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Group 3 Metal Stilbene Complexes: Synthesis, Reactivity, and Electronic Structure Studies

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Periodicity is one of the most important discoveries of chemical sciences. Ever since Dmitri Mendeleev created the periodic table of elements, scientists have used this intuitive tool to explain and predict physical and chemical properties of elements and their compounds. Unlike main group and transition metals, rare-earths (group 3 metals and lanthanides) and actinides do not show clear periodicity trends. For example, rare-earths show similar chemical reactivity within the series despite a different number of f electrons, because these electrons are shielded.1, 2 On the other hand, actinides, of which uranium and thorium are studied the most, show involvement of f electrons in bonding,3,4 and uranium has several oxidation states accessible.5 The differences between lanthanides and early actinides are most striking in their organometallic chemistry.5, 6

Group 3 metals (scandium, yttrium, lanthanum, and lutetium) usually show chemistry representative of all rare earths and their compounds are easier to characterize because of their diamagnetic nature.3, 9 Their classification with lanthanides rather than with transition metals is supported by the fact that, with few exceptions,9 their complexes contain the metal in the +3 oxidation state, while transition metals display multiple oxidation states. Recently, our group reported the synthesis of group 3 metal naphthalene10-12 and biphenyl complexes13 supported by a ferrocene diamide ligand (Chart 1a). The metal naphthalene complexes, with the general formula [(NN\textsubscript{TBS})(THF)\textsubscript{2}](\textit{μ}-\textit{η}^{4}:\textit{η}^{1}\textit{C}_{10}\textit{H}_{8})(\textit{M}_{2}-\textit{naph}, \textit{M} = \text{Sc}, \textit{x} = 0; \text{M} = \text{Y}, \text{La}, \text{Lu}, \textit{x} = 1), contain a naphthalene diamianion bridging the two metal centers through different phenyl rings. The metal biphenyl complexes, with the general formula [(NN\textsubscript{TBS})(THF)\textsubscript{2}](\textit{μ}-\textit{η}^{4}:\textit{η}^{1}\textit{C}_{10}\textit{H}_{8})(\textit{M}_{2}-\textit{biph}, M = \text{Sc}, \text{Y}, \text{La}, \text{Lu}, \textit{solvent} = \text{toluene, tetrahydrofuran, diethyl ether, or 18-crown-6}), contain a biphenyl tetraanion bridging the two rare-earth centers through the same phenyl ring. While the negative charges in \textit{M}_{2}-\textit{naph} are equally distributed over the entire naphthalene fragment, the four electron reduction is mainly localized on the coordinating phenyl ring in \textit{M}_{2}\textit{K}_{2}-\textit{biph} and results in a 6\textit{C}, 10\textit{π}-electron aromatic system. DFT calculations on the naphthalene and biphenyl complexes showed π overlap for the former and δ overlap for the latter between the metal orbitals and arene π* orbitals.

![Chart 1](image)

Chart 1: (a) Rare-earth arene complexes supported by a ferrocene diamide ligand; (b) Uranium arene complexes supported by a ketimide ligand.

This bonding dichotomy is in sharp contrast to diuranium inverse sandwich arene complexes of biphenyl, \textit{p}-terphenyl, naphthalene, and \textit{(E)}-stilbene supported by the same ketimide ligand (Chart 1b).15 Despite the different nature of the arene, the resulting complexes shared analogous electronic structures, featuring δ overlap between LUMOs of one phenyl ring and the two uranium centers. The related diuranium inverse sandwich benzene or toluene complexes have been synthesized with various ancillary ligands and present a similar bonding character.16-21 As mentioned, the δ interaction is also present in \textit{M}_{2}\textit{K}_{2}-\textit{biph},13 but to a lesser extent than in the corresponding uranium compounds. Since group 3 metal arene complexes supported by the ferrocene diamide ligand showed discrepancy in the binding mode of naphthalene and biphenyl, we became interested in synthesizing the corresponding \textit{(E)}-stilbene complexes; the presence of multiple sites for reduction and binding, i.e., the \textit{C}=\textit{C} bond and the
phenyl rings, will offer insight into the binding preference of rare-earths in comparison with uranium.

In spite of the abundance of rare-earth naphthalene complexes in literature,\textsuperscript{8, 22, 23} (E)-stilbene complexes are rare. Evans et al. reported the synthesis of [(C:Me)=:Sm±(E)-stilbene] in the presence of (C-Me)\textsubscript{2}Sm and (E)-stilbene.\textsuperscript{24} The structure of [(C:Me)=:Sm±(E)-stilbene] was established based on connectivity data derived from X-ray crystallography; however, the poor quality of the data prevented an accurate interpretation of the structural parameters. The analogous samarium styrene and butadiene complexes showed two electron reduction of the C=C bond and concomitant oxidation of Sm(II) to Sm(III).\textsuperscript{25} Related yttrium and lanthanum complexes were reported with similar structural features.\textsuperscript{26, 27}

Addition of 1.25 equiv KC\textsubscript{8} to a pre-mixed THF solution of (NN\textsuperscript{TBS})\textsubscript{2}Y(THF)\textsubscript{2} and 0.5 equiv (E)-stilbene at -78 °C resulted in an immediate color change to dark green (Scheme 1). After stirring at 0 °C for 1 h, the color gradually changed to red. The \textsuperscript{1}H NMR spectrum of the crude reaction mixture indicated the formation of a single product. Crystals suitable for single X-ray diffraction were obtained. The synthesis of M\textsubscript{2}-stilbene (M = Y and La) mimics that of M\textsubscript{2}-naph: when excess KC\textsubscript{8} was used, the formation of a heterobimetallic complex, [(NN\textsuperscript{TBS})\textsubscript{2}Y(THF)]\textsubscript{2}(E)-stilbene-K\textsubscript{8}], took place (Scheme 1). This is different from the synthesis of M\textsubscript{2-K2-biph}: M\textsubscript{2-K2-biph} was the only observed rare-earth product regardless of the KC\textsubscript{8} stoichiometry employed. It is interesting to note that adding KC\textsubscript{8} to isolated Y\textsubscript{2-stilbene} did not afford further reduction but rather exclusion of one (NN\textsuperscript{TBS})\textsubscript{2}Y(THF) fragment to form Y\textsubscript{2-stilbene-K} (Scheme 1). In addition, Y\textsubscript{2-stilbene-K} could be generated from the reaction of Y\textsubscript{2-K2-biph} and (E)-stilbene (see the ESI for details). Attempts to obtain single crystals of Y\textsubscript{2-stilbene-K} were not successful due to incorporation of labile potassium ions. However, using 18-crown-6, single crystals of [(NN\textsuperscript{TBS})\textsubscript{2}Y(THF)](E)-stilbene-K\textsubscript{8}-[18-crown-6] (Y\textsubscript{2-stilbene-K-crown}) were grown from a hexanes solution and its molecular structure was determined by X-ray crystallography (Figure 2).

Disorder in the molecular structures of M\textsubscript{2}-stilbene (M = Y, La) is caused by flipping of the central C-C bond; the resulting two conformations were solved separately and only one is shown in Figure 1 (see the ESI for details and additional parameters). Since they are isostructural, Y\textsubscript{2-stilbene} will be discussed as a representative. The bridging (E)-stilbene ligand coordinates equally to the two yttrium centers in an \(\eta^1\)-fashion through the central C-C bond and one \(\eta^2\)-coordinated carbon, with Y-C distances of 2.60, 2.58, and 2.74 Å, respectively. An additional contact between Y and one ortho-carbon of 2.99 Å is also present but is longer than the sum of the covalent radii of yttrium and carbon.\textsuperscript{28} This symmetrical coordination mode is different from the asymmetrical coordination mode suggested for [(C:Me)=:Sm±(E)-stilbene],\textsuperscript{24} but is reasonable with the less sterically demanding NN\textsuperscript{TBS}. The C1-C1A distance of 1.52 Å is consistent with a single bond character, while the shortened C1-C3 distances of 1.43 Å and elongated C3-C4 distance of 1.46 Å indicate charge delocalization. Y\textsubscript{2-stilbene-K-crown} exhibits a similar coordination mode for yttrium as Y\textsubscript{2-stilbene}, while K\textsuperscript{8} is \(\eta^1\)-coordinated to one of the phenyl rings (Figure 2).

**Scheme 1:** Synthesis of M\textsubscript{2}-stilbene, Y\textsubscript{2-stilbene-K}, and transformation of Y\textsubscript{2-stilbene} to Y\textsubscript{2-stilbene-K-crown}.

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**Figure 1:** Molecular structure of Y\textsubscript{2-stilbene}. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms and disordered counterparts were omitted for clarity.

Since the synthesis of Y\textsubscript{2-stilbene} echoed that of M\textsubscript{2-naph}, we were interested to determine the relative reducing strength of Y\textsubscript{2-stilbene} with respect to that of the other rare-earth arene complexes. Based on arene exchange experiments (Scheme 2a and 2b), we found that the reducing power decreases in the order Y\textsubscript{2-stilbene} > Y\textsubscript{2-anth} > M\textsubscript{2}-naph. The reaction of Y\textsubscript{2-stilbene} and 2,2'-bipyridine (bipy) or phenylacetylene (PhCCH) resembled the reactivity of Sc\textsubscript{2}-naph and yielded (NN\textsuperscript{TBS})\textsubscript{2}Y(THF)(bipy) and [(NN\textsuperscript{TBS})\textsubscript{2}Y(THF)]CCPh\textsubscript{2} with the concomitant formation of (E)-stilbene and bibenzyl, respectively (Scheme 2c and 2d).\textsuperscript{12} However, addition of excess pyridine did not yield the corresponding C-C coupled complex but rather an intractable mixture of products; no formation of (E)-stilbene was observed by \textsuperscript{1}H NMR spectroscopy. This suggests that the dianion of (E)-stilbene is not innocent in this reaction.
Scheme 2: Relative reducing strength of Y2-stilbene (a, b) and its reactivity with organic substrates (c, d).

In summary, we successfully synthesized group 3 metal (E)-stilbene complexes through reduction of (E)-stilbene by the (NN\text{NBS})MI(THF)/KCs system. The resulting complexes, M2-stilbene, showed similar reactivity to M2-naph complexes. Both experimental and computational data suggest that the reduction takes place at the C=C bond instead of the phenyl ring. This contrasts the case of uranium and indicates different binding preferences for rare-earths that are similar to those of transition metals and not actinides. Our synthetic route also allows access to rare-earth alkene complexes, which were previously limited to samarium.30 This work was supported by NSF (CAREER Grant 0847735 to PLD and CHE-1048804 for NMR spectroscopy). The authors thank the Kaner group (UCLA) for generous gifts of KCs.

Notes and references

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