 7$ Hz, m-Ph), 7.00–6.91 (m, 4H, m-Dipp), 6.83 (t br, 2H, $J = 7$ Hz, PhNO), 6.75 (s br, 2H, PhNO), 2.69 (septet, 2H, $J = 7$ Hz, CH(CH$_3$)$_2$), 2.63 (septet, 2H, $J = 7$ Hz, CH(CH$_3$)$_2$), 1.49 (d, 6H, $J = 7$ Hz, CH(CH$_3$)$_2$), 1.22 (d, 6H, $J = 7$ Hz, CH(CH$_3$)$_2$), 1.18 (d, 6H, $J = 7$ Hz, CH(CH$_3$)$_2$), 1.13 (d, 6H, $J = 7$ Hz, CH(CH$_3$)$_2$) ppm. $^{13}$C$\{^1$H$\}$ NMR (125.7 MHz, C$_6$D$_6$, 20 °C): $\delta =$ 162.4 (ON-C$_{\text{ipso}}$), 159.1 (C≡N), 146.4, 146.3, 139.6, 134.3, 129.9, 129.7, 128.5, 128.4, 128.3, 128.2, 123.7, 123.5, 122.7, 120.1, 31.5 (CH(CH$_3$)$_2$), 31.4 (CH(CH$_3$)$_2$), 24.0 (CH(CH$_3$)$_2$), 24.7 (CH(CH$_3$)$_2$), 24.2 (CH(CH$_3$)$_2$), 24.0 (CH(CH$_3$)$_2$) ppm. FTIR (KBr pellet): ($\nu_{\text{CN}}$) 2135 cm$^{-1}$ also 3062, 2960, 2926, 2867, 1580, 1474, 1459, 1450, 1416, 1384, 1363, 1081, 1054, 803, 792, 755 cm$^{-1}$. Anal. calcd. for C$_{111}$H$_{126}$N$_6$O$_3$Pd$_3$: C, 69.75; H, 6.64; N, 4.40. Found: C, 69.82; H, 6.67; N, 4.70.

**Synthesis of Pd($\eta^2$-O,N-m-TolNO)(CNAr$^{\text{Dipp}^2}$)$_2$** (25). To a solution of Pd(CNAr$^{\text{Dipp}^2}$)$_2$ (0.050 g, 0.052 mmol) in benzene (2 mL) was added a solution of m-TolNO (0.006 g, 0.052 mmol, 1.0 equiv) in benzene (2 mL). Upon addition, the reaction mixture turned red in color. The reaction mixture was stirred for 1 h, and then the solvent was removed under reduced pressure. To the resulting residue was added a 3:1 n-pentane/(Me$_3$Si)$_2$O solution (0.6 mL total). Filtration and slow evaporation of this solution overnight at room temperature produced red-orange crystals suitable for
X-ray analysis, which were collected and dried in vacuo. Yield: 0.035 g, 0.033 mmol, 63 %. $^1$H NMR (500.1 MHz, C$_6$D$_6$, 20 °C): $\delta$ = 7.34 (s, 1H, o-ArNO), 7.30 (t, 4H, $J$ = 8 Hz, $p$-Dipp), 7.18 (d, 8H, $J$ = 8 Hz, $m$-Dipp), 7.09 (d, 1H, $J$ = 8 Hz, o-ArNO), 7.03 (t, 1H, $J$ = 8 Hz, $m$-ArNO), 6.92–6.88 (m, 7H, 7H, $p$-ArNO, $m$-Ph and $p$-Ph), 2.61 (septet, 8H, $J$ = 7 Hz, CH(CH$_3$)$_2$), 2.33 (s, 3H, ON-Tol-C$_3$H$_3$), 1.22 (d, 24H, $J$ = 7 Hz, CH(CH$_3$)$_2$), 1.10 (d, 24H, $J = 7$ Hz, CH(CH$_3$)$_2$) ppm. $^{13}$C{$^1$H} NMR (125.7 MHz, C$_6$D$_6$, 20 °C): $\delta$ = 162.8 (ON-C$_{ipso}$), 159.3 (C≡N), 146.4, 139.4, 137.5, 134.4, 130.0, 129.8, 128.5, 128.3, 124.5, 123.6, 120.2, 118.9, 100.3, 31.4 (CH(CH$_3$)$_2$), 24.6 (CH(CH$_3$)$_2$), 24.4 (CH(CH$_3$)$_2$), 21.7 (ON-Tol-CH$_3$) ppm. FTIR (KBr pellet): (νCN) 2148 and 2108 cm$^{-1}$ also 3062, 2962, 2868, 1636, 1460, 1416, 1384, 1363, 1253, 1058, 1047, 806, 794, 758 cm$^{-1}$. Anal. calcd. for C$_{69}$H$_{81}$N$_3$OPd: C, 77.10; H, 7.60; N, 3.91. Found: C, 76.97; H, 7.37; N, 3.69.

**Synthesis of Pd($\eta^2$-O,N-$p$-TolNO)(CNAr$^{Dipp^2}$)$_2$ (26).** To a solution of Pd(CNAr$^{Dipp^2}$)$_2$ (0.050 g, 0.052 mmol) in benzene (2 mL) was added a solution of $p$-TolNO (0.006 g, 0.052 mmol, 1.0 equiv) in benzene (2 mL). Upon addition, the reaction mixture turned red in color. The reaction mixture was stirred for 1 h, and then the solvent was removed under reduced pressure. To the resulting residue was added a 3:1 n-pentane/(Me$_3$Si)$_2$O solution (0.6 mL total). Filtration and slow evaporation of this solution overnight at room temperature produced red-orange crystals suitable for X-ray analysis, which were collected and dried in vacuo. Yield: 0.029 g, 0.027 mmol, 52 %. $^1$H NMR (500.1 MHz, C$_6$D$_6$, 20 °C): $\delta$ = 7.30 (t, 4H, $J = 8$ Hz, $p$-Dipp), 7.24 (d, 2H, $J = 8$ Hz, o-ArNO), 7.18 (d, 8H, $J = 8$ Hz, $m$-Dipp), 6.92 (d, 2H, $J = 8$ Hz, m-
ArNO), 6.90 (m, 6H, m-Ph and p-Ph), 2.61 (septet, 8H, J = 7 Hz, CH(CH₃)₂), 2.16 (s, 3H, ON-Tol-CH₃), 1.22 (d, 24H, J = 7 Hz, CH(CH₃)₂), 1.09 (d, 24H, J = 7 Hz, CH(CH₃)₂) ppm. ¹³C{¹H} NMR (125.7 MHz, C₆D₆, 20 °C): δ = 160.7 (ON-Cipso), 159.6 (C≡N), 146.4, 139.4, 134.5, 132.1, 130.0, 129.7, 129.1, 128.4, 128.4, 123.5, 120.4, 31.4 (CH(CH₃)₂), 24.6 (CH(CH₃)₂), 24.4 (CH(CH₃)₂), 21.6 (ON-Tol-CH₃) ppm.

FTIR (KBr pellet): (νCN) 2137 and 2117 cm⁻¹ also 3061, 2961, 2926, 2867, 1579, 1458, 1415, 1384, 1363, 1252, 1056, 804, 792, 756 cm⁻¹. Anal. calcd. for C₆₉H₈₁N₃OPd: C, 77.10; H, 7.60; N, 3.91. Found: C, 77.63; H, 7.72; N, 4.03.

Synthesis of Pd(η²-O,N-p-F-C₆H₄NO)(CNArDipp₂)₂ (27). To a solution of Pd(CNArDipp₂)₂ (0.050 g, 0.052 mmol) in benzene (2 mL) was added a solution of p-F-C₆H₄NO (0.007 g, 0.052 mmol, 1.0 equiv) in benzene (2 mL). Upon addition, the reaction mixture turned red in color. The reaction mixture was stirred for 1 h, and then the solvent was removed under reduced pressure. To the resulting residue was added a 3:1 n-pentane/(Me₃Si)₂O solution (0.6 mL total). Filtration and slow evaporation of this solution overnight at room temperature produced red crystals suitable for X-ray analysis, which were collected and dried in vacuo. Yield: 0.017 g, 0.016 mmol, 31 %.

¹H NMR (500.1 MHz, C₆D₆, 20 °C): δ = 7.29 (t, 4H, J = 8 Hz, p-Dipp), 7.17–7.14 (m, 10H, m-Dipp and o-ArNO), 6.88 (m, 6H, m-Ph and p-Ph), 6.81 (t, 2H, J = 9 Hz, m-ArNO), 2.59 (septet, 8H, J = 7 Hz, CH(CH₃)₂), 1.19 (d, 24H, J = 7 Hz, CH(CH₃)₂), 1.09 (d, 24H, J = 7 Hz, CH(CH₃)₂) ppm. ¹³C{¹H} NMR (125.7 MHz, C₆D₆, 20 °C): δ = 159.7 (d, ¹JCF = 240 Hz, C-F), 159.0 (ON-Cipso), 158.6 (C≡N), 146.4, 139.4, 134.3, 130.1, 129.8, 128.7, 123.6, 121.6 (d, JCF = 8 Hz), 115.1 (d, JCF = 22 Hz), 31.4
(CH(CH₃)₂), 24.5 (CH(CH₃)₂), 24.4 (CH(CH₃)₂) ppm. $^{19}$F{$^{1}$H} NMR (282.3 MHz, C₆D₆, 20 °C) δ = −120.7 (m) ppm. FTIR (KBr pellet): (νCN) 2138, 2074 cm⁻¹ also 3061, 2961, 2927, 2867, 1595, 1579, 1490, 1459, 1384, 1363, 1227, 1177, 1093, 1057, 804, 792, 756 cm⁻¹. Anal. calcd. for C₆₈H₇₈FN₃OPd: C, 75.71; H, 7.29; N, 3.90. Found: C, 73.32; H, 7.48; N, 3.72.

**Synthesis of Pd(η²-O,N-m-Cl-C₆H₄NO)(CNArDipp₂)₂ (28).** To a solution of Pd(CNArDipp₂)₂ (0.050 g, 0.052 mmol) in benzene (2 mL) was added a solution of m-Cl-C₆H₄NO (0.007 g, 0.052 mmol, 1.0 equiv) in benzene (2 mL). Upon addition, the reaction mixture turned red in color. The reaction mixture was stirred for 1 h, and then the solvent was removed under reduced pressure. To the resulting residue was added a 3:1 n-pentane/(Me₃Si)₂O solution (0.6 mL total). Filtration and slow evaporation of this solution overnight at room temperature produced red-orange crystals suitable for X-ray analysis, which were collected and dried in vacuo. Yield: 0.037 g, 0.034 mmol, 65%. $^{1}$H NMR (500.1 MHz, C₆D₆, 20 °C): δ = 7.55 (q, 1H, J = 2 Hz, O-ArNO), 7.34 (t, 4H, J = 7 Hz, p-Dipp), 7.20 (d, 8H, J = 7 Hz, m-Dipp), 7.01 (dt, 2H, J = 8, 2 Hz, m-ArNO and p-ArNO), 6.89 (m, 6H, m-Ph and p-Ph), 6.80 (td, 1H, J = 8, 2 Hz, o-ArNO), 2.59 (septet, 8H, J = 6 Hz, CH(CH₃)₂), 1.20 (s br, 24H, CH(CH₃)₂), 1.09 (dd, 24H, J = 7, 2 Hz, CH(CH₃)₂) ppm. $^{13}$C{$^{1}$H} NMR (125.7 MHz, C₆D₆, 20 °C): δ = 164.0 (ON-Cipso), 158.2 (C≡N), 146.4, 139.5, 134.9, 134.2, 130.1, 129.9, 129.5, 128.8, 123.6, 122.8, 119.8, 119.2, 119.1, 31.4 (CH(CH₃)₂), 24.6 (CH(CH₃)₂), 24.4 (CH(CH₃)₂) ppm. FTIR (KBr pellet): (νCN) 2154 and 2111 cm⁻¹ also 1580, 1457,
1417, 1383, 1363, 1066, 807, 792, 759 cm$^{-1}$. Anal. calcd. for C$_{68}$H$_{78}$ClN$_3$OPd: 
C, 74.57; H, 7.18; N, 3.84. Found: C, 74.47; H, 7.05; N, 3.74.

**Synthesis of Pd($\eta^2$-O$_2$N-p-Cl-C$_6$H$_4$NO)(CNAr$^{Dipp2}$)$_2$ (29).** To a solution of Pd(CNAr$^{Dipp2}$)$_2$ (0.050 g, 0.052 mmol) in benzene (2 mL) was added a solution of p-Cl-C$_6$H$_4$NO (0.007 g, 0.052 mmol, 1.0 equiv) in benzene (2 mL). Upon addition, the reaction mixture turned red in color. The reaction mixture was stirred for 1 h, and then the solvent was removed under reduced pressure. To the resulting residue was added a 3:1 $n$-pentane/(Me$_3$Si)$_2$O solution (0.6 mL total). Filtration and slow evaporation of this solution overnight at room temperature produced dark red crystals suitable for X-ray analysis, which were collected and dried in vacuo. Yield: 0.036 g, 0.033 mmol, 63 %.

$^1$H NMR (500.1 MHz, C$_6$D$_6$, 20 °C): $\delta$ = 7.30 (t, 4H, $J$ = 8 Hz, p-Dipp), 7.15–7.12 (m, 10H, m-Dipp and o-ArNO), 7.01 (d, 2H, $J$ = 8 Hz, m-ArNO), 6.87 (m, 6H, m-Ph and p-Ph), 2.58 (septet, 8H, $J$ = 7 Hz, CH(CH$_3$)$_2$), 1.18 (d, 24H, $J$ = 7 Hz, CH(CH$_3$)$_2$), 1.08 (d, 24H, $J$ = 7 Hz, CH(CH$_3$)$_2$) ppm. $^{13}$C{$^1$H} NMR (125.7 MHz, C$_6$D$_6$, 20 °C): $\delta$ = 161.1 (ON-C$_{ipso}$), 158.2 (C≡N), 146.4, 139.5, 134.3, 130.1, 129.9, 129.3, 128.7, 128.6, 128.5, 128.4, 125.7, 123.6, 121.6, 31.4 (CH(CH$_3$)$_2$), 24.5 (CH(CH$_3$)$_2$), 24.4 (CH(CH$_3$)$_2$) ppm. FTIR (KBr pellet): ($\nu$CN) 2150 and 2121 cm$^{-1}$ also 3062, 3024, 2961, 2927, 2867, 1460, 1413, 1383, 1348, 1177, 1066, 1056, 805, 791, 757 cm$^{-1}$. Anal. calcd. for C$_{68}$H$_{78}$ClN$_3$OPd: C, 74.57; H, 7.18; N, 3.84. Found: C, 74.68; H, 7.28; N, 3.74.
Synthesis of Pd($\eta^2$-O,N-$m$-Br-C$_6$H$_4$NO)(CNArDipp)$^2_2$ (30). To a solution of Pd(CNArDipp)$^2_2$ (0.050 g, 0.052 mmol) in benzene (2 mL) was added a solution of $m$-Br-C$_6$H$_4$NO (0.010 g, 0.052 mmol, 1.0 equiv) in benzene (2 mL). Upon addition, the reaction mixture turned red in color. The reaction mixture was stirred for 1 h, and then solvent was removed under reduced pressure. To the resulting residue was added a 3:1 $n$-pentane/(Me$_3$Si)$_2$O solution (0.6 mL total). Filtration and slow evaporation of this solution overnight at room temperature produced dark red crystals suitable for X-ray analysis, which were collected and dried in vacuo. Yield: 0.037 g, 0.032 mmol, 71 %.

$^1$H NMR (500.1 MHz, C$_6$D$_6$, 20 °C): δ = 7.69 (s, 1H, o-ArNO), 7.34 (t br, 4H, $J = 7$ Hz, p-Dipp), 7.20 (s br, 8H, $m$-Dipp), 7.15 (s, 1H, o-ArNO), 7.02 (d, 1H, $J = 8$ Hz, p-ArNO), 6.89 (m, 6H, m-Ph and p-Ph), 6.72 (t, 1H, $J = 8$ Hz, m-ArNO), 2.59 (septet, 8H, $J = 7$ Hz, CH(CH$_3$)$_2$), 1.19 (br, 24H, CH(CH$_3$)$_2$), 1.09 (d, 24H, $J = 7$ Hz, CH(CH$_3$)$_2$) ppm. $^{13}$C($^1$H) NMR (125.7 MHz, C$_6$D$_6$, 20 °C): δ = 164.1 (ON-C$_{ipso}$), 146.4, 139.5, 134.2, 130.1, 129.9, 128.8, 125.7, 123.6, 123.4, 121.9, 120.3, 31.4 (CH(CH$_3$)$_2$), 24.6 (CH(CH$_3$)$_2$), 24.4 (CH(CH$_3$)$_2$) ppm (extended scanning (12 h) failed to locate the C$_{iso}$ $^{13}$C resonance for this complex). FTIR (KBr pellet): (ν$_{CN}$) 2155 and 2112 cm$^{-1}$ also 3060, 2961, 2925, 2866, 1579, 1563, 1455, 1416, 1388, 1363, 1253, 1090, 1053, 806, 792, 758 cm$^{-1}$. Anal. calcd. for C$_{68}$H$_{78}$BrN$_3$OPd: C, 71.66; H, 6.90; N, 3.69. Found: C, 71.80; H, 6.92; N, 3.70.

Synthesis of Pd($\kappa^1$-N-$p$-TolNO)$_2$(CNArDipp)$^2_2$ (31). A mixture of Pd(CNArDipp)$^2_2$ (0.100 g, 0.105 mmol) and $p$-TolNO (0.025 g, 0.210 mmol, 2.0 equiv) was stirred in 2 mL of Et$_2$O for 15 min. The resulting red solution was filtered and
stored at −35 °C overnight to produce dark brown crystals suitable for X-ray analysis, which were collected, washed with thawed *n*-pentane, and dried *in vacuo*. Yield: 0.087 g, 0.073, 70 %. $^1$H NMR (500.1 MHz, C$_6$D$_6$, 20 °C): $\delta = 7.43$ (d, 4H, $J = 8$ Hz *o*-Tol), 7.31 (t, 4H, $J = 8$ Hz, *p*-Dipp), 7.19 (d, 8H, $J = 8$ Hz, *m*-Dipp), 6.90 (m, 6H, *m*-Ph and *p*-Ph), 6.83 (d, 4H, $J = 8$ Hz, *m*-ArNO), 2.62 (septet, 8H, $J = 7$ Hz, CH(CH$_3$)$_2$), 1.99 (s, 6H, ON-Tol-C$_3$H), 1.23 (d, 24H, $J = 7$ Hz, CH(CH$_3$)$_2$), 1.10 (d, 24H, $J = 7$ Hz, CH(CH$_3$)$_2$) ppm. $^{13}$C{$^1$H} NMR (125.7 MHz, C$_6$D$_6$, 20 °C): $\delta = 162.9$ (ON-C$_{ipso}$), 159.4 (*C=*=N), 146.4, 139.4, 134.4, 130.1, 129.8, 129.4, 128.6, 128.4, 123.6, 123.4, 120.8, 31.4 (CH(CH$_3$)$_2$), 24.6 (CH(CH$_3$)$_2$), 24.4 (CH(CH$_3$)$_2$), 21.5 (ON-Tol-CH$_3$) ppm. FTIR (KBr pellet): (**) 2180, 2141, 2113 cm$^{-1}$ also 3064, 2962, 2926, 2868, 1596, 1579, 1460, 1412, 1385, 1363, 1314, 1179, 1056, 823, 800, 756 cm$^{-1}$. Anal. calcd. for C$_{76}$H$_{88}$N$_4$O$_2$Pd: C, 76.32; H, 7.42; N, 4.68. Found: C, 76.18; H, 7.37; N, 4.56.

**Synthesis of Pd($\kappa^1$-N-*p*-F-C$_6$H$_4$NO)$_2$(CNAr$_{Dipp}^2$)$_2$ (32).** To a solution of Pd(CNAr$_{Dipp}^2$)$_2$ (0.100 g, 0.105 mmol) in Et$_2$O (1 mL) was added a solution of *p*-F-C$_6$H$_4$NO (0.026 g, 0.210 mmol, 2.0 equiv) in Et$_2$O (1 mL). Upon addition, the reaction mixture turned red in color. The reaction mixture was stirred for 15 min, filtered, and stored at −35 °C overnight to produce dark brown crystals suitable for X-ray analysis, which were collected, washed with thawed *n*-pentane, and dried *in vacuo*. Yield: 0.064 g, 0.053 mmol, 50 %. $^1$H NMR (500.1 MHz, C$_6$D$_6$, 20 °C): $\delta = 7.30$–7.26 (m, 8H, *p*-Dipp and *o*-ArNO), 7.15 (d, 8H, $J = 8$ Hz, *m*-Dipp), 6.88 (m, 6H, *m*-Ph and *p*-Ph), 6.65 (t, 4H, $J = 9$ Hz, *m*-ArNO), 2.59 (septet, 8H, $J = 7$ Hz, CH(CH$_3$)$_2$), 1.19 (d, 24H, $J = 8$ Hz, CH(CH$_3$)$_2$), 1.08 (d, 24H, $J = 7$ Hz, CH(CH$_3$)$_2$) ppm. $^{13}$C{$^1$H} NMR (125.7
MHz, C₆D₆, 20 °C): δ = 158.6 (C≡N), 146.4, 139.4, 134.3, 130.1, 129.8, 128.7, 123.6, 115.6 (d, J₀ ≈ 23 Hz), 31.4 (CH(CH₃)₂), 24.5 (CH(CH₃)₂), 24.4 (CH(CH₃)₂) ppm (extended scanning (12 h) failed to locate the C-F and ON-C ipso ¹³C resonances for this complex). ¹⁹F{¹H} NMR (282.3 MHz, C₆D₆, 20 °C) δ = −121.2 (m) ppm. FTIR (KBr pellet): (vCN) 2188, 2143, 2117 cm⁻¹ also 3063, 2962, 2868, 1596, 1579, 1475, 1463, 1413, 1385, 1363, 1316, 1214, 1057, 807, 757 cm⁻¹. Anal. calcd. for C₇₄H₈₂F₂N₄O₂Pd: C, 73.83; H, 6.87; N, 4.65. Found: C, 74.31; H, 7.03; N, 4.78.

**Synthesis of Pd(κ¹-N-ₘ-Cl-C₆H₄NO)₂(CNArDipp₂)₂ (33).** A mixture of Pd(CNArDipp₂)₂ (0.100 g, 0.105 mmol) and ṁ-Cl-C₆H₄NO (0.026 g, 0.210 mmol, 2.0 equiv) was stirred in 2 mL of Et₂O for 15 min. The resulting red solution was filtered and stored at −35 °C overnight to produce dark brown crystals suitable for X-ray analysis, which were collected, washed with thawed n-pentane, and dried in vacuo. Yield: 0.084 g, 0.068 mmol, 65 %. ¹H NMR (500.1 MHz, C₆D₆, 20 °C): δ = 7.46 (s br, 2H, o-ArNO), 7.33 (t br, J = 7 Hz, 4H, p-Dipp), 7.20 (d, 8H, J = 8 Hz, m-Dipp), 6.98 (d, 2H, J = 6 Hz, o-ArNO), 6.89 (m, 6H, m-Ph and p-Ph), 6.78 (m br, 2H, ArNO), 6.53 (m br, 2H, m-ArNO), 2.59 (septet, 8H, J = 6 Hz, CH(CH₃)₂), 1.19 (br, 24H, CH(CH₃)₂), 1.09 (d, 24H, J = 7 Hz, CH(CH₃)₂) ppm. ¹³C{¹H} NMR (125.7 MHz, C₆D₆, 20 °C): δ = 146.3, 139.5, 134.2, 130.7, 129.9, 128.1, 123.6, 31.3 (CH(CH₃)₂), 24.5 (CH(CH₃)₂), 24.4 (CH(CH₃)₂) ppm (extended scanning (12 h) failed to locate the ON-C ipso and C iso ¹³C resonances for this complex). FTIR (KBr pellet): (vCN) 2185, 2151, 2118 cm⁻¹ also 3063, 2961, 2926, 2867, 1566, 1456, 1415, 1384, 1363, 1320,
Synthesis of \( \text{Pd}(\kappa^1-N-p-\text{Cl-C}_6\text{H}_4\text{NO})_2(\text{CNAr}^{\text{Dipp}2})_2 \) (34). A mixture of \( \text{Pd}(\text{CNAr}^{\text{Dipp}2})_2 \) (0.100 g, 0.105 mmol) and \( p-\text{Cl-C}_6\text{H}_4\text{NO} \) (0.026 g, 0.210 mmol, 2.0 equiv) was stirred in 2 mL of \( \text{Et}_2\text{O} \) for 15 min. The resulting red solution was filtered and stored at \(-35 \, ^\circ\text{C}\) overnight to produce dark brown crystals suitable for X-ray analysis, which were collected, washed with thawed \( n \)-pentane, and dried \textit{in vacuo}. Yield: 0.091 g, 0.074 mmol, 70 %. \(^1\)H NMR (500.1 MHz, \( \text{C}_6\text{D}_6 \), 20 °C): \( \delta = 7.29 \) (t, \( J = 8 \, \text{Hz}, 4\text{H}, p-\text{Dipp} \)), 7.20 (d, 8H, \( J = 8 \, \text{Hz}, m-\text{Dipp} \)), 6.95 (m br, 4H, \( o-\text{ArNO} \)), 6.88 (m, 6H, \( m-\text{Ph} \) and \( p-\text{Ph} \)), 6.53 (m br, 4H, \( m-\text{ArNO} \)), 2.58 (septet, 8H, \( J = 7 \, \text{Hz}, \text{CH(CH}_3)_2 \)), 1.18 (d, 24H, \( J = 7 \, \text{Hz}, \text{CH(CH}_3)_2 \)), 1.08 (d, 24H, \( J = 7 \, \text{Hz}, \text{CH(CH}_3)_2 \)) ppm. \(^{13}\)C\{\(^1\)H\} NMR (125.7 MHz, \( \text{C}_6\text{D}_6 \), 20 °C): \( \delta = 146.4, 139.4, 134.2, 130.1, 129.8, 129.2, 128.8, 123.6, 121.8, 31.4 \) (CH(CH\(_3\)_2)), 24.5 (CH(CH\(_3\)_2)), 24.4 (CH(CH\(_3\)_2)) ppm (extended scanning (12 h) failed to locate the ON-\text{C}_{ipso} \) and \( \text{C}_{iso} \) \(^{13}\)C resonances for this complex). FTIR (KBr pellet): (\( \nu_{\text{CN}} \)) 2187, 2146, 2117 \text{cm}^{-1} \) also 3063, 3056, 2962, 2926, 2868, 1581, 1465, 1410, 1385, 1363, 1320, 1176, 1079, 1057, 1046, 807, 795, 757 \text{cm}^{-1}. Anal. calcd. for \( \text{C}_{74}\text{H}_{82}\text{Cl}_2\text{N}_4\text{O}_2\text{Pd} \): C, 71.86; H, 6.68; N, 4.53. Found: C, 70.71; H, 6.99; N, 4.47.

Synthesis of \( \text{Pd}(\kappa^1-N-m-\text{Br-C}_6\text{H}_4\text{NO})_2(\text{CNAr}^{\text{Dipp}2})_2 \) (35). A mixture of \( \text{Pd}(\text{CNAr}^{\text{Dipp}2})_2 \) (0.100 g, 0.105 mmol) and \( m-\text{Br-C}_6\text{H}_4\text{NO} \) (0.039 g, 0.210 mmol, 2.0 equiv) was stirred in 2 mL of \( \text{Et}_2\text{O} \) for 15 min. The resulting brown solution was
filtered and stored at −35 °C overnight to produce dark green crystals suitable for X-ray analysis, which were collected, washed with thawed n-pentane, and dried in vacuo.

Yield: 0.072 g, 0.054 mmol, 51 %. $^1$H NMR (500.1 MHz, C$_6$D$_6$, 20 °C): $\delta = 7.58$ (s br, 2H, o-ArNO), 7.34 (t, 4H, $J = 7$ Hz, p-Dipp), 7.20 (m br, 8H, m-Dipp), 6.89 (m, 6H, m-Ph and p-Ph), 6.76 (s br, 2H, o-ArNO), 6.64 (s br, 2H, p-ArNO), 6.52 (s br, 2H, m-ArNO), 2.59 (septet, 8H, $J = 7$ Hz, CH(CH$_3$)$_2$), 1.19 (d br, 24H, $J = 5$ Hz, CH(CH$_3$)$_2$), 1.09 (d, 24H, $J = 7$ Hz, CH(CH$_3$)$_2$) ppm. $^{13}$C{1H} NMR (125.7 MHz, C$_6$D$_6$, 20 °C): $\delta$ = 146.4, 139.5, 136.5, 134.2, 131.1, 130.1, 129.9, 128.4, 128.2, 128.1, 127.9, 123.6, 122.1, 31.4 (CH(CH$_3$)$_2$), 24.6 (CH(CH$_3$)$_2$), 24.4 (CH(CH$_3$)$_2$) ppm (extended scanning (12 h) failed to locate the ON-C$_{ipso}$ and C$_{iso}$ $^{13}$C resonances for this complex). FTIR (KBr pellet): (ν$_{CN}$) 2188, 2149, 2118 cm$^{-1}$ also 3061, 2962, 2927, 2868, 1579, 1561, 1455, 1414, 1384, 1363, 1319, 1056, 1046, 805, 794, 756 cm$^{-1}$. Anal. calcd. for C$_{74}$H$_{82}$Br$_2$N$_4$O$_2$Pd: C, 67.04; H, 6.23; N, 4.23. Found: C, 67.04; H, 6.23; N, 4.23.

**Synthesis of Pd($\kappa^1$-N-p-Br-C$_6$H$_4$NO)$_2$(CNAr$^{Dipp^2}$)$_2$ (36).** A mixture of Pd(CNAr$^{Dipp^2}$)$_2$ (0.100 g, 0.105 mmol) and p-Br-C$_6$H$_4$NO (0.039 g, 0.210 mmol, 2.0 equiv) was stirred in 2 mL of Et$_2$O for 15 min. The resulting brown solution was filtered and stored at −35 °C overnight to produce dark brown crystals suitable for X-ray analysis, which were collected, washed with thawed n-pentane, and dried in vacuo.

Yield: 0.080 g, 0.060 mmol, 57 %. $^1$H NMR (400.1 MHz, C$_6$D$_6$, 20 °C): $\delta = 7.30$ (t, $J = 8$ Hz, 4H, p-Dipp), 7.27 (d, 2H, $J = 8$ Hz, o-ArNO), 7.13 (d, 8H, $J = 8$ Hz, m-Dipp), 7.05 (d, 2H, $J = 8$ Hz, o-ArNO), 6.87 (m, 6H, m-Ph and p-Ph), 2.58 (septet, 8H, $J = 7$ Hz, CH(CH$_3$)$_2$), 1.19 (d, 24H, $J = 7$ Hz, CH(CH$_3$)$_2$), 1.08 (d, 24H, $J = 7$ Hz,
CH(CH₃)₂ ppm. ¹³C{¹'H} NMR was not obtained due to the tendency of the complex to undergo oxidative addition. FTIR (KBr pellet): (νCN) 2188, 2147, 2117 cm⁻¹ also 3062, 3026, 2962, 2926, 2868, 1579, 1463, 1404, 1385, 1363, 1320, 1064, 807, 794, 757 cm⁻¹. Anal. calcd. for C₇₄H₈₂Br₂N₄O₂Pd: C, 67.04; H, 6.23; N, 4.23. Found: C, 67.04; H, 6.23; N, 4.23.

**Synthesis of trans-PdBr(C₆H₄NO)(CNArDipp)₂ (37).** To a solution of Pd(CNArDipp)₂ (0.100 g, 0.105 mmol) in C₆H₆ (2 mL) was added a solution of p-Br-C₆H₄NO (0.020 g, 0.105 mmol, 1.0 equiv) in C₆H₆ (2 mL). The reaction mixture was stirred for 20 h, during which it gradually changed in color from red to golden brown, and then the solvent was removed under reduced pressure. The resulting residue was washed with thawed n-pentane to obtain a beige powder, which was dried in vacuo. Yield: 0.064 g, 0.056 mmol, 53 %. Yellow crystals suitable for X-ray analysis were obtained by slow evaporation of a 4:1 n-pentane/C₆H₆ solution (0.6 mL total) of trans-Pd(p-PhNO)Br(CNArDipp)₂ over 2 d at room temperature. ¹H NMR (400.1 MHz, C₆D₆, 20 °C): δ = 7.41 (d, 2H, J = 8 Hz, m-ArNO), 7.30 (t, J = 8 Hz, 4H, p-Dipp), 7.12 (d, 8H, J = 8 Hz, m-Dipp), 6.80 (m, 6H, m-Ph and p-Ph), 6.42 (d, 2H, J = 8 Hz, o-ArNO), 2.41 (septet, 8H, J = 7 Hz, CH(CH₃)₂), 1.09 (d, 24H, J = 7 Hz, CH(CH₃)₂), 0.96 (d, 24H, J = 7 Hz, CH(CH₃)₂) ppm. ¹³C{¹'H} NMR (100.6 MHz, C₆D₆, 20 °C): δ = 167.2 (ON-C_ipso), 159.2 (C≡N), 146.3, 143.6, 139.9, 137.0, 133.4, 130.0, 129.9, 129.7, 126.2, 123.7, 119.2, 31.3 (CH(CH₃)₂), 24.7 (CH(CH₃)₂), 24.0 (CH(CH₃)₂) ppm. FTIR (KBr pellet): (νCN) 2182 cm⁻¹ also 3060, 2962, 2926, 2868, 1572, 1478, 1463,
1430, 1385, 1363, 1118, 1048, 820, 807, 793, 759 cm$^{-1}$. Anal. calcd. for C$_{68}$H$_{78}$BrN$_3$OPd: C, 71.66; H, 6.90; N, 3.69. Found: C, 70.72; H, 7.16; N, 3.51.

**Synthesis of Pd($\kappa^1$-N-$p$-OCH-C$_6$H$_4$NO)$_2$(CNArDipp$_2$)$_2$ (38).** A mixture of Pd(CNArDipp$_2$)$_2$ (0.150 g, 0.157 mmol) and $p$-OCH-C$_6$H$_4$NO (0.043 g, 0.315 mmol, 2.0 equiv) was stirred in a 2:1 Et$_2$O/THF solution (3 mL total) for 20 min, during which dark purple crystals suitable for X-ray analysis formed from the resulting solution. These crystals were isolated, washed with thawed n-pentane, and dried in vacuo. The mother liquor was concentrated under reduced pressure and stored at $-35^\circ$C overnight to produce a second crop of crystals, which were further isolated, washed with thawed n-pentane, and dried in vacuo. Yield: 0.105 g, 0.086 mmol, 55 %. $^1$H NMR (400.1 MHz, C$_6$D$_6$, 20 °C): $\delta$ = 7.29 (t, $J = 8$ Hz, $p$-Dipp), 6.96–6.87 (m), 6.76 (m br), 6.48 (m br), 2.57 (m br, CH(CH$_3$)$_2$), 1.08 (d, $J = 6$ Hz, CH(CH$_3$)$_2$), 1.03 (m br, CH(CH$_3$)$_2$) ppm. $^{13}$C{${^1}$H} NMR was not obtained due to crystallization of the complex in solution over time at room temperature. FTIR (KBr pellet): (v$_{CN}$) 2190, 2155, 2121 cm$^{-1}$ also 3063, 2962, 2926, 2867, 1673, 1575, 1550, 1459, 1427, 1385, 1363, 1334, 1214, 1130, 1101, 1056, 821, 805, 758 cm$^{-1}$. Anal. calcd. for C$_{76}$H$_{84}$N$_4$O$_4$Pd: C, 74.58; H, 6.92; N, 4.58. Found: C, 75.21; H, 7.16; N, 4.44. $\mu_{\text{eff}}$ (Evans method, C$_6$D$_6$ with (Me$_3$Si)$_2$O, 300.1 MHz, 20 °C) = 1.9(±0.2) $\mu_B$ (average of 3 independent measurements).

**Synthesis of 3-nitrosotoluene ($m$-TolNO).** To a 100 mL roundbottom flask containing a vigorously stirring solution of $m$-toluidine (1.61 g, 15 mmol) in CHCl$_3$
(25 mL) was added PhSeSePh (0.23 g, 0.75 mmol, 5 mol %) and 30 % aqueous H₂O₂ (3.75 mL, 33 mmol, 2.2 equiv). This reaction mixture was left stirring for 20 h, then the aqueous layer was removed and extracted with Et₂O (2 x 5 mL). The organic layers were combined, dried over sodium sulfate, and distilled under static vacuum to remove the solvents. The desired pure product was obtained as a pale yellow powder by sublimation from the brown residue. Yield: 0.450 g, 3.71 mmol, 25 %. ¹H NMR (400.1 MHz, C₆D₆, 20 °C): δ = 7.58 (d, 1H, J = 8 Hz, o-H), 7.42 (s, 1H, o-H), 6.91–6.84 (m, 2H, m-H and p-H), 1.88 (s, 3H, m-CH₃) ppm. ¹³C{¹H} NMR (125.7 MHz, C₆D₆, 20 °C): δ = 166.6 (ON-C ipso), 139.4, 135.8, 129.1, 120.9, 118.9, 20.7 (CH₃) ppm. FTIR (KBr pellet): 1612, 1487, 1411, 1390, 1287, 1230, 1161, 1097, 1017, 978, 926, 860, 817, 802, 790, 696, 666 cm⁻¹. HRMS (EI) m/z calcd. for C₇H₇NO: 121.0522. Found: (M)⁺, 121.0521.

**Synthesis of 4-nitrosotoluene (p-TolNO).**⁶⁵ To a 100 mL roundbottom flask containing a vigorously stirring solution of p-toluidine (1.61 g, 15 mmol) in CHCl₃ (25 mL) was added PhSeSePh (0.23 g, 0.75 mmol, 5 mol %) and 30 % aqueous H₂O₂ (3.75 mL, 33 mmol, 2.2 equiv). This reaction mixture was left stirring for 20 h, then the aqueous layer was removed and extracted with Et₂O (2 x 5 mL). The organic layers were combined, dried over sodium sulfate, and distilled under static vacuum to remove the solvents. The desired pure product was obtained as a pale yellow powder by sublimation from the brown residue. Yield: 0.164 g, 1.35 mmol, 9 %. ¹H NMR (500.1 MHz, C₆D₆, 20 °C): δ = 7.61 (d, 2H, J = 8 Hz, o-H), 6.75 (d, 2H, J = 8 Hz, m-H), 1.82 (s, 3H, p-CH₃) ppm. ¹³C{¹H} NMR (125.7 MHz, C₆D₆, 20 °C): δ = 165.9
(ON-C_{ipso}), 146.7, 129.8, 121.1, 21.4 (CH_{3}) ppm. FTIR (KBr pellet): 1601, 1508, 1457, 1410, 1296, 1255, 1165, 1120, 1017, 954, 823, 760 cm^{-1}. HRMS (EI) m/z calcd. for C_{7}H_{7}NO: 121.0522. Found: (M)^+, 121.0523.

**Synthesis of 1-fluoro-4-nitrosobenzene (p-F-C_{6}H_{4}NO).** To a stirred solution of K[p-F-C_{6}H_{4}BF_{3}] (0.202 g, 1.00 mmol) in MeCN (3 mL) was added solid NOBF_{4} (0.120 g, 1.03 mmol, 1.03 equiv). The reaction mixture immediately turned dark green in color, then turned gray and became warm to the touch. The reaction mixture was left stirring for 1 min, and addition of water (20 mL) restored the dark green color. The resulting mixture was then extracted with methylene chloride (3 x 10 mL). The organic layers were combined, dried over magnesium sulfate, filtered, and distilled under static vacuum to remove the solvents. The desired pure product was obtained as a pale yellow powder. Yield: 0.039 g, 0.312 mmol, 31 %. \(^{1}\)H NMR (500.1 MHz, C\textsubscript{6}D\textsubscript{6}, 20 °C): \(\delta = 7.43\) (m, 2H, o-H), 6.54 (m, 2H, m-H) ppm. \(^{13}\)C{\(^{1}\)H} NMR (125.7 MHz, C\textsubscript{6}D\textsubscript{6}, 20 °C): \(\delta = 166.4\) (d, \(^{1}\)J\textsubscript{CF} = 259 Hz, C-F), 163.5 (ON-C_{ipso}), 123.4 (d, \(J\textsubscript{CF} = 9\) Hz), 115.9 (m) ppm. \(^{19}\)F{\(^{1}\)H} NMR (282.3 MHz, C\textsubscript{6}D\textsubscript{6}, 20 °C) \(\delta = -101.9\) (m) ppm. FTIR (KBr pellet): 1598, 1506, 1414, 1303, 1269, 1256, 1235, 1158, 1113, 1094, 867, 839, 775, 589, 519 cm^{-1}. HRMS (EI) m/z calcd. for C\textsubscript{6}H\textsubscript{4}NOF: 125.0271. Found: (M)^+, 125.0273.

**Synthesis of 1-chloro-3-nitrosobenzene (m-Cl-C_{6}H_{4}NO).** To a 100 mL roundbottom flask containing a vigorously stirring solution of 3-chloroaniline (1.57 mL, 15 mmol) in CHCl\textsubscript{3} (25 mL) was added PhSeSePh (0.23 g, 0.75 mmol, 5 mol %)
and 30 % aqueous H₂O₂ (3.75 mL, 33 mmol, 2.2 equiv). This reaction mixture was left stirring for 20 h, then the aqueous layer was removed and extracted with Et₂O (2 x 5 mL). The organic layers were combined, dried over sodium sulfate, and distilled under static vacuum to remove the solvents. The desired pure product was obtained as a pale yellow powder by sublimation from the brown residue. Yield: 1.00 g, 7.06 mmol, 47 %. ¹H NMR (400.1 MHz, C₆D₆, 20 °C): δ = 7.47 (d, 1H, J = 8 Hz, o-H), 7.31 (s, 1H, o-H), 6.91 (d, 1H, J = 8 Hz, p-H), 6.61 (t, 1H, J = 8 Hz, m-H) ppm. ¹³C{¹H} NMR (125.7 MHz, C₆D₆, 20 °C): δ = 165.1 (ON-C ipso), 135.9, 134.5, 130.6, 121.0, 118.7 ppm. FTIR (KBr pellet): 1585, 1472, 1431, 1251, 1184, 1164, 1078, 1000, 914, 892, 863, 788, 713, 675 cm⁻¹. HRMS (EI) m/z calcd. for C₆H₄NOCl: 140.9976. Found: (M)+, 140.9974.

Synthesis of 1-chloro-4-nitrosobenzene (p-Cl-C₆H₄NO). To a 100 mL roundbottom flask containing a vigorously stirring solution of 4-chloroaniline (1.91 g, 15 mmol) in CHCl₃ (25 mL) was added PhSeSePh (0.23 g, 0.75 mmol, 5 mol %) and 30 % aqueous H₂O₂ (3.75 mL, 33 mmol, 2.2 equiv). This reaction mixture was left stirring for 20 h, then the aqueous layer was removed and extracted with Et₂O (2 x 5 mL). The organic layers were combined, dried over sodium sulfate, and distilled under static vacuum to remove the solvents. The desired pure product was obtained as a pale yellow powder by sublimation from the brown residue. Yield: 0.63 g, 4.45 mmol, 30 %. ¹H NMR (500.1 MHz, C₆D₆, 20 °C): δ = 7.25 (d, 2H, J = 8 Hz, o-H), 6.82 (d, 2H, J = 8 Hz, m-H) ppm. ¹³C{¹H} NMR (125.7 MHz, C₆D₆, 20 °C): δ = 163.8 (ON-C ipso), 141.8, 129.6, 121.9 ppm. FTIR (KBr pellet): 1581, 1482, 1404, 1290, 1257, 1161,
1091, 1014, 857, 820, 810, 714 cm$^{-1}$. HRMS (EI) $m/z$ calcd. for C$_6$H$_4$NOCl: 140.9976. Found: (M)$^+$, 140.9978.

**Synthesis of 1-bromo-3-nitrosobenzene (m-Br-C$_6$H$_4$NO).**$^{67}$ To a 100 mL roundbottom flask containing a vigorously stirring solution of 3-bromoaniline (1.63 mL, 15 mmol) in CHCl$_3$ (25 mL) was added PhSeSePh (0.23 g, 0.75 mmol, 5 mol %) and 30 % aqueous H$_2$O$_2$ (3.75 mL, 33 mmol, 2.2 equiv). This reaction mixture was left stirring for 20 h, then the aqueous layer was removed and extracted with Et$_2$O (2 x 5 mL). The organic layers were combined, dried over sodium sulfate, and distilled under static vacuum to remove the solvents. The desired pure product was obtained as a pale yellow powder by sublimation from the brown residue. Yield: 0.51 g, 2.74 mmol, 18 %. $^1$H NMR (400.1 MHz, C$_6$D$_6$, 20 °C): $\delta = 7.51$ (d, 1H, $J = 8$ Hz, o-H), 7.47 (s, 1H, o-H), 7.07 (d, 1H, $J = 8$ Hz, p-H), 6.53 (t, 1H, $J = 8$ Hz, m-H) ppm. $^{13}$C{$^1$H} NMR (125.7 MHz, C$_6$D$_6$, 20 °C): $\delta = 165.2$ (ON-C$_{ipso}$), 137.4, 130.9, 123.9, 121.7, 121.4 ppm. FTIR (KBr pellet): 1579, 1531, 1467, 1426, 1349, 1265, 1254, 1069, 998, 883, 855, 769, 695, 670 cm$^{-1}$. HRMS (EI) $m/z$ calcd. for C$_6$H$_4$NOBr: 184.9471. Found: (M)$^+$, 184.9468.

**Synthesis of 1-bromo-4-nitrosobenzene (p-Br-C$_6$H$_4$NO).**$^{67}$ To a 100 mL roundbottom flask containing a vigorously stirring solution of 4-bromoaniline (2.58 g, 15 mmol) in CHCl$_3$ (25 mL) was added PhSeSePh (0.23 g, 0.75 mmol, 5 mol %) and 30 % aqueous H$_2$O$_2$ (3.75 mL, 33 mmol, 2.2 equiv). This reaction mixture was left stirring for 20 h, then the aqueous layer was removed and extracted with Et$_2$O (2 x 5
mL). The organic layers were combined, dried over sodium sulfate, and distilled under static vacuum to remove the solvents. The desired pure product was obtained as a pale yellow powder by sublimation from the brown residue. Yield: 0.64 g, 3.44 mmol, 23 %.

$^1$H NMR (400.1 MHz, C$_6$D$_6$, 20 °C): $\delta = 7.17$ (d, 2H, $J = 8$ Hz, $o$-H), 7.02 (d, 2H, $J = 8$ Hz, $m$-H) ppm. $^{13}$C$\{^1$H$\}$ NMR (125.7 MHz, C$_6$D$_6$, 20 °C): $\delta = 163.9$ (ON-C$_{ipso}$), 132.6, 131.2, 121.9 ppm. FTIR (KBr pellet): 1577, 1479, 1401, 1286, 1258, 1102, 1066, 1012, 857, 806, 707, 657, 626 cm$^{-1}$. HRMS (EI) $m$/z calcd. for C$_6$H$_4$NOBr: 184.9471. Found: (M)$^+$, 184.9473.

**Synthesis of 4-nitrosobenzaldehyde (p-OCH-C$_6$H$_4$NO).**

To a stirred solution of K[p-OCH-C$_6$H$_4$BF$_3$] (0.212 g, 1.00 mmol) in MeCN (3 mL) was added solid NOBF$_4$ (0.120 g, 1.03 mmol, 1.03 equiv). The reaction mixture immediately turned dark green in color, then turned yellow and became warm to the touch. The reaction mixture was left stirring for 1 min, and water (20 mL) was added. The resulting mixture was then extracted with methylene chloride (3 x 10 mL). The organic layers were combined, dried over magnesium sulfate, filtered, and distilled under static vacuum to remove the solvents. The desired pure product was obtained as a pale yellow powder by sublimation from the crude residue. Yield: 0.057 g, 0.496 mmol, 42 %. $^1$H NMR (500.1 MHz, C$_6$D$_6$, 20 °C): $\delta = 9.40$ (s, 1H, OCH-ArNO), 7.37 (d, 2H, $J = 8$ Hz), 7.28 (d, 2H, $J = 8$ Hz) ppm. $^{13}$C$\{^1$H$\}$ NMR (125.7 MHz, C$_6$D$_6$, 20 °C): $\delta = 190.5$ (OCH-ArNO), 130.7, 127.9, 120.7 (extended scanning (12 h) failed to locate the ON-C$_{ipso}$ resonance for this complex) ppm. FTIR (KBr pellet): 1694, 1591,
1388, 1260, 1202, 1101, 872, 843, 829, 791, cm⁻¹. HRMS (EI) m/z calcd. for C₁₇H₁₅NO₂: 135.0315. Found: (M)⁺, 135.0314.

4.9 X-ray Absorption Spectroscopy

X-ray absorption spectra (XAS) measurements were conducted by Dr. Stephen Sproules and Professor Serena DeBeer at the Stanford Synchrotron Radiation Lightsource (SSRL) with the SPEAR storage ring containing between 80 and 100 mA at 3.0 GeV. Pd K-edge data were collected on the structural molecular biology XAS beamline 7-3 operating with a wiggler field of 2 T. A Si(220) double-crystal monochromator was used. Beamline 7-3 is equipped with a rhodium-coated vertical collimating mirror upstream of the monochromator, and a downstream bent-cylindrical focusing mirror (also rhodium-coated). Harmonic rejection was accomplished by detuning the intensity of the incident radiation at the end of the scan by 50 %. Incident and transmitted X-ray intensities were monitored using argon- or nitrogen-filled ionization chambers. X-ray absorption was measured in transmittance mode. During data collection, samples were maintained at a temperature of approximately 10 K using an Oxford Instruments liquid helium flow cryostat. Internal energy calibrations were performed by simultaneous measurement of the Pd reference foil placed between the second and third ionization chamber with the inflection point assigned at 24350 eV. Data represent 3–5 scan averages and were processed by fitting a second-order polynomial to the pre-edge region and subtracting this background from the entire spectrum. A three-region cubic spline was used to model the smooth
background above the edge. The data were normalized by subtracting the spline and normalizing the postedge to 1.0. Because of the intermediate nature of the pre-edge transitions, the position of the edge for each compound was taken to be the energy at a normalized absorption intensity of 0.5.

4.10 SQUID Magnetometry

The SQUID magnetometry data for Pd(κ1-N-PhNO)2(CNArDipp2)2 (13) was obtained by Dr. Thomas Weyhermüller at the Max-Planck-Institut für Bioanorganische Chemie, Mülheim an der Ruhr, Germany. Variable temperature (4–300 K) magnetization data were recorded in a 1 T magnetic field on a SQUID magnetometer (MPMS Quantum Design). The experimental magnetic susceptibility data were corrected for underlying diamagnetism using Pascal’s constants, and an additional diamagnetic correction was applied to account for a diamagnetic impurity (free ligand) in the sample.

4.11 Computational Details

The computational work reported in this chapter was conducted by Dr. Neil C. Tomson at the Max-Planck-Institut für Bioanorganische Chemie, Mülheim an der Ruhr, Germany. All density functional theory (DFT) calculations were performed with the ORCA program package.69 Geometry optimizations for (PhNO)1− and the Pd(PhNO) complexes (Pd(κ1-N-PhNO)2(CNArDipp2)2 (13) and PdCl2(κ1-N-PhNO)2)
were carried out at the BP86\textsuperscript{70,71} and the B3LYP\textsuperscript{72-74} level of DFT, respectively. Single-point calculations on the optimized geometries were performed using the B3LYP functional. Unless otherwise stated, the crystallographically determined atomic coordinates were used as starting geometries for all optimization calculations.

The all-electron Gaussian basis sets developed by the Ahlrichs group\textsuperscript{39, 40} were used in all calculations. For calculations on (PhNO)\textsuperscript{+1}, the def2-TZVP standard basis sets and def2-TZV/J auxiliary basis sets\textsuperscript{41, 42} were used on all atoms, and the Conductor-like Screening Model (COSMO)\textsuperscript{53} was applied, using the dielectric constant and refractive index of water. The zeroth-order regular approximation (ZORA) method\textsuperscript{46-48} was implemented for all calculations involving Pd. For these calculations, the standard (ZORA-TZVP and ZORA-SV(P))\textsuperscript{49} and auxiliary (def2-TZVP/J) basis sets\textsuperscript{41, 42} for each calculation were used, with the auxiliary basis sets\textsuperscript{43-45} (used to expand the electron density in the resolution-of-identity (RI) approach) being chosen to match the orbital basis. The DFT integration grid used for the COSX approximation was increased by one step from the default value, and the final grid was turned off. All calculations have been performed using an empirical van der Waals correction to the DFT energy.\textsuperscript{50-52}

The SCF calculations were tightly converged ($1 \times 10^{-8}$ \textit{E}_h in energy, $1 \times 10^{-7}$ \textit{E}_h in the density change, and $5 \times 10^{-7}$ in the maximum element of the DIIS error vector). In all cases the geometries were considered converged after the energy change was less than $1 \times 10^{-6}$ \textit{E}_h, the gradient norm and maximum gradient element were smaller than $3 \times 10^{-4}$ \textit{E}_h-Bohr\textsuperscript{-1} and $1 \times 10^{-4}$ \textit{E}_h-Bohr\textsuperscript{-1}, respectively, and the root-mean-square and maximum displacements of all atoms were smaller than $6 \times 10^{-4}$.
Bohr and $1 \times 10^{-3}$ Bohr, respectively. The geometry optimizations for all complexes were carried out in redundant internal coordinates without imposing symmetry constraints, except in the case of the nonplanar form of PhNO, for which the unconstrained optimized geometry was used as a starting point, but the O–N–C–C dihedral angle was changed to 90°; the subsequent geometry optimization run was performed by constraining the dihedral angle as indicated.

The computational results for $\text{Pd} (\kappa^1\text{-N-PhNO})_2 (\text{CNAr}^{\text{Dipp}2})_2$ (13) were described using the broken symmetry (BS) approach of Ginsberg (56) and Noodleman et al. (57) Because several broken symmetry solutions to the spin-unrestricted Kohn-Sham equations may be obtained, the general notation BS($m,n$) (58) was adopted, where $m(n)$ denotes the number of spin-up (spin-down) electrons at the two interacting fragments. The geometry optimized structure was obtained from B3LYP optimization using the BS(1,1) flag (−8344.974637 Eₜₐₜ.), which gave the best agreement between experimental and calculated bond lengths and angles. Canonical, unrestricted-corrresponding (UCO), (59) and quasi-restricted (QRO) (60) orbitals (iso-electron density surfaces = 95 %) were generated with the program Molekel, v4.3. (61) The magnetic coupling $J$ was calculated using the method developed by Yamaguchi and co-workers: (62, 63)

$$J = \frac{E_{\text{HS}} - E_{\text{BS}}}{\langle \hat{S}^2 \rangle_{\text{HS}} - \langle \hat{S}^2 \rangle_{\text{BS}}}$$

The radial integration accuracy for Balch’s complex $\text{PdCl}_2 (\kappa^1\text{-N-PhNO})_2$ was improved by setting the radial resolution parameters to 14, 10, 5, 5, 5, and 5 for the Pd, Cl, O, N, C, and H atoms, respectively. Single point unrestricted calculations
including the broken symmetry formalism on both the crystallographically-determined and geometry optimized structures yielded only the closed-shell solution.

4.12 Variable Temperature Studies

All $^1$H NMR measurements were recorded on either a Varian Mercury 400 MHz or a Jeol ECA 500 MHz spectrometer. Samples were prepared in the glovebox and loaded into J Young tubes as toluene-$d_8$ solutions (0.6 mL total) containing 7 mM of Pd compound. A series of $^1$H NMR spectra were then recorded for these samples from $-80 \, ^\circ C$ to $+20 \, ^\circ C$ at 10 °C intervals. The samples were subjected to a 10 min equilibration period at each temperature prior to data collection. All data were processed with the MestReNova software.

Supplemental ambient temperature (20 °C) $^1$H NMR (400.1 MHz) data for Pd($\kappa^1$-N-PhNO)$_2$(CNAr$^{\text{Dipp}_2}$)$_2$ (13) and Pd($\kappa^1$-$N$-$p$-OCH-$C_6H_4NO$)$_2$(CNAr$^{\text{Dipp}_2}$)$_2$ (38) in toluene-$d_8$:

$\text{Pd}(\kappa^1$-N-PhNO)$_2$(CNAr$^{\text{Dipp}_2}$)$_2$ (13). $\delta = 7.38$ (m br, 4H, PhNO), 7.25–7.22 (m, 6H, $p$-Dipp and PhNO), 7.13 (d, 8H, $J = 8$ Hz, $m$-Dipp), 6.90 (m, 6H, $J = 8$ Hz, $m$-Ph and $p$-Ph), 2.57 (septet, 8H, $J = 7$ Hz, CH(CH$_3$)$_2$), 1.19 (d, 24H, $J = 7$ Hz, CH(CH$_3$)$_2$), 1.08 (d, 24H, $J = 7$ Hz, CH(CH$_3$)$_2$) ppm.

$\text{Pd}(\kappa^1$-$N$-$p$-OCH-$C_6H_4NO$)$_2$(CNAr$^{\text{Dipp}_2}$)$_2$ (38). $\delta = 7.25$ (t, $J = 8$ Hz, $p$-Dipp), 7.13 (m), 6.88 (m), 6.50 (m br), 2.54 (m br, CH(CH$_3$)$_2$), 1.06 (d, $J = 7$ Hz, CH(CH$_3$)$_2$), 1.03 (m br, CH(CH$_3$)$_2$) ppm.
Variable temperature IR spectra were recorded on a Bruker Equinox 55 FTIR spectrometer equipped with a Specac optical cryostat. Samples were prepared in the glovebox as toluene solutions containing 12 mM of Pd compound and injected into an air-tight Specac solution cell with CaF$_2$ windows and 0.1 mm spacers. A series of spectra were then recorded for these samples from $-80 \, ^\circ C$ to $+20 \, ^\circ C$ at 10 °C intervals. The samples were subjected to a 10 min equilibration period at each temperature prior to data collection. Toluene solvent peaks were digitally subtracted from all spectra by comparison with authentic spectra obtained from $-80 \, ^\circ C$ to $+20 \, ^\circ C$.

### 4.13 Evans Method Magnetic Moment Determinations

**Table 4.7.** Average $\mu_{\text{eff}}$ Values Determined by Evans Method for Pd Complexes ($(\text{Me}_3\text{Si})_2\text{O/C}_6\text{D}_6$, 20 °C)

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<tr>
<th>Complex</th>
<th>Number of Independent Runs</th>
<th>Field (MHz)</th>
<th>Average $\mu_{\text{eff}}$</th>
<th>Std Dev</th>
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<tr>
<td>PdCl$_2$(CNArt$_2$)$_2$ (1)</td>
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<tr>
<td>Pd(CNArt$_2$)$_2$ (2)</td>
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<td>400</td>
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<td>0</td>
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<tr>
<td>Pd($\eta^4$-O$_2$N-PhNO)(CNArt$_2$)$_2$ (12)</td>
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<td>300</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Pd($\kappa^1$-N-PhNO)$_2$(CNArt$_2$)$_2$ (13)</td>
<td>3</td>
<td>400</td>
<td>0.35</td>
<td>0.04</td>
</tr>
<tr>
<td>Pd($\kappa^1$-N-$p$-OCH$_2$-C$_6$H$_4$NO)$_2$(CNArt$_2$)$_2$ (38)</td>
<td>3</td>
<td>300</td>
<td>1.99</td>
<td>0.24</td>
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</table>
4.14 Crystallographic Structure Determinations

**General considerations.** Single crystal X-ray structure determinations were carried out at low temperature on a Bruker Kappa, Photon, or Apollo Diffractometer equipped with a Bruker APEX detector. All structures were solved by direct methods with SIR 2004\(^75\) and refined by full-matrix least-squares procedures utilizing SHELXL-97.\(^76\) Crystallographic data collection and refinement information are listed in Tables 4.7–4.12. The crystallographic routine SQUEEZE\(^77\) was performed on disordered Et\(_2\)O, C\(_6\)H\(_6\), and toluene molecules of co-crystallization in the structures of Pd(\(\eta^2\)-O,N-\(\eta\)-O-TolNO)(CNAr\(^{\text{Dipp2}}\))\(_2\) (23), trans-PdBr(C\(_6\)H\(_4\)NO)(CNAr\(^{\text{Dipp2}}\))\(_2\) (37), and Pd(\(\kappa^1\)-N-\(\eta\)-OCH-C\(_6\)H\(_4\)NO)(CNAr\(^{\text{Dipp2}}\))\(_2\) (38), respectively. The crystal structure of [Pd(\(\eta^2\)-O,N-PhNO)(CNAr\(^{\text{Dipp2}}\))]\(_3\) (24) contains positional disorder on the Pd atoms, as well as the N and C atoms of the PhNO ligands, which were modeled and refined. The crystal structures of Pd(\(\eta^2\)-O,N-\(m\)-TolNO)(CNAr\(^{\text{Dipp2}}\))\(_2\) (25), Pd(\(\eta^2\)-O,N-\(\eta\)-\(p\)TolNO)(CNAr\(^{\text{Dipp2}}\))\(_2\) (26), Pd(\(\eta^2\)-O,N-\(p\)-F-C\(_6\)H\(_4\)NO)(CNAr\(^{\text{Dipp2}}\))\(_2\) (27), Pd(\(\eta^2\)-O,N-\(m\)-Cl-C\(_6\)H\(_4\)NO)(CNAr\(^{\text{Dipp2}}\))\(_2\) (28), and Pd(\(\eta^2\)-O,N-\(m\)-Br-C\(_6\)H\(_4\)NO)(CNAr\(^{\text{Dipp2}}\))\(_2\) (30) all contain isopropyl-group positional disorder, which was modeled and refined. The crystal structure of Pd(\(\eta^2\)-O,N-\(m\)-TolNO)(CNAr\(^{\text{Dipp2}}\))\(_2\) (25) additionally contains phenyl-group positional disorder on the central arene ring of one of the CNAr\(^{\text{Dipp2}}\) ligands, while the crystal structures of Pd(\(\eta^2\)-O,N-\(m\)-Cl-C\(_6\)H\(_4\)NO)(CNAr\(^{\text{Dipp2}}\))\(_2\) (28), Pd(\(\eta^2\)-O,N-\(m\)-Br-C\(_6\)H\(_4\)NO)(CNAr\(^{\text{Dipp2}}\))\(_2\) (30), and Pd(\(\kappa^1\)-N-\(p\)-OCH-C\(_6\)H\(_4\)NO)(CNAr\(^{\text{Dipp2}}\))\(_2\) (38) additionally contain positional disorder on the Cl, Br, and
formyl substituents on the ArNO rings. These disordered components were also modeled and refined.

Table 4.8. Crystallographic Data Collection and Refinement Information for Pd(\(\eta^2\)-O,N-o-TolNO)(C\(\text{NAr}^{\text{Dipp}2}\))\(_2\)•0.5Et\(_2\)O, OC\(\text{NAr}^{\text{Dipp}2}\)•CH\(_2\)Cl\(_2\), and [Pd(\(\eta^2\)-O,N-PhNO)(C\(\text{NAr}^{\text{Dipp}2}\))]\(_3\).

<table>
<thead>
<tr>
<th></th>
<th>Pd((\eta^2)-O,N-o-TolNO) (C(\text{NAr}^{\text{Dipp}2}))(_2)•0.5Et(_2)O (23)</th>
<th>OC(\text{NAr}^{\text{Dipp}2})•CH(_2)Cl(_2)</th>
<th>[Pd((\eta^2)-O,N-PhNO)(C(\text{NAr}^{\text{Dipp}2}))](_3) (24)</th>
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<tr>
<td>Formula</td>
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<td>C(<em>{55.5})H(</em>{63})N(_3)O(_1).5Pd</td>
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<td>Monoclinic P(_2_1/c)</td>
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<tr>
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<td>GOF</td>
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<td>1.043</td>
<td>1.042</td>
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Table 4.9. Crystallographic Data Collection and Refinement Information for Pd(η^2-O,N-m-TolNO)(CNAr_Dipp^2)_2, Pd(η^2-O,N-p-TolNO)(CNAr_Dipp^2)_2•C_6H_6, and Pd(η^2-O,N-p-F-C_6H_5NO)(CNAr_Dipp^2)_2•C_6H_6.

<table>
<thead>
<tr>
<th>Formula</th>
<th>C_{60}H_{58}N_2OPd</th>
<th>C_{75}H_{67}N_2OPd</th>
<th>C_{62}H_{64}FN_2OPd</th>
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<td>Monoclinic</td>
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<td>P-1</td>
<td>Cc</td>
<td>Cc</td>
</tr>
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<td>a, Å</td>
<td>11.7787(7)</td>
<td>14.2644(8)</td>
<td>14.0835(8)</td>
</tr>
<tr>
<td>b, Å</td>
<td>13.4861(8)</td>
<td>20.3118(8)</td>
<td>20.4568(8)</td>
</tr>
<tr>
<td>c, Å</td>
<td>20.8151(13)</td>
<td>22.2729(10)</td>
<td>21.9700(11)</td>
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<tr>
<td>a, deg</td>
<td>72.022(2)</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>β, deg</td>
<td>77.910(2)</td>
<td>96.304(3)</td>
<td>95.090(3)</td>
</tr>
<tr>
<td>γ, deg</td>
<td>76.771(2)</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>V, Å³</td>
<td>3027.0(3)</td>
<td>6413.0(5)</td>
<td>6304.7(5)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Radiation (λ, Å)</td>
<td>Mo-Kα 0.71073</td>
<td>Mo-Kα 0.71073</td>
<td>Mo-Kα 0.71073</td>
</tr>
<tr>
<td>ρ (calcd.), g/cm³</td>
<td>1.179</td>
<td>1.194</td>
<td>1.219</td>
</tr>
<tr>
<td>μ, mm⁻¹</td>
<td>0.350</td>
<td>0.335</td>
<td>0.343</td>
</tr>
<tr>
<td>Temp, K</td>
<td>100(2)</td>
<td>100(2)</td>
<td>100(2)</td>
</tr>
<tr>
<td>θ max, deg</td>
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<td>25.47</td>
<td>25.40</td>
</tr>
<tr>
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<td>10692/747</td>
<td>10909/728</td>
</tr>
<tr>
<td>R₁</td>
<td>0.0284</td>
<td>0.0372</td>
<td>0.0697</td>
</tr>
<tr>
<td>wR₁</td>
<td>0.0883</td>
<td>0.1065</td>
<td>0.1617</td>
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<td>GOF</td>
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<td>1.019</td>
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Table 4.10. Crystallographic Data Collection and Refinement Information for Pd(η^2-O,N-m-Cl-C_6H_5NO)(CNAr_Dipp^2)_2, Pd(η^2-O,N-p-Cl-C_6H_5NO)(CNAr_Dipp^2)_2•0.5C_6H_6, and Pd(η^2-O,N-m-Br-C_6H_5NO)(CNAr_Dipp^2)_2.

<table>
<thead>
<tr>
<th>Formula</th>
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<th>C_{75}H_{81}ClN_2OPd</th>
<th>C_{66}H_{83}BrN_2OPd</th>
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<td>Crystal System</td>
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<td>Monoclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space Group</td>
<td>P2₁/c</td>
<td>P2₁/n</td>
<td>P2₁/c</td>
</tr>
<tr>
<td>a, Å</td>
<td>25.5580(7)</td>
<td>16.7271(11)</td>
<td>25.8348(8)</td>
</tr>
<tr>
<td>b, Å</td>
<td>11.7890(3)</td>
<td>17.1511(14)</td>
<td>11.8191(3)</td>
</tr>
<tr>
<td>c, Å</td>
<td>20.0170(5)</td>
<td>21.9018(15)</td>
<td>20.1027(5)</td>
</tr>
<tr>
<td>a, deg</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>β, deg</td>
<td>100.3930(11)</td>
<td>93.309(4)</td>
<td>102.2680(10)</td>
</tr>
<tr>
<td>γ, deg</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>V, Å³</td>
<td>5932.2(3)</td>
<td>6272.9(8)</td>
<td>5998.1(3)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Radiation (λ, Å)</td>
<td>Mo-Kα 0.71073</td>
<td>Mo-Kα 0.71073</td>
<td>Mo-Kα 0.71073</td>
</tr>
<tr>
<td>ρ (calcd.), g/cm³</td>
<td>1.226</td>
<td>1.201</td>
<td>1.262</td>
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<tr>
<td>μ, mm⁻¹</td>
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<td>0.382</td>
<td>1.019</td>
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<td>Temp, K</td>
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<td>100(2)</td>
<td>100(2)</td>
</tr>
<tr>
<td>θ max, deg</td>
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<td>25.42</td>
<td>25.40</td>
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<td>11525/710</td>
<td>10989/699</td>
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<td>R₁</td>
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<td>0.0373</td>
<td>0.0400</td>
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<td>wR₁</td>
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<td>0.0845</td>
<td>0.1046</td>
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<td>GOF</td>
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<td>1.077</td>
<td>1.047</td>
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</table>
Table 4.11. Crystallographic Data Collection and Refinement Information for Pd(κ¹-N-p-TolNO)₂(CNAr²Dipp)₂•2Et₂O, Pd(κ¹-N-p-F-C₆H₄NO)₂(CNAr²Dipp)₂•2Et₂O, and Pd(κ¹-N-m-Cl-C₆H₄NO)₂(CNAr²Dipp)₂•2Et₂O.

<table>
<thead>
<tr>
<th>Formula</th>
<th>Crystal System</th>
<th>Space Group</th>
<th>a, Å</th>
<th>b, Å</th>
<th>c, Å</th>
<th>a, deg</th>
<th>β, deg</th>
<th>γ, deg</th>
<th>V, Å³</th>
<th>Z</th>
<th>Radiation (λ, Å)</th>
<th>ρ (calcd.), g/cm³</th>
<th>μ, mm⁻¹</th>
<th>Temp, K</th>
<th>θ max, deg</th>
<th>data/parameters</th>
<th>R_f</th>
<th>wR_f</th>
<th>GOF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd(κ¹-N-p-TolNO)₂(CNAr²Dipp)₂•2Et₂O (31)</td>
<td>Monoclinic</td>
<td>P2₁/c</td>
<td>13.973(2)</td>
<td>17.461(3)</td>
<td>16.912(3)</td>
<td>90</td>
<td>113.135(2)</td>
<td>90</td>
<td>3794.4(10)</td>
<td>4</td>
<td>Mo-Kα, 0.71073</td>
<td>1.176</td>
<td>0.295</td>
<td>100(2)</td>
<td>28.28</td>
<td>8777/432</td>
<td>0.0517</td>
<td>0.1181</td>
<td>1.027</td>
</tr>
<tr>
<td>Pd(κ¹-N-p-F-C₆H₄NO)₂(CNAr²Dipp)₂•2Et₂O (32)</td>
<td>Monoclinic</td>
<td>P2₁/n</td>
<td>13.8874(10)</td>
<td>17.1486(12)</td>
<td>16.7177(12)</td>
<td>90</td>
<td>113.685(3)</td>
<td>90</td>
<td>3646.0(5)</td>
<td>2</td>
<td>Mo-Kα, 0.71073</td>
<td>1.232</td>
<td>0.311</td>
<td>100(2)</td>
<td>25.43</td>
<td>6598/437</td>
<td>0.0426</td>
<td>0.0890</td>
<td>1.031</td>
</tr>
<tr>
<td>Pd(κ¹-N-m-Cl-C₆H₄NO)₂(CNAr²Dipp)₂•2Et₂O (33)</td>
<td>Monoclinic</td>
<td>C2/c</td>
<td>21.312(5)</td>
<td>14.111(4)</td>
<td>25.056(6)</td>
<td>90</td>
<td>97.197(3)</td>
<td>90</td>
<td>7476(3)</td>
<td>4</td>
<td>Mo-Kα, 0.71073</td>
<td>1.231</td>
<td>0.371</td>
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<td>28.33</td>
<td>8788/419</td>
<td>0.0742</td>
<td>0.1972</td>
<td>1.041</td>
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</table>

Table 4.12. Crystallographic Data Collection and Refinement Information for Pd(κ¹-N-p-Cl-C₆H₄NO)₂(CNAr²Dipp)₂•2Et₂O, Pd(κ¹-N-m-Br-C₆H₄NO)₂(CNAr²Dipp)₂•2Et₂O, and Pd(κ¹-N-p-Br-C₆H₄NO)₂(CNAr²Dipp)₂•2Et₂O.

<table>
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<th>Formula</th>
<th>Crystal System</th>
<th>Space Group</th>
<th>a, Å</th>
<th>b, Å</th>
<th>c, Å</th>
<th>a, deg</th>
<th>β, deg</th>
<th>γ, deg</th>
<th>V, Å³</th>
<th>Z</th>
<th>Radiation (λ, Å)</th>
<th>ρ (calcd.), g/cm³</th>
<th>μ, mm⁻¹</th>
<th>Temp, K</th>
<th>θ max, deg</th>
<th>data/parameters</th>
<th>R_f</th>
<th>wR_f</th>
<th>GOF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd(κ¹-N-p-Cl-C₆H₄NO)₂(CNAr²Dipp)₂•2Et₂O (34)</td>
<td>Monoclinic</td>
<td>P2₁/c</td>
<td>13.967(3)</td>
<td>17.490(4)</td>
<td>16.936(5)</td>
<td>90</td>
<td>114.091(3)</td>
<td>90</td>
<td>3776.8(15)</td>
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<td>Mo-Kα, 0.71073</td>
<td>1.218</td>
<td>0.367</td>
<td>100(2)</td>
<td>28.28</td>
<td>8716/425</td>
<td>0.0367</td>
<td>0.0853</td>
<td>1.021</td>
</tr>
<tr>
<td>Pd(κ¹-N-m-Br-C₆H₄NO)₂(CNAr²Dipp)₂•2Et₂O (35)</td>
<td>Monoclinic</td>
<td>P2₁/n</td>
<td>12.130(2)</td>
<td>24.738(4)</td>
<td>12.783(2)</td>
<td>90</td>
<td>99.112(3)</td>
<td>90</td>
<td>3787.3(11)</td>
<td>2</td>
<td>Mo-Kα, 0.71073</td>
<td>1.292</td>
<td>1.351</td>
<td>100(2)</td>
<td>26.07</td>
<td>7450/431</td>
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<td>0.1259</td>
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<tr>
<td>Pd(κ¹-N-p-Br-C₆H₄NO)₂(CNAr²Dipp)₂•2Et₂O (36)</td>
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<td>P2₁/c</td>
<td>14.1466(14)</td>
<td>17.5910(18)</td>
<td>17.0139(18)</td>
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<td>114.0900(10)</td>
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<td>7289/431</td>
<td>0.0422</td>
<td>0.1067</td>
<td>1.039</td>
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Table 4.13. Crystallographic Data Collection and Refinement Information for \textit{trans}\textsuperscript{-}PdBr(C\textsubscript{6}H\textsubscript{4}NO)(CNAr\textsubscript{Dipp}\textsubscript{2})\textsubscript{2}•1.5C\textsubscript{6}H\textsubscript{6}, Pd(κ\textsuperscript{1}N-p-OCH-C\textsubscript{6}H\textsubscript{4}NO)\textsubscript{2}(CNAr\textsubscript{Dipp}\textsubscript{2})\textsubscript{2}•0.5Tol (38).

<table>
<thead>
<tr>
<th></th>
<th>\textit{trans}-PdBr(C\textsubscript{6}H\textsubscript{4}NO)(CNAr\textsubscript{Dipp}\textsubscript{2})\textsubscript{2}•1.5C\textsubscript{6}H\textsubscript{6} (37)</th>
<th>Pd(κ\textsuperscript{1}N-p-OCH-C\textsubscript{6}H\textsubscript{4}NO)\textsubscript{2}(CNAr\textsubscript{Dipp}\textsubscript{2})\textsubscript{2}•0.5Tol (38)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C\textsubscript{77}H\textsubscript{87}BrN\textsubscript{3}O Pd</td>
<td>C\textsubscript{39.7}H\textsubscript{43.7}N\textsubscript{2}O\textsubscript{2}Pd0.50</td>
</tr>
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<td>Monoclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space Group</td>
<td>C\textsubscript{2}/c</td>
<td>\textit{P}2\textsubscript{1}/\textit{n}</td>
</tr>
<tr>
<td>(a), Å</td>
<td>48.4775(18)</td>
<td>14.3005(9)</td>
</tr>
<tr>
<td>(b), Å</td>
<td>10.8499(4)</td>
<td>17.1080(11)</td>
</tr>
<tr>
<td>(c), Å</td>
<td>27.7602(10)</td>
<td>16.6238(11)</td>
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<td>(α), deg</td>
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<td>90</td>
</tr>
<tr>
<td>(β), deg</td>
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<td>113.702(2)</td>
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<td>(γ), deg</td>
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<td>90</td>
</tr>
<tr>
<td>(V), Å\textsuperscript{3}</td>
<td>13289.3(8)</td>
<td>3724.0(4)</td>
</tr>
<tr>
<td>(Z)</td>
<td>8</td>
<td>4</td>
</tr>
<tr>
<td>Radiation ((λ), Å)</td>
<td>Mo-K\textsubscript{α}, 0.71073</td>
<td>Mo-K\textsubscript{α}, 0.71073</td>
</tr>
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</tr>
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<td>GOF</td>
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<td>1.011</td>
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4.15 References


(69) Neese, F. *Orca, an ab initio, DFT and Semiempirical Electronic Structure Package*; versions 2.7 and 2.8; Insitut für Physikalische und Theoretische Chemie, Universität Bonn: Bonn, Germany, 2009-2010.


### 4.16 Acknowledgments

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