PENTAMETHYLCYCLOPENTADIENYL AND BIS(TRIMETHYLSILYL) AMIDO COMPLEXES OF THE DI- AND TRIVALENT LANTHANIDES

Terry Don Tilley
(Ph.D. thesis)

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PENTAMETHYLCYCLOPENTADIENYL AND BIS(TRIMETHYLSILYL)AMIDO COMPLEXES
OF THE DI- AND TRIVALENT LANTHANIDES

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to my parents
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Pentamethylcyclopentadienyl and Bis(trimethylsilyl)amido Complexes of the Di- and Trivalent Lanthanides

Terry Don Tilley

ABSTRACT

The reaction of the divalent iodides YbI₂ and EuI₂ with NaN(SiMe₃)₂ has provided pentane-soluble, monomeric derivatives of the divalent lanthanides. These compounds are isolated as the solvated species Eu[N(SiMe₃)₂]₂L₂ (L = thf or 1,2-dme), Yb[N(SiMe₃)₂]₂(thf)ᵡ₁.₅ and Yb[N(SiMe₃)₂]₂L₂ (L = 1,2-dme or OEt₂), or as the sodium salts NaN[SiMe₃]₂₃ (M = Eu or Yb). The crystal structure of NaEu[N(SiMe₃)₂]₃ reveals four short Eu-C(methyl) contacts that appear to result from electrostatic attractions between the metal and the methyl carbon atoms. Diethyl ether and NaN(SiMe₃)₂ can be displaced from Yb[N(SiMe₃)₂]₂(OEt₂)₂ and NaEu[N(SiMe₃)₂]₃, respectively, to yield phosphine coordination complexes. Thus, Yb[N(SiMe₃)₂]₂(dmpe), Yb[N(SiMe₃)₂]₂L₂ (L = Pn-Bu₃, dpm), Eu[N(SiMe₃)₂]₂(dmpe)₁.₅ and Eu[N(SiMe₃)₂]₂(Pn-Bu₃)₂ are obtained. The crystal structure of Yb[N(SiMe₃)₂]₂(dmpe) provides the first structural evidence for lanthanide-phosphine bonding, and exhibits two metal-C(methyl) interactions.

The pentamethylcyclopentadienyl ligand has been used to obtain trivalent derivatives of the type (C₅Me₅)₂MCl₂M'Lₓ (M = Nd, Sm or Yb; M' = Li or Na; L = OEt₂ or tmed) or (C₅Me₅)₂MCl(thf) (M = Nd or Yb). These compounds undergo metathesis reactions that yield (C₅Me₅)₂MO₂CR, (C₅Me₅)₂MS₂CNEt₂ or (C₅Me₅)₂MN(SiMe₃)₂ (M = Nd or Yb).
The interaction of NaC₅Me₅ with EuCl₃ yields only the divalent (C₅Me₅)₂EuL (L = thf or OEt₂). Analogous compounds of ytterbium are obtained by reaction of YbI₂ with NaC₅Me₅ in thf or OEt₂. Displacement of the ether ligands by aromatic amines yields (C₅Me₅)₂ML₂ complexes (M = Eu, L = 1/2bipy; M = Yb, L = py, 1/2bipy or p-Me₂NC₅H₄N). The ytterbium amine complexes are weakly paramagnetic, apparently due to charge transfer from ytterbium to the aromatic rings. The divalent phosphine complexes (C₅Me₅)₂ML (M = Eu or Yb; L = dmpe or dmpm) are also described.

Whereas oxidizing agents fail to yield isolable Eu(III) species, the (C₅Me₅)₂Yb(L) complexes are taken to trivalent (C₅Me₅)₂YbX(L) derivatives (X = Cl, I or O₂CR). The (C₅Me₅)₂Yb(OEt₂) is shown to reduce binary transition metal carbonyls, affording the Yb(III) species [(C₅Me₅)₂Yb][Mo(CO)₅], [(C₅Me₅)₂Yb(thf)][Co(CO)₄], [(C₅Me₅)₂Yb(thf)]₂[Fe(CO)₄] and [(C₅Me₅)₂Yb]₂[Fe₃(CO)₁₁]. Infrared and X-ray crystallographic data reveal the presence of isocarbonyl (YbOCM) linkages. In [(C₅Me₅)₂Yb(thf)][Co(CO)₄], one isocarbonyl linkage is observed in the crystal structure. The structure of [(C₅Me₅)₂Yb][Fe₃(CO)₁₁] shows an unusual bent geometry for the triiron fragment, with only two Fe-Fe bonds. Four carbonyls bridge the Fe-Fe bonds, and form two chelating, Fe(CO)₂Yb rings.
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CHAPTER 1

INTRODUCTION

Since 1956, when Wilkinson first described the preparations of the trivalent tris(cyclopentadienyl) lanthanides [1], interest in organometallic lanthanide chemistry has grown steadily. To date, most of this chemistry has been developed with the six-electron (three-coordinate) cyclopentadienide as a solubilizing ligand, though α-bonded complexes (with two-electron donor groups) such as Ln(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>(thf)<sub>2</sub> [2,3], [Li(thf)<sub>4</sub>][Ln(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>4</sub>] [2,3], [Li(thf)<sub>4</sub>][Ln(CMe<sub>3</sub>)<sub>4</sub>] [4], [Li(tmed)]<sub>3</sub>[LnMe<sub>6</sub>] [5], [Li(thf)<sub>4</sub>][Ln(CH(SiMe<sub>3</sub>)<sub>2</sub>)<sub>3</sub>Cl] [2] and [Li(thf)<sub>4</sub>][LnAr<sub>4</sub>] [6,7], where Ar is phenyl or 2,6-dimethylphenyl, have been reported.

The development of mixed-ligand cyclopentadienyl complexes was pioneered by Dubeck et al., who reported preparations for the halide derivatives LnCp<sub>2</sub>X (X = halide) [8] and LnCpCl<sub>2</sub>(thf)<sub>3</sub> [9]. These compounds were readily obtained by the following methods:

\[
\text{ LnCl}_3 + 2\text{NaCp} \rightarrow \text{LnCp}_2\text{Cl} \\
2\text{LnCp}_3 + \text{LnCl}_3 \rightarrow \text{LnCp}_2\text{Cl} \\
\text{LnCp}_3 + \text{HCl} \rightarrow \text{LnCp}_2\text{Cl} \\
\text{LnCp}_3 + \text{I}_2 \rightarrow \text{LnCp}_2\text{I} + \text{CpI} \\
\text{LnCp}_3 + 2\text{LnCl}_3 + 3\text{thf} \rightarrow \text{LnCpCl}_2(\text{thf})_3
\]
More recently, Dornberger et al. have shown that SmCp₂Cl and 
YbCp₂Cl can be conveniently synthesized by protonation of a 
C₅H₅ 
ligand with ammonium chloride [10]: 

\[ \text{LnCp}_3 + \text{NH}_4\text{Cl} \rightarrow \text{LnCp}_2\text{Cl} + \text{NH}_3 + \text{C}_5\text{H}_6 \]

The bis(cyclopentadienyl)chloro species have proven to be useful 
starting materials for the preparations of a variety of substituted 
LnCp₂X derivatives. Chloride-metathesis reactions have generated 
bis(cyclopentadienyl)-carboxylate [8], -alkyl [11], -alkynyl [11], 
-(n°-allyl) [12], -hydride [13], -borohydride [14], -phosphide [15],
-stannyl [16] and -germyl [16] derivatives. A number of excellent 
reviews covering organometallic lanthanide chemistry have appeared 
recently [17-19].

Divalent lanthanide chemistry has received much less attention. 
Liquid ammonia solutions of europium(II) and ytterbium(II) cations, 
prepared by dissolving the metals in liquid ammonia, have been used to 
obtain the insoluble species LnCp₂ [20], Ln(COT) [21] and Ln(C ≡ CR)₂ 
[22,23], upon reaction with the appropriate hydrocarbon. The prepara-
tion of YbCp₂ from the metal and diene in liquid ammonia is not 
straightforward, since two ytterbium(III) products, YbCp₃ and 
Yb₂Cp₄N₂H₄, have also been isolated from this reaction [24]. 
An alternative synthetic scheme, reduction of YbCp₂Cl by sodium or 
ytterbium metal in tetrahydrofuran, has been devised [25]. Ytterbium, 
samarium and europium analogues to Grignard reagents, RLnX, can be
prepared by the reaction of the metal and the alkyl halide in tetrahydrofuran [26]. Ytterbium metal also reacts with Hg(C₆F₅)₂ [22] or Hg(C≡CPh)₂ [22] to give the ether-soluble Yb(C₆F₅)₂(thf)₄ or Yb(C≡CPh)₂. An insoluble, purple, paramagnetic (3.6 B.M.) derivative of samarium(II), SmCp₂(thf), is isolated from reduction of SmCp₃ with potassium naphthalene in tetrahydrofuran [27]. Johnson has produced a detailed review of divalent lanthanide chemistry, including discussions on the electronic and thermodynamic factors influencing relative stabilities of the di- and trivalent oxidation states [28].

The difficulty in studying the solution chemistry of the divalent compounds results from their lack of solubility in hydrocarbon solvents. This property is undoubtedly related to the tendency of these large, electropositive metals to achieve a high coordination number via polymerization. The divalent EuCp₂ and YbCp₂ have been shown to be isostructural with SrCp₂ and CaCp₂ [20], respectively. The CaCp₂ compound has been shown to have a polymeric structure, with n⁵-C₅H₅, n³-C₅H₅, and n¹-C₅H₅ bonding [29]. The structure of Yb(C₅H₄Me)₂(thf)₂ reveals a polymeric structure with C₅H₄Me groups bridging two ytterbium atoms by penta-hapto bonding to both metals [30].

The bonding in all lanthanide compounds is thought to be highly ionic, and much of the coordination chemistry of these metals reflects this. The lanthanide ions, which have a high charge-to-ionic radius ratio, can be considered as hard Lewis acids, which typically bind to
as many donor ligands as is sterically possible. Therefore, typical coordination numbers are high, ranging from seven to eleven. The question of valence-orbital participation in bonding is somewhat controversial, but since the 4f orbitals are well-shielded by the 5s^2 and 5p^6 shells, little covalency is to be expected. The possible role of 5d orbital participation in bonding is unclear, though these orbitals may play a role as acceptor-orbitals in coordination by donor ligands [31].

So far, lanthanide research has resulted in little reason to expect chemical properties that are strikingly unique to the lanthanide series. The placement of the lanthanide series in the periodic table suggests properties intermediate between those of the alkaline earth metals and the Group IV transition metals. This observation is substantiated by known chemical properties. However, a number of fundamental questions remain unanswered. For instance, how do chemical and redox properties change from metal to metal? Also, the capacity of soft donor molecules, for example CO, olefins and acetylenes, to serve as ligands in lanthanide complexes is still an open question, since no evidence for such bonding has been observed. This may be a result of the inability of these potential ligands to compete with harder Lewis bases that are generally present at some point during the preparation of the lanthanide compounds. Evans has reported that lanthanide metal vapors condense with butadienes to yield the compounds Ln(C_4H_6)_3 [32], where Ln is La, Nd, Sm and Er, and Ln(Ne_2C_4H_6)_2, where Ln is La or Er. The mode of bonding to the butadiene ligands has
not been established, but the metals in these complexes are most likely not trivalent. Another interesting observation is that SmCp₃ is known to trimerize phenylacetylene and to polymerize olefins [33].

It is reasonable to expect to find new and interesting reactivity patterns among more reactive lanthanide systems, such as ones exhibiting a low coordination number and/or low oxidation state. The reaction chemistry of these compounds with various organic and inorganic substrate molecules can best be studied if solubility in non-coordinating hydrocarbons can be obtained. This will eliminate complications due to coordination of polar solvents, such as tetrahydrofuran.

The aim of the research reported here is to investigate the use of sterically demanding ligands in preparing hydrocarbon-soluble derivatives of the lanthanides. Bulky ligands that can block coordination sites around the metal should lead to monomeric, electron-poor species that might display new and interesting chemical properties. Of particular interest are coordinatively unsaturated, hydrocarbon-soluble divalent compounds.

Two ligands that fit this description are the pentamethylcyclopentadienyl and bis(trimethylsilyl)amide groups. The utility of the pentamethylcyclopentadienyl ligand in this regard is illustrated by the observation that 1cyclopentadienylmanganese has a polymeric constitution in the solid state [34], whereas bis(pentamethylcyclopentadienyl) manganese is monomeric and pentane-soluble [35].

Although the coordination chemistry of bis(trimethylsilyl)amide has been extensively investigated for main group metals, first-row
transition metals and the actinides [36], its use in lanthanide chemistry has been largely unexplored. Exhaustive reviews on the chemistry of this ligand have appeared [37-39]. It is potentially a very valuable ligand in lanthanide systems due to its steric bulk, and has been used to prepare monomeric, three-coordinate \( \text{Ln}[\text{N(SiMe}_3]_2]_3 \) complexes [40]. In addition, the tendency of the silylamide ligand to bridge two metal atoms, resulting in associated species, is relatively low. The basicity of the lone pair of electrons on nitrogen is much less than that of the lone pairs in dialkylamides, due to the electron-withdrawing effect of the SiMe\(_3\) groups. The SiMe\(_3\) group is more electron-withdrawing than an alkyl group, and possesses low-lying \( d_\pi \)-orbitals that may be able to delocalize the lone pair on nitrogen. However, there are a few examples of silylamide bridged species in low-coordination number complexes. The alkali-metal derivatives are associated, as is the divalent Mn[\text{N(SiMe}_3]_2]_2, which has been shown to exist as dimeric units in the solid state, with each manganese atom bound to one terminal and two bridging silylamides [41].

The divalent chemistry will focus upon europium and ytterbium, since the thermodynamic stability of these divalent metals is greatest among the lanthanides [28]. This is a consequence of the stability of the half-filled 4f shell \( (4f^7) \) in europium(II), and the full 4f shell \( (4f^{14}) \) in ytterbium(II).

During the course of this research, the compound \([\text{Li(tnf)}_2] \) \([[(\text{C}_5\text{Me}_5)_2\text{NdCl}_2] \) was briefly described by Evans [42], and the preparation of \( \text{Yb(C}_5\text{Me}_5)_2\text{(thf)}_2 \) was communicated [43]. The
latter publication also reports some halo and alkyl-pentamethylenecyclopentadienyl derivatives of ytterbium(III).

Chapter 1 References


CHAPTER 2

EXPERIMENTAL DETAILS

General

Infrared spectra were recorded on a Perkin-Elmer 597 spectrometer as Nujol mulls between CsI windows. Mass spectra were obtained with an AEI-MS 12 mass spectrometer. The $^1$H (90 MHz), $^{13}$C($^1$H) (22.5 MHz) and $^{31}$P($^1$H) (36.2 MHz) nuclear magnetic resonance spectra were recorded on a JEOL FX-90Q spectrometer and referenced to Me$_4$Si (δ 0, $^1$H and $^{13}$C spectra) or 85 percent H$_3$PO$_4$ (δ 0, $^{31}$P spectra).

Elemental analyses were performed by the analytical laboratories at the University of California, Berkeley. Melting points were taken in sealed capillaries and are uncorrected.

Low temperature magnetic susceptibility studies were conducted on solid samples using a Princeton Applied Research Model 155 vibrating sample magnetometer, equipped with a Janus Research Model 153 liquid helium dewar. The spectrometer was calibrated with HgCo(SCN)$_4$, and field strength was monitored with a George Associates rotating coil gaussmeter. Temperatures were measured with a calibrated GaAs diode. Solution magnetic moments were obtained using the Evans' NMR method [1].

All operations were conducted under a nitrogen atmosphere, using standard Schlenk techniques or a vacuum atmospheres inert atmosphere box. For reactions carried out under elevated pressures, a Fischer-Porter bottle, equipped with a pressure release valve, was used.
Reagent grade diethyl ether, tetrahydrofuran, 1,2-dimethoxyethane, pentane, benzene and toluene were distilled from sodium benzophenone ketyl under nitrogen. Pyridine and N,N,N',N'-tetramethylethylene-diamine were distilled from sodium. Deuterated solvents for NMR studies were stored over molecular sieves and degassed prior to use. All other chemicals were of reagent grade quality unless specified otherwise.

The preparation of 1,2,3,4,5-pentamethylcyclopentadiene was according to the method of Threlkel and Bercaw [2]. Sodium pentamethylcyclopentadienide was prepared by adding the diene to NaNH₂ in liquid ammonia. The crude product was purified by extraction with tetrahydrofuran, evaporating the solvent and washing the residue with diethyl ether. The grey residue was dried in vacuo. Unlike LiC₅Me₅, which is insoluble in ethers, Na(C₅Me₅) is soluble in tetrahydrofuran and 1,2-dimethoxyethane, but not diethyl ether.

Sodium bis(trimethylsilyl)amide [3], the lanthanide dihalides [4], and the Ln[N(SiMe₃)₂]₃ [5] were prepared according to literature procedures.

The phosphine 1,2-dimethylphosphinoethane was prepared by reaction of bis(1,2-dichlorophosphino)ethane with methyl magnesium chloride [6]. The 1,2-dimethylphosphinomethane was prepared by the method of Schmidbaur [7].

Tetra(n-butyl)ammonium borohydride, [n-Bu₄N][BH₄], was prepared by soxhlet extraction of a sodium borohydride-tetra(n-butyl)-ammonium bromide mixture [8]. Sodium 2,2-dimethylpropionate (which is insoluble
in diethyl ether and tetrahydrofuran) was prepared by stirring equal molar amounts of sodium hydride and pivalic acid in diethyl ether for 12 h. Lithium diethylamide was prepared by the addition of n-butyl lithium to diethyl amine in pentane at 0°C. Ferrocinium hexafluorophosphate was obtained by combining ferrocinium tetrachloroferrate (8 g) and potassium hexafluorophosphate (3.8 g) in 120 mL of water. After stirring for 30 min., the mixture was cooled to 0°C, and the product isolated by filtration.
Experimental Procedures for Chapter 3

Attempted Preparation of Bis[bis(trimethylsilyl)amido]chloro-europium(III)

Tris[bis(trimethylsilyl)amido]europium(III) (1.12 g, 1.77 mmol) in tetrahydrofuran (75 mL) was added to EuCl₃ (0.23 g, 0.89 mmol) in tetrahydrofuran (50 mL). After 24 h of stirring, during which time the EuCl₃ dissolved, the solution was filtered. Attempts to crystallize a product by concentration and cooling failed.

Attempted Preparations of Bis[bis(trimethylsilyl)amido]chlorosamarium(III)

1) Tris[bis(trimethylsilyl)amido]samarium(III) (1.47 g, 2.33 mmol) in tetrahydrofuran (75 mL) was added to SmCl₃ (0.30 g, 1.2 mmol) in tetrahydrofuran (50 mL). The solution was stirred for 24 h, the solvent was removed under vacuum, and the residue was extracted with pentane (50 mL). Concentration and cooling (-10°C) resulted in crystallization of the starting material, Sm[N(SiMe₃)₂]₃, characterized by its infrared spectrum and melting point. 2) Sodium bis(trimethylsilyl)amide (1.12 g, 6.11 mmol) in tetrahydrofuran (75 mL) was added to SmCl₃ (0.70 g, 3.1 mmol) in tetrahydrofuran (50 mL) and the solution was stirred for 12 h. The solvent was removed under vacuum and the residue extracted with pentane (40 mL). Concentration and cooling (-10°C) led to isolation of only Sm[N(SiMe₃)₂]₃, as shown by its infrared spectrum and melting point.
Attempted Preparation of Bis[bis(trimethylsilyl)amido]-iodosamarium(III)

Iodine (0.24 g, 0.96 mmol) in diethyl ether (25 mL) was added to Tris[bis(trimethylsilyl)amido]samarium(III) (1.21 g, 1.92 mmol) in diethyl ether (25 mL). A white precipitate formed immediately. The reaction mixture was stirred for 12 h, the volatile material was removed under vacuum, and the residue was extracted with pentane. Concentration and cooling (-10°C) yielded Sm[N(SiMe₃)₂]₃, as shown by IR and melting point. No attempt was made to characterize the insoluble product of the residue.

Attempted Preparation of Bis[bis(trimethylsilyl)amido]-chloroytterbium(III)

Sodium bis(trimethylsilyl)amide (2.02 g, 11.0 mmol) in tetrahydrofuran (30 mL) was added to YbCl₃ (1.54 g, 5.51 mmol) in tetrahydrofuran (50 mL), and the solution stirred for 12 h. The solvent was removed under vacuum and the residue was extracted with pentane (40 mL). Concentration and cooling (-10°C) resulted in the crystallization of Yb[N(SiMe₃)₂]₃, as shown by its IR spectrum and melting point.

Attempted Preparations of Bis[bis(trimethylsilyl)amido]-samarium(III) Complexes

1) A solution of sodium naphthalene (0.055 M, 50 mL, 2.7 mmol) in tetrahydrofuran was added to a solution prepared by adding Sm[N(SiMe₃)₂]₃ (1.14 g, 1.81 mmol) in tetrahydrofuran (30 mL) to SmCl₃ (0.23 g, 0.90 mmol) in tetrahydrofuran (50 mL). An intense purple color developed immediately that yielded a reddish-brown color.
after ca. 2 h. After 12 h of stirring, the solvent was removed and
naphthalene was sublimed (40°C, 10⁻² mm Hg). The residue was
extracted with pentane, from which only Sm[N(SiMe₃)₂]₃ could be
crystallized (by IR and mp) in very low yield.

2. A sodium naphthalene solution (one molar equivalent in
tetrahydrofuran, 50 mL) was added to SmCl₃ (0.76 g, 2.96 mmol) in
tetrahydrofuran (50 mL). The purple solution was stirred for 12 h, and
the tetrahydrofuran removed under vacuum. The dark brown-red residue
was washed with toluene (2 x 75 mL), and sodium bis(trimethylsilyl)amide
(1.08 g, 5.89 mmol) in 75 mL of tetrahydrofuran was added. The purple
solution was stirred for 24 h, and the volatile material removed under
vacuum. Addition of pentane gave a dark red solution, from which only
the white Sm[N(SiMe₃)₂]₃ (by IR, mp) could be obtained.
Bis[bis(trimethylsilyl)amide]bis(tetrahydrofuran)europium(II),
Eu[N(SiMe₃)₂]₂(thf)₂
Sodium bis(trimethylsilyl)amide (2.13 g, 11.6 mmol) and europium
diiodide (2.36 g, 5.82 mmol) were stirred together in tetrahydrofuran
(70 mL) for 8 h. After removal of the solvent, pentane (100 mL) was
added, and the solution filtered. Concentration and cooling (-10°C)
gave orange-yellow prisms, m.p. = 128-130°C, in an overall yield of
73 percent (2.62 g). The mass spectrum contained peaks at m/e 471 and
473, corresponding to ¹⁵¹Eu[N(SiMe₃)₂]₂ and ¹⁵³Eu[N(SiMe₃)₂]₂.
The Eu[N(SiMe₃)₂]₂(thf)₂ sublimes with much decomposition,
100-110°C/10⁻² mm Hg. It is soluble in hydrocarbons and ethers.

Anal. Calcd. for C₂₀H₅₂N₂Eu₂O₂Si₄: C, 38.9; H, 8.50; N, 4.54.
Found: C, 39.4; H, 7.73; N, 4.63. IR data: 1245 s, 1008 w sh, 998 s, 987 s, 865 m, 835 s br, 788 m, 770 m, 753 w, 668 m, 602 m, 447 w, 442 m, 375 m cm⁻¹.

**Bis[bis(trimethylsilyl)amido]bis(1,2-dimethoxyethane)europium(II),**

**Eu[N(SiMe₃)₂]₂(dme)₂**

Europium diiodide (1.78 g, 4.39 mmol), sodium bis(trimethylsilyl) amide (1.61 g, 8.78 mmol) and 1,2-dimethoxyethane (75 mL) were added to a flask, and the mixture stirred for 10 h. After removal of solvent, the residue was extracted and crystallized from pentane (ca. 30 mL, -10°C) in an overall yield of 79 percent (2.26 g), m.p. = 83-86°C (the compound turned orange at ca. 77°C). The compound follows Curie behavior from 5 to 45 K with C = 8.82 and μeff = 8.43 B.M. Yellow Eu[N(SiMe₃)₂]₂(dme)₂ is soluble in hydrocarbons and ethers. **Anal. Caled. for C₂₀H₅₆N₂O₄Si₄Eu: C, 36.8; H, 8.64; N, 4.29. Found: C, 35.7; H, 8.40; N, 4.28. IR data: 1303 m, 1245 s br, 1212 w, 1188 m, 1120 w sh, 1102 s, 1063 s, 1020 vs br, 988 w sh, 977 w, 929 w, 873 s br, 852 w sh, 822 vs br, 758 w sh, 745 m br, 692 w, 654 s, 603 m, 584 m, 562 w, 453 w br, 363 m cm⁻¹.**

**Bis[bis(trimethylsilyl)amido](bipyridine)europium(II),**

**Eu[N(SiMe₃)₂]₂(bipy)**

2,2'-Bipyridine (0.064 g, 0.41 mmol) in benzene (30 mL) was added to Eu[N(SiMe₃)₂]₂(thf)₂ (0.25 g, 0.41 mmol) in benzene (20 mL). The dark brown solution was stirred for 1 h, and the solvent removed under vacuum. The residue was extracted with toluene (10 mL), the toluene extract filtered, and the volume decreased to ca. 5 mL. Yellow
needles were obtained upon cooling (0°C) in a yield of 0.16 g (62 percent), m.p. = 85-87°C (decomp). The Eu[N(SiMe₃)₂]₂(bipy) is soluble in toluene, benzene and ethers. It is only slightly soluble in saturated hydrocarbons. Anal. Calcd. for C₂₂H₄₄N₄Si₄Eu: C, 42.0; H, 7.05; N, 8.91. Found: C, 42.0; H, 6.66; N, 8.85. IR data: 1600 m, 1594 m, 1580 w, 1575 w, 1568 w, 1558 w, 1490 w, 1438 m, 1324 m, 1240 vs br, 1170 m, 1152 m, 1098 w, 1088 w, 1049 w, 1029 w, 1014 m, 1006 w, 965 vs br, 881 s, 866 m, 830 vs br, 775 w, 756 s, 738 m, 693 w, 666 m br, 643 m, 625 w, 602 m br, 428 m br, 415 w sh, 377 m cm⁻¹. Sodium Tris[bis(trimethylsilyl)amido]europate(II), NaEu[N(SiMe₃)₂]₃

Europium diiodide (5.41 g, 0.0133 mol) and sodium bis(trimethylsilyl)amide (4.89 g, 0.0267 mol) were stirred together for 14 h in diethyl ether (100 mL). The diethyl ether was removed under reduced pressure, and the residue extracted with toluene (60 mL). The yellow toluene solution was filtered, the volume was reduced to ca. 15 mL under vacuum and cooled (-10°C) to give large yellow prisms (m.p. = 132-134°C) in an overall yield of 41 percent (3.58 g). The compound was dissolved in benzene and hydrolyzed with D₂O. Only the resonance due to UN(SiMe₃)₂ was observed in the ¹H NMR spectrum of the benzene extract. A qualitative test for sodium (with uranyl zinc acetate reagent) was positive. Anal. Calcd. for C₁₈H₅₄N₃Si₆NaEu: C, 32.9; H, 8.30; N, 6.40. Found: C, 30.8; H, 8.11; N, 5.45. IR data: 1240 s, 1206 w, 1069 s, 982 s, 858 s, 811 vs br, 753 m, 739 w sh, 720 w sh, 652 s, 602 w, 577 m, 389 m, 359 m cm⁻¹.
When extraction and crystallization were carried out with pentane or diethyl ether rather than toluene, a compound having different physical properties was obtained. The yellow needles (m.p. = 152-153°C) that crystallized from pentane (-10°C) or diethyl ether (-70°C) also contained sodium (by a qualitative test with uranyl zinc acetate reagent) and did not contain solvent of crystallization (by examination of hydrolysis products in benzene by $^1$H NMR). The mass spectrum of this compound contained a peak due to the Eu[N(SiMe$_3$)$_2$]$_2$ species at m/e = 473, as well as groups of higher mass peaks centered at 504, 515, 536, 552, 603, 618, 625, 697 and 712. The compound crystallizes in space group $P\bar{1}$, with $Z = 4$ and a unit cell volume of 3454 Å$^3$ [9]. This volume is roughly one-half the unit cell volume observed for the product crystallized from toluene, 6996 Å$^3$ (space group $P2_1/n$, $Z = 8$) [9]. These data suggest that the compound crystallized from pentane or diethyl ether can also be formulated as NaEu[N(SiMe$_3$)$_2$]$_3$, and that this compound simply crystallizes in a different form from pentane and diethyl ether. Anal. C, 29.0; H, 7.26; N, 5.50 IR data: 1242 m sh, 1232 s, 1006 s, 868 m, 850 w, 817 s, 756 m, 718 m, 653 m, 602 w, 587 m, 551 w, 390 m, 364 m cm$^{-1}$.

Bis[bis(trimethylsilyl)amido]europium(II)-1,2-dimethylphosphinoethane complex, Eu[N(SiMe$_3$)$_2$]$_2$(dmpe)$_{1.5}$

To NaEu[N(SiMe$_3$)$_2$]$_3$ (0.49 g, 0.75 mmol) in pentane (20 mL) was added 1,2-dimethylphosphinoethane (0.32 g, 2.1 mmol), and the resulting orange solution was stirred for 6 h. The solution was filtered, concentrated to ca. 10 mL and cooled (-10°C) to yield large orange prisms in an overall yield of 67 percent (0.35 g). When heated
in a sealed capillary, the compound partially melted at 78-80°C and the
remaining solid melted at 94-96°C. The compound was hydrolyzed in
benzene with D2O. The \(^1H\) NMR spectrum of the benzene extract con-
tained resonances due to DN(SiMe\(_3\)\(_2\)) and dmp [10]. The mass
spectrum contained an envelope of peaks centered at m/e 623 due to
Eu[Na(SiMe\(_3\)\(_2\))]\(_2\).Anal. Calcd. for C\(_{21}\)H\(_{60}\)N\(_2\)P\(_3\)Si\(_4\)Eu:
C, 36.1; H, 8.67; N, 4.01; P, 13.3. Found: C, 35.4; H, 8.34; N, 3.80;
P, 13.0. IR data: 1424 m, 1300 w, 1282 w, 1243 s, 1173 w, 1147 w,
1094 w, 1046 s, 986 w, 938 m, 925 w sh, 864 s, 822 s, 751 m, 740 w sh,
718 w, 652 m, 570 m, 578 m, 356 s, 238 w cm\(^{-1}\).

Bis[bis(trimethylsilyl)amido]bis[tri(n-butyl)phosphine]europium(II)

Eu[Na(SiMe\(_3\)\(_2\))]\(_2\)[PBU\(_3\)]\(_2\)

Tri(n-butyl)phosphine (1.6 mL, 6.4 mmol) was added to
NaEu[Na(SiMe\(_3\)\(_2\))]\(_3\) (1.00 g, 1.52 mmol) dissolved in pentane (50
mL). After stirring for 12 h, the pentane solution was filtered,
concentrated to ca. 10 mL under reduced pressure and cooled (-70°C).
The orange crystals (m.p. = 48-49°C) were isolated and dried in vacuo.
Yield was 48 percent (0.64 g). The hydrolysate of this compound in
benzene consisted of tri(n-butyl)phosphine and HN(SiMe\(_3\)\(_2\)) in a 1:1
molar ratio (by \(^1H\) NMR). The \(^31P\{^1H\} NMR spectrum of the above
solution contained a single resonance at \(s -29.7\) due to free tri-
(n-butyl)phosphine [11]. The mass spectrum contained groups of peaks
centered at m/e 783, 873 and 944. The Eu[Na(SiMe\(_3\)\(_2\))]\(_2\)[PBU\(_3\)]\(_2\)
requires 877. The effective magnetic moment, determined by Evans'
method (30°C, benzene) was 7.4 B.M. Anal. Calcd. for
C\(_{36}\)H\(_{90}\)N\(_2\)P\(_2\)Si\(_4\)Eu: C, 49.3; H, 10.3; N, 3.19; P, 7.06. Found:
C, 49.0; H, 10.2; N, 2.79; P, 6.82. When heated to 100°C under vacuum,
tri(n-butyl)phosphine is slowly evolved from the compound. IR data: 1413 w, 1339 w, 1241 s, 1043 s, 978 s, 861 s, 817 s, 749 s, 653 m, 598 m, 577 w, 380 w sh, 361 m cm⁻¹.

**Bis[bis(trimethylsilyl)amido]ytterbium(II)-tetrahydrofuran complex,**

\[
\text{Yb}[\text{N(SiMe}_3\text{)}_2]_2(\text{thf})_{2.5}
\]

Sodium bis(trimethylsilyl)amide (2.30 g, 13.0 mmol) and ytterbium diiodide (2.78 g, 6.51 mmol) were stirred together in tetrahydrofuran (75 mL) for 12 h. After removal of solvent, the orange residue was extracted with pentane (50 mL). The pentane solution was filtered, concentrated (to ca. 15 mL) and cooled to -10°C. The orange prisms (m.p. = 173-174°C) were collected and dried in vacuum in an overall yield of 68 percent (3.0 g). This compound can also be prepared by the addition of tetrahydrofuran to Yb[N(SiMe₃)₂]₂(OEt₂)₂ in pentane, followed by crystallization from pentane. \(^1\text{H NMR (26°C, d}_6\text{-PhH):} \delta 0.49 (s, 36H, N(SiMe₃)₂), 1.40 (m, 10H, α-protons of thf) and 3.68 (m, 10H, α-protons of thf). \(^{13}\text{C}^1\text{H) NMR (-30°C, d}_8\text{-PhMe):} \delta 5.47, N(SiMe₃)₂; 25.0, α-carbons of thf and 69.6, α-carbons of thf. The highest mass peak observed in the mass spectrum was at 494, corresponding to Yb[N(SiMe₃)₂]₂. **Anal. Calc'd. for** C\(_{22}\)H\(_{56}\)N\(_2\)O\(_{2.5}\)Si\(_4\)Yb: C, 39.2; H, 8.37; N, 4.16. Found: C, 35.3; H, 8.02; N, 3.57. IR data: 1250 s, 1182 w, 1079 m, 1047 s, 972 s, 866 s, 832 s, 776 m, 756 m, 664 s, 609 m, 590 m, 369 s cm⁻¹.

**Bis[bis(trimethylsilyl)amido]bis(1,2-dimethoxyethane)ytterbium(II),**

\[
\text{Yb}[\text{N(SiMe}_3\text{)}_2]_2(\text{dime})_2
\]

Ytterbium diiodide (3.92 g, 9.18 mmol), sodium bis(trimethylsilyl)amide (3.37 g, 18.4 mmol) and 1,2-dimethoxyethane (75 mL) were added
to a flask, and the mixture was stirred for 10 h, resulting in a blue
solution. Removal of solvent under vacuum gave a blue residue, which
was extracted with toluene (40 mL). Concentration of the filtrate (to
c.a. 10 mL) and cooling (-10°C) led to crystallization of blue prisms
(m.p. = 162-165°C) in an overall yield of 63 percent (3.9 g). The mass
spectrum contained a parent peak at m/e 674. Anal. Calcd. for
C_{20}H_{56}N_{2}O_{4}Si_{4}Yb: C, 35.6; H, 8.37; N, 4.16. Found: C,
34.5; H, 8.07; N, 4.11. IR data: 1248 s, 1194 w, 1127 m, 1086 s,
1062 w sh, 968 s, 864 m, 832 s, 776 m, 757 m, 662 s, 601 m, 587 w, 387
m sh, 372 m cm⁻¹.

Bis[bis(trimethylsilyl)amido](1,2-dimethoxyethane)ytterbium(II),
Yb[N(SiMe₃)₂]₂(dme)

Blue Yb[N(SiMe₃)₂]₂(dme)₂ (1.78 g, 2.64 mmol) was dissolved
in pentane (40 mL) giving a red solution. Concentration to ca. 10 mL
and cooling (-10°C) led to crystallization of red prisms (m.p. = 118-
120°C) in quantitative yield. ¹H NMR (30°C, d₆-PhH): δ 0.42 (s,
36H, N(SiMe₃)₂), 2.93 (s, 6H, OCH₃) and 3.26 (m, 4H, MeOCH₂).
The mass spectrum contained a parent peak at m/e 584. Anal. Calcd. for
C_{16}H_{46}N_{2}O_{2}Si_{4}Yb: C, 32.9; H, 7.94; N, 4.80. Found: C,
33.1; H, 7.95; N, 4.60. IR data: 1249 s, 1238 w sh, 1112 w sh, 1092
w sh, 1054 s, 1024 w sh, 962 s, 887 w sh, 862 m, 828 s, 749 m, 602 m,
604 w, 589 w, 373 w sh, 363 m cm⁻¹.

Bis[bis(trimethylsilyl)amido](1,2-dimethoxyethane)iodoytterbium(III),
Yb[N(SiMe₃)₂]₂I(dme)

A solution of blue Yb[N(SiMe₃)₂]₂(dme)₂ (0.74 g, 1.10 mmol)
in toluene (40 mL) was added to solid silver iodide (0.26 g, 1.1 mmol)
with stirring. The resulting yellow solution, with a very dark suspended solid, was stirred for 5 h. After removal of toluene under reduced pressure, diethyl ether (ca. 50 mL) was used to extract the product from the residue and for crystallization of the product (-10°C, ca. 8 mL). The yellow needles (m.p. = 153-155°C) were obtained in 49 percent yield. A qualitative test for iodide (with silver nitrate solution) was positive. Anal. Calcd. for C_{16}H_{46}N_{2}O_{2}Si_{4}IYb:
C, 27.0; H, 6.52; N, 3.94. Found: C, 26.7; H, 6.54; N, 3.93. IR data:
1302 w, 1261 w sn, 1200 m, 1203 w sh, 1192 w, 1079 m, 1031 s, 989 w sh, 970 w sh, 953 m, 933 s, 889 w sh, 856 m, 832 s, 780 w, 759 w, 669 m, 620 m, 402 w, 383 m cm⁻¹.

Bis[bis(trimethylsilyl)amido]bis(diethyl ether)ytterbium(II),
Yb[N(SiMe₃)₂]₂(OEt₂)₂

Diethyl ether (125 mL), cooled to 0°C, was added to a flask containing ytterbium diiodide (4.76 g, 11.2 mmol) and sodium bis(trimethylsilyl)amide (4.09 g, 22.3 mmol). The blue reaction mixture was stirred at 0°C for 1 h. Upon warming to room temperature, the solution color changed to red. After 10 h of additional stirring, the solution was filtered, concentrated (to ca. 20 mL) and cooled (-70°C). The yellow prisms that were isolated gradually turned orange upon warming to ambient temperature. The orange crystals (m.p. 69-71°C) were isolated in 56 percent (4.0 g) yield. The compound gives a red solution in aromatic or aliphatic hydrocarbons. \(^1\)H NMR (26°C, d₆-PhH):
\(\delta\) 0.41 (s, 36 H, N(SiMe₃)₂), 1.06 (t, 12H, OCH₂CH₃) and 3.51 (q, 8H, OCH₂CH₃). \(^{13}\)C{\(^1\)H} NMR (26°C, d₆-PhH): \(\delta\) 5.57 (N(SiMe₃)₂), 14.1 (OCH₂CH₃) and 65.2 (OCH₂CH₃). Mass
spectrum: m/e 639 (Yb[N(SiMe$_3$)$_2$)$_2$(OEt$_2$)$_2$ - 3), 567
(Yb[N(SiMe$_3$)$_2$)$_2$(OEt$_2$) - 1) and 493 (Yb[N(SiMe$_3$)$_2$]$_2$ - 1).
IR data: 1249 s, 1187 m, 1151 m, 1122 m, 1091 w, 1040 m br, 968 s,
862 m sh, 830 s br, 774 m, 753 w sh, 732 w sh, 663 w sh, 662 m, 609 m,
592 w, 503 w, 391 m, 372 m cm$^{-1}$. Anal. Calcd. for
C$_{20}$H$_{56}$N$_2$O$_2$Si$_4$Yb: C, 37.4; H, 8.79; N, 4.36. Found: C,
33.3; H, 8.06; N, 4.18.

The complex was freed of diethyl ether by stirring it (0.56 g,
0.87 mmol) in toluene (30 mL) at 80°C for 5 h, then removing the solvent
under reduced pressure at 80°C. The resulting red compound (0.14 g)
was crystallized from pentane (6 mL, -10°C). $^1$H NMR (26°C,
d$_6$-PhMe): δ 0.32, s, N(SiMe$_3$)$_2$. $^{13}$C($^1$H) NMR (26°C,
d$_6$-PhMe): δ 6.45, s, N(SiMe$_3$)$_2$. IR data: 1252 s, 1022 s, 927 s,
876 s, 818 s, 763 s, 659 s, 604 w sh, 594 m, 412 m, 391 w sh, 374 m,
363 w sh, 284 w, 244 w cm$^{-1}$.

**Sodium Tris[bis(trimethylsilyl)amido]ytterbate(II), NaYb[N(SiMe$_3$)$_2$]$_3$**

Sodium bis(trimethylsilyl)amide (3.76 g, 0.0205 mol) and ytterbium
diodide (4.38 g, 0.0103 mol) were stirred together in diethyl ether
(100 mL) at 0°C for 1 h. The mixture was then warmed to room tempera-
ture and stirred for an additional 10 h. After removal of the diethyl ether,
the residue was extracted with toluene (60 mL) to give a red
solution. This solution was evaporated to dryness under vacuum, and
the red residue dissolved in pentane (40 mL). The red pentane solution
was filtered, concentrated to ca. 15 mL and cooled (-10°C). The red
needles (m.p. = 154-157°C) were isolated in 46 percent yield (3.20 g).
$^1$H NMR (26°C, d$_6$-PhH): δ 0.24, s, N(SiMe$_3$)$_2$. $^{13}$C($^1$H) NMR
(26°C, d₆-PhH): δ 6.38, s, N(SiMe₃)₂. Upon lowering the temperature to -80°C, the silylamide resonance in the ¹³C{¹H} NMR spectrum (d₈-PhMe) gradually decreased in intensity as a broad resonance (δ 7.01, ν₁/₂ = ca. 120 Hz) increased in intensity. A qualitative test for sodium (with uranyl zinc acetate reagent) was positive. Anal. Calcd. for C₁₈H₅₄N₆Si₆NaYb: C, 31.9; H, 8.04; N, 6.20. Found: C, 28.9; H, 7.29; N, 5.36. IR data: 1241 s, 1203 w, 1046 s, 964 s, 857 s, 818 s, 752 s, 653 m, 602 w, 579 w, 392 m, 357 m cm⁻¹.

Bis(1,2-dimethylphosphinomethane)bis(trimethylsilyl)ytterbium(II), 

Yb[N(SiMe₃)₂]₂(dpm)₂

The addition of 1,2-dimethylphosphinomethane (0.14 mL, 0.83 mmol) to a pentane solution (20 mL) of Yb[N(SiMe₃)₂]₂(0Et₂)₂ (0.53 g, 0.83 mmol) resulted in a deep red colored solution. The solution was stirred for 3 h, filtered and concentrated to ca. 6 mL. Cooling to -10°C resulted in crystallization of thin, dark red plates (m.p. = 60-61°C). The compound dissolves in diethyl ether to give a solution that has the orange-yellow color characteristic of Yb[N(SiMe₃)₂]₂

(0Et₂)₂. ¹H NMR (26°C, d₈-PhMe): δ 0.35 (s, 36H, N(SiMe₃)₂); 0.87 (s, 24H, PMe₂) and 1.14 (t, JₚH = 3Hz, 4H, PCH₂P). ¹³C{¹H} NMR (26°C, d₈-PhMe): δ 5.91 (s, N(SiMe₃)₂); 14.9 (s, PMe₂) and 31.6 (s, PCH₂P). ³¹P{¹H} NMR (-40°C to +25°C, d₈-PhMe): δ -44.7.

The mass spectrum did not contain a parent ion (m/e = 766), but peaks at 825, 756 and 639 were observed, as well as the Yb[N(SiMe₃)₂]₂⁻¹ peak (493). Anal. Calcd. for C₂₂H₆₄N₂P₂Si₄Yb: C, 34.5; H, 8.42; N, 3.66; P, 16.2. Found: C, 33.9; H, 8.25; N, 3.38; P, 15.8.
IR data: 1423 m, 1414 m, 1291 m, 1278 w, 1238 s, 1030 s, 968 s, 932 s, 860 s, 822 s, 748 s, 723 w sh, 710 w, 654 s, 600 m, 584 m, 387 w sh, 361 s cm⁻¹.

(1,2-Dimethylphosphinoethane)bis[bis(trimethylsilyl)amido]ytterbium(II), Yb[N(SiMe₃)₂]₂(dmpe)

To orange Yb[N(SiMe₃)₂]₂(0Et₂)₂ (0.57 g, 0.89 mmol) in pentane (30 mL) was added 1,2-dimethylphosphinoethane (0.3 mL, ca. 2 mmol). The color of the solution turned purple. After stirring for 2 h, the solution was filtered, concentrated to ca. 13 mL and cooled (-10° C). Purple prisms (m.p. = 195-197° C) were isolated in 70 percent yield (0.4 g). The color of Yb[N(SiMe₃)₂]₂(dmpe) is discharged by dissolution in diethyl ether to give the yellow-orange color of Yb[N(SiMe₃)₂]₂(0Et₂)₂. ¹H NMR (26°C, d₆-PhH): δ 0.46 (s, 36H, N(SiMe₃)₂), 0.86 (s, 12H, PCH₂₂P) and 1.04 (t, 4H, PCH₂CH₂P).

¹³C(¹H) NMR (26°C, d₆-PhH): δ 5.75, N(SiMe₃)₂; 11.6, PMe₂ and 25.8, t (JPC = 8 Hz), PCH₂CH₂P. ³¹P (¹H) NMR (26°C, d₆-PhH): δ -40.9, s. The mass spectrum gave a molecular ion for Yb[N(SiMe₃)₂]₂(dmpe), m/e = 644. Anal. Calcd. for C₁₈H₅₂N₂P₂Si₄Yb: C, 33.6; H, 8.14; N, 4.35; P, 9.62. Found: C, 31.6; H, 7.98; N, 3.81; P, 9.02. IR data: 1423 m, 1300 w, 1283 w, 1243 s, 1245 w, 1052 s, 962 s, 940 s sh, 862 s, 821 s, 748 s, 722 w sh, 692 w, 656 s, 600 m, 579 m, 455 w, 369 s, 352 s cm⁻¹.

Bis[bis(trimethylsilyl)amido]bis[tri(n-butyl)phosphine]ytterbium(II), Yb[N(SiMe₃)₂]₂(PBu₃)₂

Tri(n-butyl)phosphine (0.34 mL, 1.4 mmol) was added to a pentane solution (20 mL) of Yb[N(SiMe₃)₂]₂(0Et₂)₂ (0.43 g, 0.67 mmol). After 14 h of stirring, the solution was filtered,
concentrated to ca. 10 mL under reduced pressure and cooled (-70°C). Brown-red prisms (m.p. = 46-48°C) crystallized in 70 percent yield (0.42 g). In the mass spectrum, groups of peaks centered at m/e 493 (Yb[N(SiMe₃)₂]₂ - 1), 505, 517, 531, 543, 567, 581, 593, 605, 617, 639, 655, 693 and 705 were observed. _¹H NMR (26°C, d₆-PhH): δ 0.48 (s, 36H, N(SiMe₃)₂), 1.00 (t, 18H, P(CH₂)₃CH₃) and 1.49 (s, 36H, P(CH₂)₃CH₃). _¹³C{¹H} NMR (26°C, d₆-PhH): δ 6.27 (s, N(SiMe₃)₂), 14.0 (s, P(CH₂)₃CH₃), 24.9 (d, J_PC = 10 Hz, -CH₂-), 26.9 (d, J_PC = 10 Hz, -CH₂-) and 28.3 (d, J_PC = 11 Hz, -CH₂-). _³¹P{¹H} NMR (26°C, d₆-PhH): δ 29.6. _Anal._ Calcd. for C₃₆H₉₀N₂P₂Si₄Yb: C, 48.1; H, 10.1; N, 3.12; P, 6.89. Found: C, 48.8; H, 10.0; N, 2.87; P, 7.47. IR data: 1413 w, 1244 s, 1089 w, 1031 m, 964 s, 862 m, 824 s, 769 w, 749 w, 656 w, 602 w, 586 w, 386 w, 367 m cm⁻¹.

_Bis[bis(trimethylsilyl)amido][1,2-diphenylphosphinoethane]ytterbium(II), Yb[N(SiMe₃)₂]₂(disphos)_

A solution of NaYb[N(SiMe₃)₂]₃ (0.81 g, 1.20 mmol) in pentane (50 ML) was added to 1,2-diphenylphosphinoethane (0.48 g, 1.20 mmol), and the solution was stirred for 12 h. The product separated from solution as a red solid. The pentane was filtered off, and the red solid washed with pentane (2 x 40 mL). The compound is sparingly soluble in toluene, from which it was crystallized (0.11 g from 15 mL at -10°C, after extraction with 60 mL). When heated in a sealed capillary, the compound gradually moistens above ca. 140°C and melts at 206-209°C. _Anal._ Calcd. for C₃₈H₆₀N₂P₂Si₄Yb: C, 51.2; H, 6.78; N, 3.14; P, 6.94. Found: C, 51.3; H, 6.50; N, 2.79; P, 6.64.
IR data: 1583 w, 1570 w, 1433 w, 1246 w sh, 1233 s, 1174 m, 1154 w, 1098 w, 1052 s, 1023 w sh, 997 w, 929 m, 882 m, 869 m, 822 s, 749 m sh, 741 m, 726 w, 691 s, 661 m, 590 m, 551 w, 510 m, 502 w sh, 480 w, 448 w, 379 w sh, 363 m, 243 w cm\(^{-1}\).

Bis[bis(trimethylsilyl)amido]tris(t-butylnitrile)ytterbium(II), Yb[N(SiMe\(_3\)]\(_2\)]\(_2\)(NCCMe\(_3\)]\(_3\)

To Yb[N(SiMe\(_3\)]\(_2\)]\(_2\)(OEt\(_2\)]\(_2\) (0.55 g, 0.86 mmol) in toluene (10 mL) was added t-butylnitrile (0.40 mL, 3.6 mmol) in toluene (25 mL). The reaction mixture was stirred for 10 h, the toluene removed under vacuum, and the residue extracted with pentane (40 mL). The red pentane solution was concentrated to ca. 6 mL and cooled (-10°C) to afford dark red prisms (m.p. = 68-70°C) in 38 percent yield (0.24 g).

\(^1\)H NMR (26°C, d\(_6\)-PhH): \(\delta\) 0.63 (s, N(SiMe\(_3\)]\(_2\)) and 1.62 (s, \(\nu_{1/2} = 41\) Hz, NCCMe\(_3\]). \(^{13}\)C{\(^1\)H} NMR (26°C, d\(_6\)-PhH): \(\delta\) 5.89, N(SiMe\(_3\)]\(_2\)) and 28.3, NCCMe\(_3\). No other resonances were observed.

Anal. Calcd. for C\(_{27}\)H\(_{63}\)N\(_5\)Si\(_4\)Yb: C, 43.6; H, 8.54; N, 9.42.

Found: C, 42.5; H, 8.33; N, 9.13. IR data: 2254 m, 1242 s, 1207 w, 1041 s, 940 w, 884 w sh, 873 m, 817 s, 763 m, 742 m, 689 m, 652 s, 593 m, 360 m cm\(^{-1}\).

Reaction of methyl lithium with Yb[N(SiMe\(_3\)]\(_2\)]\(_2\)I(dme)

Methyl lithium (1.3 mL of a 0.6 M solution in diethyl ether, 0.78 mmol) was added to Yb[N(SiMe\(_3\)]\(_2\)]\(_2\)I(dme) in diethyl ether at 0°C. The solution was stirred for 6 h, the solvent removed and the residue extracted with pentane (40 mL). The Li(OEt\(_2\)]N(SiMe\(_3\)]\(_2\)), identified by m.p. and IR, was crystallized from the pentane solution (ca. 8 mL, -10°C).
Reaction of phenylacetylene with Yb[N(SiMe$_3$)$_2$]$_2$(OEt)$_2$

Phenylacetylene (0.16 mL, 1.5 mmol) in toluene (10 mL) was added to Yb[N(SiMe$_3$)$_2$]$_2$(OEt)$_2$ (0.48 g, 0.75 mmol) in toluene (20 mL) at 0°C. After stirring for 1 h, a dark purple solid had separated from solution. This solid was isolated by filtration, and crystallized from tetrahydrofuran (8 mL, -70°C). The compound was identified as Yb(C = CPh)$_2$ by its infrared spectrum and analyses (C, 51.6; H, 2.83; C$_{16}$H$_{10}$Yb requires C, 51.2; H, 2.69) [12].

Experimental Procedures for Chapter 4

Bis(diethyl ether)sodium pentamethylcyclopentadienyldichlorononoydate(III), [Na(OEt)$_2$][(C$_5$Me$_5$)NdCl$_3$]

Sodium pentamethylcyclopentadienide (3.38 g, 0.0214 mol) in tetrahydrofuran (50 mL) was added to a stirred suspension of NdCl$_3$ (5.36 g, 0.0214 mol) in tetrahydrofuran (75 mL). The resulting solution was refluxed for 12 h. The blue-green solution was evacuated to dryness, and the residue extracted with diethyl ether (2 x 100 mL). The combined diethyl ether extracts were concentrated to ca. 80 mL and cooled to -10°C, yielding light blue prisms. Overall yield: 7.40 g (62 percent). When heated in a sealed capillary, the compound turned pink (decomp.) at ca. 125°C. Anal. Calcd. for C$_{18}$H$_{35}$O$_2$Cl$_3$Nd: C, 38.8; H, 6.33. Found: C, 38.6; H, 5.69. IR data: 2720 w, 1296 W br, 1181 w, 1150 w, 1090 s, 1063 s, 1018 w sh, 1007 m, 968 w, 911 m, 862 m, 833 w sh, 799 w, 791 w, 721 m, 588 w, 392 m cm$^{-1}$.

Bis(diethyl ether)lithium bis(pentamethylcyclopentadienyl)dichloroytterbate(III), [Li(OEt)$_2$][(C$_5$Me$_5$)$_2$YbCl$_2$]

A flask was charged with YbCl$_3$ (2.62 g, 9.38 mmol) and LiC$_5$Me$_5$ (2.67 g, 18.8 mmol). Tetrahydrofuran (75 mL) was added, and the violet
mixture was refluxed for 6 h. The tetrahydrofuran was removed under vacuum, and the residue extracted with diethyl ether (2 x 60 mL). The combined extracts were concentrated to ca. 30 mL and cooled to -10°C to give violet needles in 72 percent (4.50 g) yield. When heated in a sealed capillary, the compound decomposed (turned grey) at 128-130°C. Anal. Calcd. for C₂₈H₅₀O₂Cl₂LiYb: C 50.2; H, 7.53; Cl, 10.59. Found: C, 50.5; H, 7.59; Cl, 9.38. IR data: 2723 w, 1300 m, 1262 w, 1183 m, 1153 w, 1120 w sh, 1090 s, 1061 s, 1021 s, 911 m, 836 m, 791 m, 722 w, 592 w, 502 m, 382 vs br, 305 vs br cm⁻¹. 

(N,N,N',N'-Tetramethylethylenediamine)lithium bis(pentamethylcyclopentadienyl)dichloro ytterbiate(III), [Li(tmed)][(C₅Me₅)₂YbCl₂]. 

N,N,N',N'-Tetramethylethylenediamine (0.3 mL, ca. 2 mmol) was added to [Li(UEt₂)₂][(C₅Me₅)₂YbCl₂] (0.60 g, 0.90 mmol) in 40 mL of diethyl ether. The violet solution was stirred for 5h and the volatile material removed under vacuum to yield a pink residue. The residue was dissolved in 30 mL of diethyl ether and the volume reduced to ca. 20 mL under reduced pressure. Cooling (-10°C) resulted in crystallization of violet needles in 53 percent (0.30 g) yield. The compound turned grey (decomposed) at 254-256°C when heated in a sealed capillary. Anal. Calcd. for C₂₆H₄₆N₂Cl₂LiYb: C, 49.0; H, 7.27; N, 4.39. Found: C, 50.0; H, 7.43; N, 4.50. IR data: 2723 w, 1410 m, 1360 m, 1290 s, 1248 m, 1186 m, 1161 s, 1131 s, 1099 w, 1070 s, 1033 s, 1016 s, 947 s, 792 s, 773 m, 722 w, 631 w, 618 w, 594 m, 472 s br, 445 s, 417 m, 389 s, 357 m, 308 vs br, 240 s cm⁻¹.
Bis(diethyl ether)lithium bis(pentamethylocyclopentadienyl)dichloro-
neodymate(III), \([\text{Li(0Et}_2\text{)}_2][\text{(C}_5\text{Me}_5\text{)}_2\text{NdCl}_2]\]

Tetrahydrofuran (100 mL) was added to a flask containing NdCl₃
(3.55 g, 0.0142 mol) and LiC₅Me₅ (4.03 g, 0.0283 mol) and the dark
blue solution was refluxed for 12 h. After removal of solvent under
vacuum, the residue was extracted with diethyl ether (2 x 100 mL). The
combined red extracts were concentrated to ca. 100 mL and cooled
(-10°C), resulting in isolation of large blue prisms in 66 percent
yield (6.0 g). Heating in a sealed capillary results in decomposition
(to a white substance) at 114-116°C. Anal. Calcd. for
C₂₈H₅₀O₂Cl₂LiNd: C, 52.5; H, 7.87. Found: C, 52.2; H, 7.78.
IR data: 2728 w, 2184 w, 1949 w, 1299 m, 1128 s, 1154 m, 1089 s br,
1059 s br, 1018 s br, 909 m, 834 m, 790 s, 722 w, 632 w, 619 w, 592 w,
552 w, 503 m, 384 vs br, 304 vs br cm⁻¹.

Bis(N,N,N,N'-tetramethylethylenediamine)lithium bis(pentamethylocyclo-
pentadienyl)dichloro-neodymate(III), \([\text{Li(tmed)}_2][\text{(C}_5\text{Me}_5\text{)}_2\text{NdCl}_2]\]

N,N,N',N'-Tetramethylethylenediamine (0.3 mL, 2 mmol) was added to
\([\text{Li(0Et}_2\text{)}_2][\text{(C}_5\text{Me}_5\text{)}_2\text{NdCl}_2]\) (0.58 g, 0.91 mmol) in 30 mL of
diethyl ether. The solution was stirred for 3 h, the volatile material
removed under vacuum, and the residue extracted with diethyl ether
(30 mL). This solution was concentrated to ca. 20 mL and cooled
(-10°C) to yield small, light blue needles in 58 percent yield
(0.38 g). When heated in a sealed capillary, the compound did not
undergo an observable change below 300°C. Anal. Calcd. for
C₃₂H₆₂N₂Cl₂LiNd: C, 53.0; H, 8.62; N, 7.73. Found: C, 53.3;
H, 8.47; N, 7.69. IR data: 2720 w, 1369 m, 1290 s, 1249 m, 1188 m,
1163 s, 1131 s, 1100 m, 1070 m, 1034 s, 1017 s, 948 s, 789 s, 776 w, 
722 w, 593 m, 496 m br, 446 m, 378 m sh, 342 m, 300 s br, 229 s br 
cm\(^{-1}\).

\((N,N,N',N'-\text{Tetramethylethylene diamine})\text{lithium bis(pentamethylcyclo-}
\text{pentadienyl)dichlorosamarate(III), \([\text{Li(tmed)}][(C_5\text{Me}_5)_2\text{SmCl}_2]\]

Lithium pentamethylcyclopentadienide (2.1 g, 15 mmol) was added to 
\text{SmCl}_3 (1.94 g, 7.6 mmol) and tetrahydrofuran (60 mL) was added.
After refluxing for 8 h, the suspension was evaporated to dryness. The 
residue was extracted with toluene (50 mL) and evaporated to dryness. 
Tetrahydrofuran (10 mL) and \(N,N,N',N'-\text{tetramethylethylene diamine}\) (1.5 
\text{mL}, ca. 10 mmol) were added to the residue. After stirring the orange 
solution for 2 h, the volatile material was removed under vacuum. The 
residue was washed with pentane (20 mL), then crystallized from tetra-
hydrofuran (10 mL, -10°C) as yellow prisms in 33 percent yield (1.5 g). 
When heated in a sealed capillary, the compound turned orange at 201-
203°C and dark red at 287-289°C. \text{Anal. Calcd. for }C_{26}H_{46}N_2Cl_2LiSm: 
C, 50.8; H, 7.54; N, 4.56. \text{Found: C, 50.5; H, 7.71; N, 4.40. IR data:} 
2721 w, 1358 w, 1293 s, 1263 w sh, 1250 m, 1186 m, 1161 m, 1130 m, 
1099 w, 1067 m, 1033 s, 1014 w sh, 947 s, 913 w, 892 w, 792 s, 773 w, 
722 w, 592 w, 471 m br, 443 m, 416 w, 384 w, 309 vs, 236 s cm\(^{-1}\).

\text{Bis(diethyl ether)sodium bis(pentamethylcyclopentadienyl)dichloro-
ytterate(III), \([\text{Na(OEt}_2]_2][(C_5\text{Me}_5)_2\text{YbCl}_2]\]

To a stirred suspension of \(\text{YbCl}_3\) (3.33 g, 0.0119 mol) in 
tetrahydrofuran (25 mL) was added \(\text{NaC}_5\text{Me}_5\) (3.77 g, 0.0238 mol) in 
tetrahydrofuran (75 mL). The solution was stirred for 15 h, the 
solvent removed under vacuum and the purple residue extracted with
diethyl ether (2 x 100 mL). The diethyl ether extracts were concentrated to ca. 100 mL and cooled to -10°C to yield large violet prisms. Subsequent crystallizations from the mother liquors resulted in isolation of Yb(C₅Me₅)₂Cl(thf), which could be separated by fractional crystallization. Overall yields: [Na(OEt₂)₂][C₅Me₅]₂YbCl₂, 2.70 g (33 percent); Yb(C₅Me₅)₂Cl(thf), 2.75 g (42 percent). When heated in a sealed capillary, [Na(OEt₂)₂][C₅Me₅]₂YbCl₂ decomposed (turned grey) at 278-280°C. A sample was dissolved in benzene and hydrolyzed with D₂O. Examination of the benzene extract (¹H NMR) showed only resonances due to diethyl ether and C₅Me₅D.

The magnetic moment (5-45k) was 3.91 B.M., with g = -3.7K and C = 1.90. Anal. Calcd. for C₁₂₄H₁₅₀O₂Cl₂NaYb: C, 49.1; H, 7.36; Cl, 10.35. Found: C, 49.0; H, 7.16; C, 9.00. IR data: 2723 ν, 1307 ν, 1290 ν, 1187 w sh, 1172 w sh, 1152 m, 1124 m, 1084 vs br, 1046 ν, 1024 m, 931 m, 845 m, 824 w, 804 ν, 723 w, 598 m, 444 w, 390 m br, 309 vs br cm⁻¹.

(N,N,N',N'-Tetramethylethylenediamine)sodium bis(pentamethylcyclopentadienyl)dichlorotert-bate(III), [Na(tmed)][C₅Me₅]₂YbCl₂

N,N,N',N'-Tetramethylethylenediamine (0.30 mL, ca. 2 mmol) was added to a solution of [Na(OEt)₂][C₅Me₅]₂YbCl₂ (0.83 g, 1.2 mmol) in 30 mL of diethyl ether. The reaction mixture was stirred for 1 h, and then evacuated to dryness. Extraction with diethyl ether (2 x 50 mL), concentration of the combined extracts to ca. 40 mL and cooling (-10°C) resulted in crystallization of violet prisms in 41 percent yield (0.32 g). When heated in a sealed capillary, the
compound gradually decomposed (turned grey) above ca. 120°C. Anal.
Calcd. for C_{26}H_{46}N_{2}Cl_{2}NaYb: C, 47.8; H, 7.09; N, 4.28. Found:
C, 46.3; H, 7.05; N, 3.10. A qualitative test for sodium (uranyl zinc
acetate reagent) was positive. Attempted sublimation of the compound
at 250°C and 10^{-4} mm Hg led to decomposition. IR data: 2719 w, 1289
s, 1248 m, 1176 m, 1152 m, 1129 w, 1070 s br, 1032 w sh, 1017 s br,
943 s, 927 w sh, 913 w sh, 837 m, 782 s, 720 w, 612 w, 590 m, 550 w,
451 w, 424 m, 378 s br, 305 s br cm^{-1}.
(Diethyl ether)sodium bis(pentamethylcyclopentadienyl)dichloroeneody-
mate(III), [Na(OEt)_{2}][(C_{5}Me_{5})_{2}NdCl_{2}]

Addition of NaC_{5}Me_{5} (4.56 g, 0.0288 mol) in tetrahydrofuran
(75 mL) to NdCl_{3} (3.61 g, 0.0144 mol) suspended in tetrahydrofuran
(25 mL) resulted in a green solution. The mixture was refluxed for
8 h, evacuated to dryness and the residue extracted with diethyl ether
(2 x 10 mL). The combined extracts were concentrated to ca. 150 mL
and cooled to -10°C, resulting in crystallization of light blue prisms,
m.p. >300°C. Overall yield: 4.03 g, 48 percent. Anal. Calcd. for
C_{24}H_{40}OCl_{2}NaNd: C, 49.7; H, 6.92. Found: C, 50.1; H, 6.66. IR
data: 2722 w, 2180 w, 1943 w, 1306 w, 1186 m, 1157 m, 1123 s, 1098 s,
1069 s, 1021 s, 913 w, 841 w, 802 w, 796 w sh, 722 w, 628 w, 618 w,
594 w, 379 m br, 312 vs br cm^{-1}.
Bis(pentamethylcyclopentadienyl)chlorotetrahydrofurannenoeodymium(III),
(C_{5}Me_{5})_{2}NdCl(thf)

Upon further concentration and cooling, the mother liquors from the
above reaction also yielded green (C_{5}Me_{5})_{2}NdCl(thf), m.p.
220-223°C, in an overall yield of 1.73 g (23 percent).  *Anal.* Calcd. for C_{24}H_{38}OClnNd: C, 55.2; H, 7.33.  Found: C, 55.4; H, 7.28.  IR data: 2721 w, 1948 w, 1343 w, 1298 w, 1262 w, 1179 m, 1151 w, 1122 s, 1076 w, 1019 vs, 953 w, 917 m, 863 vs, 845 w sh, 802 w, 723 w, 671 m, 628 w, 617 w, 593 m, 551 w, 382 w, 309 vs br, 243 m cm^{-1}.  The \(^1\)H NMR spectrum (36°C, d\(_6\)-PhH) consisted of a broad resonance (v\(_{1/2}\) = 75 Hz) at \(\delta\) 2.95 due to the C\(_5\)Me\(_5\) group.  The thf resonances were not observed.

The neutral species, \((\text{C}_{5}\text{Me}_{5})_2\text{NdCl(thf)}\), may also be prepared by extraction of the residue from reaction of NaC\(_5\)Me\(_5\) (2 molar equivalents) and NdCl\(_3\) in tetrahydrofuran with pentane in 20 percent yield.  The complex was identified by IR and m.p. (Diethyl ether)sodium bis(pentamethylcyclopentadienyl)dichlorosamarate(III), [Na(OEt\(_2\))][(\text{C}_{5}\text{Me}_{5})_2\text{SmCl}_2]

Sodium pentamethylcyclopentadienide (2.19 g, 13.8 mmol) in tetrahydrofuran (75 mL) was added to a SmCl\(_3\) (1.77 g, 6.9 mmol) suspension in tetrahydrofuran (25 mL).  The resulting brown solution was stirred for 24 h, and then evaporated to dryness in vacuum.  The residue was extracted with diethyl ether (2 x 75 mL) and the combined, orange extracts were concentrated to ca. 70 mL and cooled (-10°C).  The large, orange prisms, obtained in 36 percent yield (2.9 g), were collected and dried under vacuum.  When heated in a sealed capillary, there was no observable change in the compound up to 280°C.  The \(^1\)H NMR spectrum (d\(_6\)-PhH, 26°C) consisted of a singlet at \(\delta\) 7.27, a quartet centered at \(\delta\) 3.35 (J = 7 Hz), and a triplet centered at \(\delta\) 1.20 (J = 7 Hz) in
area ratio 30:4:6 due to $\text{Me}_5\text{C}_5$, MeCH$_2$O and MeCH$_2$O, respectively. The resonances are narrow, $\nu_{1/2}$ being ca. 1 Hz. Anal. Calcd. for C$_{24}$H$_{10}$OClsNaSm: C, 49.0; H, 6.85. Found: C, 48.5; H, 6.49. IR data: 3563 w, 2725 w, 2275 w, 1305 w, 1187 m, 1157 m, 1123 s, 1098 s, 1068 s, 1022 s, 912 w, 835 m, 803 w sh, 796 m, 723 w, 629 w, 618 w, 596 w, 553 w, 506 w, 381 m br, 312 vs br, 238 m cm$^{-1}$.

$(\text{N},\text{N},\text{N}',\text{N}''\text{-Tetramethylene diamine})\text{Sodium bis(pentamethylocyclopentadienyl)dichlorosamarate(III), [Na(tmed)][(C}_5\text{Me}_5)_2\text{SmCl}_2]$  

Addition of N,N,N',N''-tetramethylene diamine (0.3 mL, ca. 2 mmol) to a solution of [Na(ΟEt$_2$)][(C$_5$Me$_5$)$_2$SmCl$_2$] (0.80 g, 1.4 mmol) in diethyl ether (15 mL) resulted in precipitation of a yellow solid that crystallized from tetrahydrofuran as yellow needles. The yellow needles did not melt or undergo a noticeable change when heated in a sealed capillary to 280°C. Overall yield: 0.56 g (65 percent). Anal. Calcd. for C$_{26}$H$_{46}$N$_2$Cl$_2$NaSm: C, 49.5; H, 7.35; N, 4.44. Found: C, 49.7; H, 7.36; N, 3.20. IR data: 2724 w, 1297 s, 1256 m, 1181 m, 1160 m, 1137 m, 1099 w, 1078 m, 1040 m sh, 1023 s, 953 s, 918 w, 896 w, 838 w, 804 w sh, 788 s, 724 m, 592 m br, 456 w, 432 w, 383 m br, 310 s br cm$^{-1}$.

$\text{Bis(pentamethylocyclopentadienyl)chlorotetrahydrofuran ytterbium(III), (C}_5\text{Me}_5)_2\text{YbCl}(\text{tnf})$  

a. By crystallization from toluene. Sodium pentamethylocyclopentadienide (4.74 g, 0.030 mol) in tetrahydrofuran (75 mL) was added to a cooled (-70°C) suspension of YbCl$_3$ (4.19 g, 0.015 mol) in tetrahydrofuran (50 mL). The blue suspension turned to red as the
solution was allowed to warm to room temperature. The red suspension was stirred for 15 h. Tetrahydrofuran was removed under vacuum and the residue extracted with toluene (2 x 100 mL). The extracts were combined, concentrated to ca. 70 mL and cooled (-10°C). The violet needles, m.p. 221-223°C, were collected and dried in vacuum. Yield was 5.2 g (63 percent). The compound is soluble in hydrocarbons and ethers. Attempted sublimation at 120-125°C and 10⁻³ mm Hg led to decomposition of the compound. A sample was dissolved in benzene and hydrolyzed with water. Examination of the benzene extract (¹H NMR) showed only resonances due to tetrahydrofuran and C₅Me₅H. The mass spectrum contained groups of peaks centered about m/e = 479, 444, 343, and 309, corresponding to the fragments Yb(C₅Me₅)₂Cl⁺, Yb(C₅Me₅)₂⁺, Yb(C₅Me₅)Cl⁺ and Yb(C₅Me₅)⁺, respectively. The magnetic moment, determined at 28°C (in PhH) by the Evans method, was 4.2 B.M. Anal. Calcd. for C₂₄H₃₈ClOYb: C, 52.4; H, 6.96; Cl, 6.44. Found: C, 52.6; H, 7.05; Cl, 6.04. IR data: 2723 w, 1612 w, 1342 w, 1297 w, 1246 w, 1178 m, 1062 w, 1036 w sh, 1014 s, 954 w, 922 m, 913 w sh, 862 s, 841 w sh, 803 w, 728 m, 693 w, 677 m, 628 w, 595 m, 552 w, 382 m, 308 vs, 258 s cm⁻¹.

b. From [Na(OEt₂)₂][C₅Me₅)₂YbCl₂]. The anionic complex (0.65 g, 9.5 mmol) was suspended in toluene (60 mL) and tetrahydrofuran (0.5 mL) was added, yielding a purple solution that was stirred for 8 h. The volatile material was removed under vacuum and the residue was crystallized from toluene (ca. 10 mL, -10°C). The m.p. and IR spectrum were identical to those of an authentic specimen.
Bis(pentamethylcyclopentadienyl)chloropyridineytterbium(III),

\[(C_5Me_5)_2YbCl(py)\]

To \((C_5Me_5)_2YbCl(\text{thf})\) (0.84 g, 1.53 mmol) dissolved in diethyl ether (10 mL) was added 1 mL of pyridine (an excess), and the solution was stirred for 2 h. The volatile material was removed under vacuum, and the residue dissolved in diethyl ether (30 mL). Upon concentration to ca. 20 mL and cooling (-10°C), purple prisms (m.p. 270-272°C) were obtained in 47 percent yield (0.4 g). Anal. Calcd. for \(C_{25}H_{35}ClYb\): C, 53.8; H, 6.32; N, 2.51; Cl, 6.35. Found: C, 54.4; H, 6.37; N, 2.53; Cl, 5.96. IR data: 3048 w, 2720 w, 1947 w, 1640 m, 1600 s, 1570 w, 1233 w, 1215 m, 1153 w, 1062 m, 1039 w, 1019 w sh, 1009 m, 959 w, 800 w, 756 s, 707 s, 627 m, 592 w, 433 m, 389 m, 310 s br cm⁻¹.

(Diethyl amine)bis(pentamethylcyclopentadienyl)chloroytterbium(III),

\[(C_5Me_5)_2YbCl(\text{NHET}_2)\]

Diethyl amine (1 mL, excess) was added to a suspension of \([\text{Na(\text{OET}_2) }][ (C_5Me_5)_2\text{YbCl}_2]\) (1.47 g, 25.1 mmol) in toluene (25 mL). The resulting solution was stirred for 6 h and then evaporated to dryness. The purple residue was crystallized from toluene (ca. 8 mL, -10°C) to give purple prisms in 84 percent yield (1.0 g). When heated in a sealed capillary, the prisms decomposed at ca. 181°C. Anal. Calcd. for \(C_{24}H_{41}ClYb\): C, 52.2; H, 7.49; N, 2.54; Cl, 6.42. Found: C, 51.9; H, 7.24; N, 2.42; Cl, 6.16. IR data: 3300 w, 2723 w, 1192 w, 1153 w, 1119 m, 1053 m, 1017 m, 963 s, 838 m, 785 s, 728 w, 593 w, 382 m, 300 s, 250 m cm⁻¹.
Tetrabutylammonium bis(pentamethylyclopentadienyl)dichloroytterbate (III), $[n$-$Bu_4$N]$[(C_5Me_5)_2YbCl_2]$  
To $[Li(UEt_2)_2][(C_5Me_5)_2YbCl_2]$ (0.77 g, 1.15 mmol) in 20 mL of toluene was added $[n$-$Bu_4$N]$[BH_4]$ (0.28 g, 1.2 mmol) in toluene (60 mL). After stirring 10 h, the solution was filtered and concentrated to ca. 15 mL. Cooling (-10°C) gave purple needles (m.p. 204-205°C) in 69 percent yield (0.6 g). $^1$H NMR (26°C, d_6-PhMe): 6 2.85 ($\nu_{1/2} = 15$ Hz), 12 H; 3.52 ($\nu_{1/2} = 37$ Hz), 30H; 4.45 ($\nu_{1/2} = 23$ Hz), 8 H; 6.75 ($\nu_{1/2} = 23$ Hz), 8H and 10.17 ($\nu_{1/2} = 23$ Hz), 8H. Anal. Calcd. for C_{36}H_{66}NCl_2Yb: C, 57.1; H, 8.79; N, 1.85. Found: C, 54.7; H, 8.46; H, 1.82. IR data: 2718 w, 1159 m, 1127 w, 1103 w, 1061 w, 1021 m, 923 w, 898 w sh, 879 m, 800 w, 782 w, 736 m, 599 w, 382 m, 296 s cm$^{-1}$.

Phenylpyridinemagnesium bis(pentamethylyclopentadienyl)bromo-chloroytterrate(III), (C_5Me_5)_2Yb(Cl)BrMgPh(py)  
The Grignard reagent PhMgBr (1.05 mL of a 1.0 M diethylether solution) was added to a diethylether solution (40 mL) of (C_5Me_5)_2YbCl(py) (0.57 g, 1.0 mmol) cooled to 0°C. After 1 h, the solution was warmed to room temperature and stirred for 8 h. The solution was then filtered, concentrated to ca. 12 mL and cooled (-10°C) to yield purple needles (m.p. 279-281°C, dec.) in 61 percent yield. The mass spectrum contained peaks due to (C_5Me_5)_2Yb(Cl)BrMg(py)$^+$ (661), (C_5Me_5)_2YbBr$^+$ (523) and (C_5Me_5)_2YbCl$^+$ (479). Anal. Calcd. for C_{31}H_{40}NBrClMgYb: C, 50.4; H, 5.45; N, 1.89. Found: C, 50.3; H, 5.99; N, 2.30. IR data: 3045 w, 2707 w, 1600 s, 1485 w, 1441 m,
1235 w, 1214 s, 1064 m, 1040 m, 1020 m, 1009 m, 757 s, 707 s, 630 m, 387 m, 306 s, 278 m, 245 m cm⁻¹.

Bis(pentamethylcyclopentadienyl)[bis(trimethylsilyl)amido]neodymium(III), (C₅Me₅)₂Nd[N(SiMe₃)₂]

Sodium bis(trimethylsilyl)amide (0.16 g, 0.87 mmol) in toluene (25 mL) was added to [Li(OEt₂)]([C₅Me₅]₂NdCl₂) (0.55 g, 0.86 mmol) in toluene (20 mL). The blue solution was stirred for 8 h, then the solvent was removed under vacuum. The residue was extracted with pentane (2 × 20 mL). The combined extracts were concentrated to ca. 13 mL and cooled (-10°C) to obtain large hexagonal needles in 51 percent yield (0.25 g). The compound does not melt below 300°C.

Anal. Calcd. for C₃₀H₄₆Nd₂S_i₂: C, 54.3; H, 8.41; N, 2.44. Found: C, 53.3; H, 8.28; N, 2.36. IR data: 2722 w, 1257 w sh, 1242 s br, 863 vs br, 813 vs br, 762 vs br, 669 m, 592 s, 383 w sh, 370 s, 290 vs br cm⁻¹.

Pentamethylcyclopentadienylbis[bis(trimethylsilyl)amido]neodymium(III), (C₅Me₅)Nd[N(SiMe₃)₂]₂

Sodium bis(trimethylsilyl)amide (0.72 g, 3.9 mmol) in toluene (50 mL) was added to [Na(OEt₂)]([C₅Me₅]NdCl₃) (1.08 g, 1.94 mmol), and the mixture was stirred for 12 h. After evaporation to dryness, the residue was extracted with pentane (50 mL). Concentration to ca. 10 mL under vacuum, followed by cooling (-10°C) resulted in crystallization of large blue prisms (m.p. 234-236°C) in 72 percent yield (0.84 g). A parent ion, an envelope of peaks centered about m/e = 600, was observed in the mass spectrum.

Anal. Calcd. for C₢₂H₅₁Nd₂S_i₄: C, 44.0; H, 8.56; N, 4.67. Found: C, 42.0; H,
8.46; N, 4.30. IR data: 1246 vs br, 990 vs br, 878 s sh, 830 s br,
763 s, 752 w sh, 723 m, 670 s, 660 w sh, 598 s, 371 s, 306 s cm⁻¹.

\[
\text{Bis(pentamethylcyclopentadienyl)bis(trimethylsilyl)amidoytterbium(III),}
\]
\[
(C_5Me_5)_2YbN(SiMe_3)_2
\]
Sodium bis(trimethylsilyl)amide (0.21 g, 1.1 mmol) in diethyl ether
(30 mL) was added to \((C_5Me_5)_2YbCl(py)\) (0.64 g, 1.1 mmol) in
diethyl ether (20 mL). After stirring for 10 h, the volatile material
was removed under reduced pressure and the residue was extracted with
pentane (50 mL). After filtration, the pentane solution was concen-
trated to ca. 10 mL. Cooling (-10°C) afforded large, purple prisms
(m.p. 294-295°C) in 61 percent yield (0.42 g). Anal. Calcd. for
\[
C_{20}H_{48}NSi_2Yb: C, 51.7; H, 8.01; N, 2.32. Found: C, 50.9; H,
7.82; N, 2.18. IR data: 2710 w, 1256 w sh, 1242 s, 988 s br, 868 s
br, 820 s br, 777 m, 749 m, 655 m, 383 m, 298 s cm⁻¹.
\]

\[
\text{Bis(pentamethylcyclopentadienyl)(2,2-dimethylpropionate)ytterbium(III),}
\]
\[
(C_5Me_5)_2YbO_2CCMe_3
\]
The anionic complex \([\text{Na(OEt}_2\text{)}_2][(C_5Me_5)_2YbCl_2]\) (1.72
g, 2.51 mmol) in diethyl ether (30 mL) was added to a suspension of
sodium 2,2-dimethylpropionate (0.31 g, 2.50 mmol) in diethyl ether
(20 mL). After stirring 6 h, the red solution was evaporated to dry-
ness and the residue extracted with 35 mL of pentane. After filtering
and cooling (-70°C), red prisms (m.p. 154-155°C) were obtained. The
yield was 48 percent (0.65 g). The mass spectrum showed dimeric peaks
at m/e = 924, 839, 820, 802, 749, 612 and 571, as well as the monomeric
peak at m/e = 545. \(^1H\) NMR (26°C, \text{d}_{8}-\text{PhMe}): \delta 10.95 (v_{1/2} = 107
Hz), 30 H, 6 -26.45 (v<sub>1/2</sub> = 21 Hz), 9 H. The magnetic susceptibility followed Curie behavior from 5-35K, with $\mu_{\text{eff}} = 3.29$ B.M. and C = 1.34. Anal. Calcd. for C<sub>25</sub>H<sub>39</sub>O<sub>2</sub>Yb: C, 55.1; H, 7.22. Found: C, 55.2; H, 7.19. IR data: 2713 w, 1503 m, 1489 m, 1430 m, 1225 s, 1169 w, 1064 w, 1026 m, 940 w, 896 s, 810 m, 793 m, 617 m, 474 w, 408 m, 388 m, 319 s cm<sup>-1</sup>.

Bis(pentamethylcyclopentadienyl)trifluoroacetatoytterbium(III),
(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>YbO<sub>2</sub>CCF<sub>3</sub>

The complex [Na(OEt<sub>2</sub>)<sub>2</sub>][(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>YbCl<sub>2</sub>] (1.08 g, 1.58 mmol) in tetrahydrofuran (30 mL) was added to NaO<sub>2</sub>CCF<sub>3</sub> (0.22 g, 1.6 mmol) in tetrahydrofuran (10 mL). The dark red solution was stirred for 12 h, the tetrahydrofuran removed under vacuum, and the residue extracted with diethyl ether (2 x 40 mL). Concentration and cooling (-10°C) of the combined extracts led to crystallization of violet prisms (m.p. 262-263°C) in 57 percent yield (0.5 g). The mass spectrum contained a molecular ion at 557. Anal. Calcd. for C<sub>22</sub>H<sub>30</sub>O<sub>2</sub>F<sub>3</sub>Yb: C, 47.5; H, 5.43. Found: C, 47.7; H, 5.49. IR data: 3140 w, 3092 w, 2726 w, 1680 s, 1204 s, 1158 s, 1023 w, 847 m, 785 m, 718 m, 614 w, 592 w, 523 w, 468 w, 385 m, 312 s cm<sup>-1</sup>.

Diethylidithiocarbamatobis(pentamethylcyclopentadienyl)ytterbium(III),
(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>YbS<sub>2</sub>CNEt<sub>2</sub>

The anionic complex, [Na(OEt<sub>2</sub>)<sub>2</sub>][(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>YbCl<sub>2</sub>]
(1.39 g, 2.03 mmol) in diethyl ether (40 mL) was added to NaS<sub>2</sub>CNEt<sub>2</sub> (0.35 g, 2.04 mmol) in diethyl ether (20 mL). After stirring for 8 h, the red diethyl ether solution was evaporated to dryness. Addition of pentane (40 mL) gave a deep purple solution, that upon concentration
and cooling (-10°C) gave purple prisms (m.p. 226-227°C) in 81 percent yield (0.97 g). The mass spectrum contained peaks at m/e = 592, Yb(C₅Me₅)₂S₂CNET₂⁺; 457, Yb(C₅Me₅)S₂CNET₂⁺; 444, Yb(C₅Me₅)⁺; 322, YbS₂CNET₂⁺; 309, YbC₅Me₅⁺. ¹H NMR (26°C, d₈-PhMe): δ 7.45 (ν₁/₂ = 61 Hz), 30 H; -5.76 (ν₁/₂ = 18 Hz), 4 H; -9.00 (ν₁/₂ = 13 Hz), 6H. The magnetic susceptibility followed Curie behavior (5-55K), with μₑffective = 3.39 B.M. and C = 1.43. Anal. Calcd. for C₂₅H₄₀NS₂Yb: C, 50.7; H, 6.81; N, 2.37; S, 10.8. Found: C, 50.7; H, 6.76; N, 2.29; S, 10.7.

IR data: 2723 w, 1487 s, 1424 s, 1360 m, 1306 w, 1277 s, 1209 m, 1089 m, 1023 w, 987 m, 911 m, 841 m, 800 w, 779 w, 608 w, 593 w, 564 m, 473 w, 392 m, 360 m, 311 s cm⁻¹.

Diethylidtniocarboxamatobis(pentamethylcyclopentadienyl)neodymium(III), (C₅Me₅)₂NdS₂CNET₂

To NaS₂CNET₂ (0.58 g, 3.39 mmol) in diethyl ether (20 mL) was added [Li(OEt₂)][(C₅Me₅)₂NdCl₂] (2.17 g, 3.39 mmol) in diethyl ether (40 mL). After 8 h of stirring, the green solution was filtered, concentrated to ca. 30 mL and cooled (-10°C). Large green prisms (m.p. 229-231°C) were obtained in an overall yield of 72 percent (1.37 g). ¹H NMR (d₈-PhMe, 70°C): δ 7.00 (ν₁/₂ = 23 Hz), 30 H; -0.10 (ν₁/₂ = 17 Hz), 4 H; -0.94 (ν₁/₂ = 16 Hz), 6H. The mass spectrum contained peaks at m/e = 562, Nd(C₅Me₅)₂S₂CNET₂⁺; 427, Nd(C₅Me₅)S₂CNET₂⁺; 414, Nd(C₅Me₅)⁺; 292, NdS₂CNET₂⁺; 279, NdC₅Me₅⁺. Anal. Calcd. for C₂₅H₄₀NS₂Nd: C, 53.3; H, 7.10; N, 2.49. Found: C, 53.2; H, 7.03;
N. 2.47. IR data: 2722 w, 1482 s, 1420 s, 1357 m, 1402 w, 1273 s, 1203 s, 1138 m, 1087 m, 1063 w, 1021 w, 979 m, 905 m, 836 m, 798 w, 773 w, 607 w, 560 m, 470 w, 430 w, 382 m, 348 m, 310 s cm$^{-1}$. The magnetic susceptibility followed Curie behavior (5-50K), with $\mu_{\text{eff}} = 2.75$ B.M. and $C = 0.94$.

**Attempted Preparation of $(\text{C}_5\text{Me}_5)_2\text{YbNET}_2$**

The anionic complex $[\text{Li(0Et}_2)_2][(\text{C}_5\text{Me}_5)_2\text{YbCl}_2]$ (0.81 g, 1.21 mmol) in 40 mL of diethyl ether was added to a cold (-70°C) suspension of lithium diethylamide (0.10 g, 1.3 mmol) in diethyl ether. After ca. 1 h, the stirred solution was allowed to warm to room temperature, and was then stirred for an additional 7 h. The red solution was filtered away from a white precipitate. Concentration of the solution and cooling (-10°C) led to isolation of only the starting material, $[\text{Li(0Et}_2)_2][(\text{C}_5\text{Me}_5)_2\text{YbCl}_2]$, in 60 percent yield. Refluxing the reactants in tetrahydrofuran for 14 h led to the same result.

**Experimental Procedures for Chapter 5**

**(Diethyl ether)bis(pentamethylcyclopentadienyl)(tetrahydrofuran) europium(II), Eu$(\text{C}_5\text{Me}_5)_2$(thf)(0Et$_2$)**

Sodium pentamethylcyclopentadienide (9.72 g, 0.0614 mol) in tetrahydrofuran (75 mL) was added to a stirred suspension of europium trichloride (5.30 g, 0.0205 mol) in tetrahydrofuran (75 mL). A blue solution developed immediately which slowly turned brown-red. The suspension was refluxed for 12 h. Tetranydrofuran was removed under vacuum, the residue was extracted with diethyl ether (2 x 150 mL), and the combined extracts were concentrated to ca. 100 mL. Cooling (-10°C)
yielded red prisms in 65 percent yield (7.5 g); m.p. 181-182°C. The complex is soluble in aliphatic and aromatic hydrocarbons and in ethereal solvents. It decomposed upon attempted sublimation under vacuum at ca. 140°C. A sample of the complex was dissolved in benzene and hydrolyzed with water. The $^1$H NMR spectrum of the benzene solution showed tetrahydrofuran and diethyl ether in equal amounts.

The compound follows Curie behavior from 5-50K with $\mu_{\text{eff}} = 7.99$ B.M. and C = 7.91. Anal. Calcd. for $C_{28}H_{48}O_2$Eu: C, 59.1; H, 8.51.

Found: C, 59.1; H, 8.43. IR data: 2713 w, 1629 w, 1313 w, 1286 w, 1248 w, 208 w, 1185 w, 1147 m, 1119 w, 1089 w, 1054 m, 1032 s, 1003 w sh, 927 w, 896 s, 837 w, 828 w, 818 w, 795 m, 777 m, 766 w, 649 w br, 624 w, 585 m, 506 m br, 353 w br, 248 s br cm$^{-1}$.

Bis(pentamethylcyclopentadienyl)(tetrahydrofuran)europium(II),

$\text{Eu(C}_5\text{Me}_5\text{)}_2(\text{thf})$

(Diethyl ether)bis(pentamethylcyclopentadienyl)(tetrahydrofuran)-europium(II) (1.5 g, 2.7 mmol) was dissolved in toluene (25 mL), and the solution was concentrated to ca. 10 mL. Cooling (-70°C) yielded red prisms in quantitative yield; m.p. 178-181°C. Recrystallization of this complex from diethyl ether yields $\text{Eu(C}_5\text{Me}_5\text{)}_2(\text{thf})(\text{OEt}_2)$.

Anal. Calcd. for $C_{24}H_{38}$EuO: C, 58.3; H, 7.74. Found: C, 58.6; H, 7.56. IR data: 2714 w, 1637 w br, 1292 w sh, 1281 w, 1243 m, 1209 m, 1027 s br, 952 w, 928 w, 898 s br, 834 w sh, 794 w, 691 w, 637 m br, 587 w, 462 w, 357 m br, 258 s br cm$^{-1}$. 
(Diethyl ether)bis(pentamethylcyclopentadienyl)europium(II),
Eu(C₅Me₅)₂(0Et₂)

Sodium pentamethylcyclopentadienide (2.18 g, 13.8 mmol) and europium diiodide (2.79 g, 6.88 mmol) were stirred together in diethyl ether (100 mL). After 12 h, the red solution was filtered, concentrated (to ca. 60 mL) and cooled (-10°C). Large red needles (m.p. = 192-195°C) were obtained in 72 percent yield (2.46 g). The highest mass peak in the mass spectrum corresponded to the base-free fragment (m/e = 423). Anal. Calcd. for C₂₄H₄₀OEu: C, 58.1; H, 8.12. Found: C, 57.9; H, 8.07. IR data: 2721 w, 1488 w, 1284 m, 1163 w, 1144 s, 1079 s, 1037 s, 1017 m, 929 m, 838 s, 819 w, 797 m, 590 m, 551 w, 442 w, 358 s, 270 s cm⁻¹.

Bis(pentamethylcyclopentadienyl)(tetrahydrofuran)ytterbium(II),
Yb(C₅Me₅)₂(thf)

Sodium pentamethylcyclopentadienide (3.97 g, 0.0251 mol) in tetrahydrofuran (75 mL) was added to a suspension of ytterbium dichloride (3.06 g, 0.0125 mol) in tetrahydrofuran (75 mL). After refluxing for 12 h, the deep purple suspension was evaporated to dryness, and the residue was extracted with diethyl ether (2 x 100 mL). The combined, green extracts were concentrated to ca. 100 mL and cooled (-10°C). The red prisms were collected and dried under vacuum; yield 5.5 g (85 percent). When heated in a sealed capillary, the complex shrank at ca. 120°C and melted at 206-209°C. The compound is soluble in aromatic hydrocarbons and ethereal solvents. The complex decomposed upon attempted sublimation under vacuum at ca. 125°C. ¹H NMR (-25°C, d₈-PhMe): s 1.41 (m, 4H, δ-protons of thf), 2.12 (s, 30H, C₅Me₅)
and 3.42 (m, 4H, \(\alpha\)-protons of thf). \(^{13}\text{C}\{^1\text{H}\})\text{ NMR} (-25^\circ\text{C}, \text{d}_{8}-\text{PhMe}): \\
\text{s 11.5 (C}_5\text{Me}_5\text{), 25.7 (OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{), 69.5 (OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{)} \\
\text{and 111 (C}_5\text{Me}_5\text{). Anal. Calcd. for C}_{24}\text{H}_{38}\text{OYb: C, 55.9; H, 7.43.} \\
\text{Found: C, 56.2; H, 7.32. IR data: 2719 w, 1646 w br, 1322 w, 1297 w,} \\
\text{1249 m br, 1221 w, 1151 w, 1093 w, 1067 w sh, 1034 s br, 916 w, 882} \\
\text{s br, 801 w, 783 w, 668 m br, 628 w, 595 m, 483 w, 472 w, 361 m br,} \\
\text{304 m, 258 s br cm}^{-1}. \\
\text{Bis(pentamethylcyclopentadienyl)(tetrahydrofuran)ytterbium(II)-} \\
\text{Hemitoluene, Yb(C}_5\text{Me}_5\text{)}_2\text{(thf)}\cdot\frac{1}{2}\text{PhMe} \\
\text{Sodium pentamethylcyclopentadienide (3.52 g, 0.0227 mol) in tetra-} \\
\text{hydrofuran (75 mL) and ytterbium dichloride (2.71 g, 0.0111 mol) in} \\
\text{tetrahydrofuran (75 mL) were refluxed for 12 h. Tetrahydrofuran was} \\
\text{removed under vacuum, the residue was extracted with toluene (150 mL),} \\
\text{and the solution was concentrated to ca. 80 mL and was cooled to -70}^\circ\text{C.} \\
\text{The brown-red prisms were collected and dried under vacuum; yield 4.6} \\
\text{g (74 percent). When heated in a sealed capillary, the complex darkened} \\
\text{at ca. 195}^\circ\text{C and melted at 204-206}^\circ\text{C. Anal. Calcd. for C}_{27.5}\text{H}_{42}\text{OYb:} \\
\text{C, 58.8; H, 7.54. Found: C, 58.5; H, 7.27. IR data: 2719 m, 1604 m,} \\
\text{1337 w, 1259 m, 1242 w sh, 1174 m br, 1079 w, 1022 s, 918 m, 868 s br,} \\
\text{843 w sh, 795 w, 730 s, 694 s, 671 m, 589 w, 481 w sh, 466 m, 360 m} \\
\text{br, 304 s br, 282 w sh, 268 s cm}^{-1}. \\
\text{(Diethyl ether)bis(pentamethylcyclopentadienyl)ytterbium(II),} \\
\text{Yb(C}_5\text{Me}_5\text{)}_2\text{(OEt)}_2 \\
\text{A flask was charged with ytterbium diiodide (6.70 g, 0.0157 mol) and} \\
sodium pentamethylcyclopentadienide (4.97 g, 0.0314 mol). Diethyl} \\
\text{ether (100 mL) was added, and the mixture stirred for 16 h. The green}
ether solution was filtered, and the residue extracted once more with
diethyl ether (100 mL). The combined extracts were concentrated to ca.
70 mL and cooled (-10°C). Green needles were isolated in an overall
yield of 73 percent (5.9 g). The compound decomposed without melting
at ca. 145°C. $^1$H NMR (35°C, d$_6$-PhH): $\delta$ 1.04 (t, 6H, CH$_3$CH$_2$O),
2.16 (s, 3OH, C$_5$Me$_5$) and 3.15 (q, 4H, CH$_3$CH$_2$O). Anal. Calcd.
for C$_{24}$H$_{40}$OYb: C, 55.7; H, 7.79. Found: C, 55.7; H, 7.58. IR
data: 2720 w, 1633 w, 1284 w, 1262 w, 1180 w sh, 1163 w sh, 1149 s,
1123 w, 1097 w sh, 1077 s br, 1041 m, 1019 w, 980 w sh, 948 w, 929 m,
839 s, 829 w sh, 797 w, 592 m, 552 w, 482 w, 443 w, 355 m br, 303 m,
268 s br cm$^{-1}$.
(Methyl vinyl ether)bis(pentamethylcyclopentadienyl)ytterbium(II),
Yb(C$_5$Me$_5$)$_2$(MeOC$_2$H$_3$)

Toluene was enriched with methyl vinyl ether by adding triglyme and
refluxing with sodium benzophenone ketyl. Ytterbium diiodide (1.25 g,
3.0 mmol), sodium pentamethylcyclopentadienide (0.94 g, 5.9 nmol) and
methyl vinyl ether-containing toluene (50 mL) were added to a flask.
The solution was stirred for 24 h, filtered, concentrated to ca. 10 mL
and cooled (-70°C). Green prisms (m.p. = 185-188°C) were isolated in
63 percent yield (0.95 g). $^1$H NMR (28°C, d$_6$-PhH): $\delta$ 2.23 (s, 30
H, C$_5$Me$_5$), $\delta$ 4.12 (m, 5H, CH=CH$_2$ and OMe) and 6.17 (q, 1H,
CH$_2$=CHO). $^{13}$C($^1$H) NMR (28°C, d$_6$-PhH): $\delta$ 11.5 (C$_5$Me$_5$),
66.2 (OMe), 90.4 (OCH=CH$_2$), 112 (C$_5$Me$_5$) and 149 (OCH=CH$_2$).
Anal. Calcd. for C$_{23}$H$_{36}$OYb: C, 55.1; H, 7.23. Found: C, 55.1; H,
7.35. The compound can be recrystallized from diethyl ether. IR data:
3120 w, 2726 w, 1637 s, 1328 m, 1288 w, 1252 w, 1208 m, 1123 m, 1200 s, 1060 w, 1040 s, 966 m, 952 m, 871 s, 829 w, 732 s, 699 m, 597 w, 470 w, 370 w, 310 m, 263 s cm\(^{-1}\).

Bis(pentamethylcyclopentadienyl)(tetrahydrofuran)(triphenylphosphine-oxide)ytterbium(II), Yb(C\(_{5}Me_{5}\))\(_{2}\)(thf)(OPPh\(_{3}\))

Triphenylphosphineoxide (0.33 g, 1.19 mmol) in diethyl ether (50 mL) was added to Yb(C\(_{5}Me_{5}\))\(_{2}\)(OEt\(_{2}\)) (0.61 g, 1.18 mmol) in diethyl ether (20 mL). The solution was stirred for 10 h, resulting in precipitation of a red-brown solid. The diethyl ether was filtered off, and the residue washed with toluene (20 mL). The residue was then dissolved in 13 mL of tetrahydrofuran-diethyl ether (3:1) and cooled (-10°C). Small purple crystals (m.p. = 188-190°C) were isolated in 56 percent yield (0.53 g). The presence of tetrahydrofuran was substantiated by \(^{1}\)H NMR (\(d_6\)-PhH) of a hydrolyzed sample, and by absorptions in the IR spectrum (1041 and 892 cm\(^{-1}\)). The mass spectrum contained a peak due to Yb(C\(_{5}Me_{5}\))\(_{2}\)(OPPh\(_{3}\)) (m/e = 721).

**Anal. Calcd. for C\(_{42}\)H\(_{53}\)PO\(_{2}\)Yb: C, 63.5; H, 6.73; P, 3.90. Found: C, 63.8; H, 6.72; P, 4.11.**

IR data: 3052 m, 2719 m, 1592 m, 1438 m, 1170 s, 1119 s, 1093 w, 1077 w, 1041 m, 999 m, 916 w, 892 m, 851 w, 761 m, 746 m, 723 s, 703 m, 695 m, 593 w, 540 s, 513 w, 469 m, 411 w, 358 m, 313 w, 289 w, 256 m cm\(^{-1}\).

(Bipyridine)bis(pentamethylcyclopentadienyl)europium(II),

Eu(C\(_{5}Me_{5}\))\(_{2}\)(bipy)

The complex was prepared by the addition of 2,2'-bipyridine (0.31 g, 2.0 mmol) in toluene (20 mL) to Eu(C\(_{5}Me_{5}\))\(_{2}\)(thf)(OEt\(_{2}\)) (1.14 g, 2.0 mmol) in toluene (15 mL). After stirring for 3 h and
removing the solvent, the resulting dark brown solid was crystallized from tetrahydrofuran (-70°C). The brown prisms did not melt below 300°C when heated in a sealed capillary. Yield was 91 percent (1.05 g). The mass spectrum contained a parent peak at m/e = 579. The compound follows Curie behavior (5-60K) with $\mu_{\text{eff}} = 7.73$ B.M. and C = 7.41. Anal. Calcd. for $C_{30}H_{38}N_2$Eu: C, 62.3; H, 6.62; N, 4.84. Found: C, 60.9; H, 6.67; N, 4.75. IR data: 3044 w, 2720 w, 1591 s, 1562 w, 1433 w, 1312 m, 1152 m, 1004 m, 757 s, 741 w, 652 w, 639 w, 621 w, 416 w, 259 s cm$^{-1}$.

(Bipyridine)bis(pentamethylcyclopentadienyl)ytterbium(II),

$Yb(C_5\text{Me}_5)_2(\text{bipy})$

Upon addition of a toluene (10 mL) solution of 2,2'-bipyridine (0.46 g, 2.95 mmol) to a green solution of $Yb(C_5\text{Me}_5)_2(\text{OEt}_2)$ (1.53 g, 2.96 mmol) in toluene (25 mL), a very deep brown solution formed. The solution was stirred for 4 h and the toluene removed under vacuum. The brown solid was dissolved in pentane (40 mL), filtered and concentrated (to ca. 25 mL). Cooling (-10°C) yielded dark brown prisms in an overall yield of 85 percent (1.5 g). When heated in a sealed capillary, the compound did not melt below 300°C. $^1H$ NMR (26°C, d$_6$-PhH): $\delta$ - 13.11, s; 4.11, s, $C_5\text{Me}_5$; 5.24, s and 25.82, s. $^{13}C$ NMR (26°C, d$_6$-PhH): $\delta$ - 3.35 (q, $C_5\text{Me}_5$), $^1J_{CH} = 123$ Hz and - 42.2 (s, $C_5\text{Me}_5$). Anal. Calcd. for $C_{30}H_{38}N_2$Yb: C, 60.1; H, 6.39; N, 4.67. Found: C, 59.9; H, 6.32; N, 4.67. The magnetic moment, obtained by Evans' method (PhH, 30°C) was 2.4 B.M. IR data: 2720 w, 1553 m, 1510 m, 1492 w sh, 1426 w, 1399 m, 1281 s br, 1259 m br, 1147 s br, 1021 m, 942 s br, 743 w, 732 m, 638 w, 608 w, 448 w, 430 w, 290 s br cm$^{-1}$. 
Bis(pentamethylcyclopentadienyl)bis(pyridine)ytterbium(II),
\[\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{py})_2\]

To a solution of \(\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)\) (1.75 g, 3.4 mmol) in toluene (20 mL) was added pyridine (1 mL, an excess). A dark green solid precipitated from solution. The mixture was stirred for 1 h, taken to dryness under vacuum, and the green residue was washed with pentane (50 mL). Extractions were taken by stirring the green residue in 100 mL of toluene overnight, filtering, and concentrating to ca. 20 mL. Cooling (-10°C) yielded ca. 300 mg of \(\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{py})_2\) (m.p. = 215-218°C). Overall yield was ca. 70 percent. \(^1\text{H}\) NMR (26°C, d\(_6\)-PhH): \(\delta\) 2.12 (s, \(\text{C}_5\text{Me}_5\)). Resonances due to the pyridine ligands were not observed. \(\text{Anal. Calcd. for C}_{30}\text{H}_{40}\text{N}_2\text{Yb}: C, 59.9; H, 6.66; N, 4.66. Found: C, 60.3; H, 6.70; N, 4.47. IR data: 3092 w, 3061 w, 3038 w, 2720 w, 1594 s, 1487 m, 1223 m, 1150 m, 1106 w br, 1069 m, 1034 m, 1000 m, 984 w, 942 w, 886 w, 800 w, 749 s, 729 w, 702 s, 652 w, 628 w, 619 w, 591 w, 418 m cm\(^{-1}\).

Bis(p-dimethylaminopyridine)bis(pentamethylcyclopentadienyl)-ytterbium(II), \(\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{p-Me}_2\text{NC}_5\text{H}_5\text{N})_2\)

To \(\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)\) (0.76 g, 1.5 mmol) in toluene (10 mL) was added p-dimethylaminopyridine (0.32 g, 2.9 mmol) in toluene (30 mL). The red color that developed in the solution gradually turned dark blue. The solution was stirred for 3 h and the toluene removed under vacuum. The blue residue was extracted with diethyl ether (2 x 100 mL) and the combined extracts concentrated (to ca. 110 mL) and cooled (-10°C). Dark blue prisms (m.p. = 241-242°C) were isolated in
an overall yield of 92 percent (0.93 g). $^1$H NMR (26°C, $d_8$-PhMe):
$\delta$ 2.18 (s, 30H, C$_5$Me$_5$), 2.28 (s, 6H, NMe$_2$), 6.18 (s, $\nu_{1/2} = 12$
Hz, 2H, aromatic) and 8.37 (s, $\nu_{1/2} = 21$ Hz, 2H, aromatic). Anal.
Calcd. for C$_{34}$H$_{50}$N$_4$Yb: C, 59.4; H, 7.33; N, 8.15. Found: C,
59.2; H, 7.56; N, 7.78. IR data: 2719 w, 1612 s, 1531 s, 1288 w, 1228
s, 1181 w, 1120 w sh, 1111 m, 1067 m, 999 s, 959 m, 806 s, 757 m, 591
w, 537 m, 483 w, 468 w, 307 w, 251 m cm$^{-1}$.

(1,2-Dimethylphosphinoethane)bis(pentamethylcyclopentadienyl)-
ytterbium(II), Yb(C$_5$Me$_5$)$_2$(dmpe)

1,2-Dimethylphosphinoethane (0.16 mL, 1 mmol) was added to
Yb(C$_5$Me$_5$)$_2$(0Et$_2$) (0.48 g, 0.93 mmol) in 25 mL of benzene.
Stirring for 1 h resulted in a green precipitate and a colorless
solution. The benzene was filtered off, and the green solid washed
with toluene (75 mL). A small amount (0.20 g) of microcrystalline
Yb(C$_5$Me$_5$)$_2$(dmpe) (m.p. 283-285°C) was obtained by extraction with
diethyl ether (70 mL), followed by concentration to ca. 20 mL and
cooling (-10°C). Anal. Calcd. for C$_{26}$H$_{46}$P$_2$Yb: C, 52.6; H, 7.81;
P, 10.4. Found: C, 51.8; H, 7.69; P, 10.0. IR data: 2721 w, 1421 m,
1302 m, 1284 w, 1150 w, 1091 w, 1015 w, 945 s, 926 m, 889 w, 829 w,
796 w, 720 s, 624 m, 672 w, 637 w, 589 w, 360 m, 349 m, 253 s cm$^{-1}$.

(1,2-Dimethylphosphinoethane)bis(pentamethylcyclopentadienyl)-
europium(II), Eu(C$_5$Me$_5$)$_2$(dmpe)

1,2-Dimethylphosphinoethane (0.17 mL, 1 mmol) was added to
Eu(C$_5$Me$_5$)$_2$(0Et$_2$) (0.51 g, 1.0 mmol) in toluene (20 mL). The
mixture was stirred for 1 h, the toluene filtered off, and the red
precipitate washed with toluene (75 mL). About 0.15 g of Eu(C₅Me₅)₂(dmpe) (m.p. 288-292°C) was crystallized from diethyl ether (ca. 20 mL, -10°C). The compound was hydrolyzed in d₆-benzene, and the resulting solution was shown to contain C₅Me₅H and dmpe [10] in a 1:1 ratio by ¹H and ³¹P(¹H) NMR. Anal. Calcd. for C₂₆H₄₆P₂Eu: C, 54.5; H, 8.10; P, 10.8. Found: C, 53.7; H, 7.83; P, 10.5. The infrared spectrum was identical to the one for Yb(C₅Me₅)₂(dmpe).

(1,2-Dimethylphosphinomethane)bis(pentamethylcyclopentadienyl)-ytterbium(II), Yb(C₅Me₅)₂(dmpe)

1,2-Dimethylphosphinomethane (0.16 mL, 1.1 mmol) was added to Yb(C₅Me₅)₂(OEt₂) in toluene (25 mL). The solution was stirred for 8 h, filtered and cooled (-10°C). Dark green needles (m.p. 250-253°C) were collected and dried under vacuum. Yield was quantitative. ¹H NMR (26°C, d₆-PhH): δ 2.17, (s, 30H, C₅Me₅), 1.78 (d, 2H, PCH₂P) and 0.95 (s, 12H, PMe₂). ¹³C(¹H)NMR (26°C, d₆-PhH): δ 112 (s, C₅Me₅), 44.6 (s, PCH₂P), 15.8 (s, PMe₂) and 12.0 (s, C₅Me₅). ³¹P(¹H) NMR (26°C, d₆-PhH): δ -39.6. Anal. Calcd. for C₂₅H₄₄P₂Yb: C, 51.8; H, 7.65; P, 10.7. Found: C, 50.6; H, 7.41; P, 10.2. IR data: 2720 w, 1420 m, 1300 m, 1284 m, 1161 w, 1109 m, 1055 w, 1015 m, 942 s, 925 m, 888 s, 830 m, 796 w, 749 s, 725 s, 705 w, 693 w, 674 w, 623 w, 589 w, 532 s, 253 s cm⁻¹.

(1,2-Dimethylphosphinomethane)bis(pentamethylcyclopentadienyl)-europium(II), Eu(C₅Me₅)₂(dmpe)

1,2-Dimethylphosphinomethane (0.30 mL, 1.8 mmol) was added to Eu(C₅Me₅)₂(OEt₂) (0.67 g, 1.8 mmol) in toluene (40 mL), and
the solution cooled (-10°C). Red needles (m.p. 251-253°C) were isolated; yield was quantitative. Hydrolysis of the compound in d$_6$-benzene gave C$_5$Me$_5$H and dmpm [7] in a 1:1 ratio (by $^1$H and $^{31}$P($^1$H) NMR). Anal. Calcd. for C$_{25}$H$_{44}$P$_2$Eu: C, 53.8; H, 7.94; P, 11.1. Found: C, 53.4; H, 7.85; P, 10.8. The infrared spectrum was identical to that for Yb(C$_5$Me$_5$)$_2$(dmpm).

Experimental Procedures for Chapter 6

(Diethyl ether)sodium Bis(pentamethylcyclopentadienyl)bis(trimethylsilyl)amidoytterbium(II), [Na(OEt$_2$)][(C$_5$Me$_5$)$_2$YbNSiMe$_3$)$_2$].

The divalent complex Yb(C$_5$Me$_5$)$_2$(OEt$_2$) (0.62 g, 1.20 mmol) in toluene (15 mL) was cooled to 0°C, and sodium bis(trimethylsilyl)-amide (0.22 g, 1.2 mmol) in toluene (30 mL) was added. After stirring for 5h, a green solid had precipitated, leaving a clear solution. The toluene was filtered and the green residue dried in vacuo. Diethyl ether (50 mL) was added to the residue and the resulting green solution was filtered, concentrated to ca. 12 mL and cooled (-10°C). Green needles (mp. > 300°C) were obtained in 59 percent yield (0.5 g). The compound is insoluble in nonpolar hydrocarbons. It was dissolved in benzene and hydrolyzed. Analysis of the benzene extract by $^1$H NMR showed resonances due to diethyl ether, C$_5$Me$_5$ and HN(SiMe$_3$)$_2$ in a 1:2:1 ratio. Anal. Calcd. for C$_{30}$H$_{58}$NOSi$_2$NaYb: C, 51.4; H, 8.34; N, 2.00. Found: C, 51.4; H, 7.55; N, 1.67. IR data:

\[
\begin{align*}
2722 \text{ w}, & \ 1242 \text{ s}, \ 1232 \text{ w sh}, \ 1038 \text{ w}, \ 983 \text{ w}, \ 871 \text{ s}, \ 823 \text{ w sh}, \ 611 \text{ s}, \ 757 \text{ m}, \ 740 \text{ w}, \ 652 \text{ m}, \ 599 \text{ w}, \ 580 \text{ w}, \ 361 \text{ m}, \ 324 \text{ m br cm}^{-1}.
\end{align*}
\]

Reaction of Yb(C$_5$Me$_5$)$_2$(thf) with NH$_4$Cl
To ammonium chloride (0.13 g, 2.4 mmol) was added Yb(C₅Me₅)₂(thf) (1.21 g, 2.3 mmol) in tetrahydrofuran (40 mL) and the mixture was stirred for 10 h. The resulting red solution was filtered from a yellow precipitate, and evaporated to dryness giving a red residue. The Yb(C₅Me₅)₂(thf) starting material was obtained by crystallization of the red residue from diethyl ether. The yield (based on the original amount of Yb(C₅Me₅)₂(thf)) was 33 percent. The yellow precipitate was washed with diethyl ether (40 mL) and dried under reduced pressure. This material was shown to be YbCl₂(thf)₂.

Anal. Calcd. for C₈H₁₆O₂Cl₂Yb: C, 24.8; H, 4.16. Found: C, 24.5; H, 3.59. IR data: 1200 w, 1069 m, 1032 m, 913 w, 880 m, 721 m, 303 s cm⁻¹.

**Reaction of Eu(C₅Me₅)₂(thf)(OEt₂) with 2,6-di(t-butyl)cresol**

2,6-Di(t-butyl)cresol (0.26 g, 1.2 mmol) in tetrahydrofuran (20 mL) was added to Eu(C₅Me₅)₂(thf)(OEt₂) (0.68 g, 1.2 mmol) in tetrahydrofuran (30 mL). After stirring for 8 h, the tetrahydrofuran was removed, and the resulting yellow solid was crystallized from diethyl ether-tetrahydrofuran (4:1) at -10°C. Yellow needles (m.p. 217-219°C) were obtained in 42 percent yield (0.41 g) based on Eu(OC₁₅H₂₃)₂(thf)₃. Anal. Calcd. for C₄₂H₇₀O₅Eu: C, 62.5; H, 8.74. Found: C, 62.7; H, 8.70. The mass spectrum contained peaks for Eu(OC₁₅H₂₃)₂ at 1178/1181 for the ¹⁵¹Eu and ¹⁵³Eu isotopes. IR data: 3651 w, 3200 w, 3144 w, 2720 w, 2561 w, 1745 w, 1602 w, 1548 w, 1412 m, 1272 s, 1217 m, 1198 m, 1121 w, 1029 s, 922 w, 911 m, 890 s, 878 s, 863 m, 818 s, 800 s, 789 m, 670 m, 632 w, 578 m, 498 s, 353 s cm⁻¹.
Reactor of 2,2-dimethylpropionic acid with Eu(C₅Me₅)₂(THF)(OEt₂)

To Eu(C₅Me₅)₂(THF)(OEt₂) (0.94 g, 1.65 mmol) in 50 mL of
diethyl ether was added 2,2-dimethylpropionic acid (0.17 g, 1.7 mmol)
in diethyl ether (20 mL). A dull yellow solid precipitated. The
diethyl ether solution was filtered off, and the residue washed with
diethyl ether (50 mL). The residue was dissolved in tetrahydrofuran,
the solution was filtered and concentrated to ca. 10 mL. Yellow micro-
crystals (ca. 0.5 g) were obtained (m.p. > 310°C). Anal. C, 37.2; H,
5.66. Eu(O₂CCMe₃)₂(THF) requires C, 39.4; H, 6.15. IR data:
1567 s, 1531 s, 1481 s, 1411 s, 1244 s, 1058 s, 892 s, 801 m, 792 m,
600 m, 543 m, 383 m cm⁻¹.

Reactor of 2,2-dimethylpropionic acid with Yb(C₅Me₅)₂(OEt₂)

A solution of Yb(C₅Me₅)₂(OEt₂) (0.90 g, 1.7 mmol) in
diethyl ether (40 mL) was cooled to 0°C. A solution of 2,2-dimethyl-
propionic acid (0.18 g, 1.8 mmol) in diethyl ether was then added
slowly. After 10 h of stirring at room temperature, a yellow solid had
precipitated from solution. The diethyl ether was filtered, and the
yellow residue dissolved in tetrahydrofuran-diethyl ether (1:1, 10 mL)
to give a red solution. Cooling (-70°C) gave a yellow powder (m.p.
164-165°C). Anal. C, 40.7; H, 6.16. Yb(O₂CCMe₃)₂(THF)₂
requires C, 41.6; H, 6.60. IR data: 1567 s, 1472 m, 1409 m, 1351 m,
1220 m, 1050 m, 1018 m, 883 m, 785 m, 370 m cm⁻¹.

Reactor of phenylacetylene with Yb(C₅Me₅)₂(OEt₂)

Phenylacetylene (0.17 mL, 1.5 mmol) in toluene (15 mL) was added
to Yb(C₅Me₅)₂(OEt₂) (0.82 g, 1.16 mmol) in toluene (15 mL).
With stirring, the green solution gradually turned red over a 12 h
period. The solution was filtered, concentrated to ca. 5 mL, and pentane (ca. 2 mL) was added. Cooling (-10°C) resulted in red prisms (m.p. = 275-278°C). The yield (based on (C₅Me₅)YbC₂Ph as the product) was 47 percent (0.31 g). The mass spectrum contained peaks due to Yb₂(C₅Me₅)₃(C₂Ph)₂ (955), Yb₂(C₅Me₅)₂(C₂Ph)₂ (820), Yb₂(C₅Me₅)(C₂Ph)₂ (685), Yb₂(C₅Me₅)(C₂Ph) (584) and Yb(C₅Me₅)(C₂Ph) (410). ^H NMR (26°C, d₆-PhH): δ 3.49, s, ν₁/₂ = 25 Hz, 30 H; 10.55, s, ν₁/₂ = 20 Hz, 1H; 12.69, s, ν₁/₂ = 20 Hz, 2H and 25.47, s, ν₁/₂ = 21 Hz, 2H. Anal. Calcd. for C₁₈H₃₀Yb: C, 52.8; H, 4.92. Found: C, 52.6; H, 5.30. IR data: 3076 w, 3047 w, 2718 w, 2040 m, 1593 w, 1571 w, 1483 m, 1441 w, 1193 m, 1070 w, 1023 m, 917 w, 756 s, 729 m, 670 s, 542 m, 502 m, 388 m, 310 s cm⁻¹.

Reaction of dichloromethane with Yb(C₅Me₅)₂(thf) 1/2PhMe

Dichloromethane (0.50 mL, 7.8 mmol) was added to a toluene solution (20 mL) of Yb(C₅Me₅)₂(thf) 1/2PhMe (0.66 g, 1.2 mmol) cooled to 0°C. After stirring at 0°C for 30 min. the volatile material was evaporated and the residue crystallized from toluene (ca. 8 mL, -10°C), in 70 percent yield (0.45 g). The m.p. and infrared spectrum were identical to those of an authentic specimen of Yb(C₅Me₅)₂Cl(thf).

Reaction of ytterbium trichloride with Yb(C₅Me₅)₂(thf) 1/2PhMe

The Yb(C₅Me₅)₂(thf) 1/2PhMe (0.52 g, 0.93 mmol), dissolved in toluene (30 mL), was added to a suspension of ytterbium trichloride (0.26 g, 0.93 mmol) in toluene (15 mL). After stirring for 12 h, the solution was filtered, concentrated to ca. 10 mL and cooled (-10°C). The violet crystals of Yb(C₅Me₅)₂Cl(thf) (0.30 g, 59 percent) were identified by their m.p. and infrared spectrum.
Chloro(1,2-dimethylphosphinomethane)bis(pentamethylcyclopentadienyl)-
ytterbium(III), Yb(C₅Me₅)₂Cl(dmpm)

The divalent Yb(C₅Me₅)₂(dmpm) (0.74 g, 1.28 mmol) in toluene
(75 mL) was added to a suspension of ytterbium trichloride (0.36 g,
1.3 mmol) in toluene (10 mL). The reaction mixture was stirred for
24 h. The compound was crystallized by filtering the solution, con-
centrating it to ca. 10 mL and cooling (-10°C). The purple prisms
(dec. ca. 208°C) were collected and dried under vacuum. Yield was
66 percent (0.52 g). The effective magnetic moment (30°C in benzene
by Evans' method) was 4.4 B.M. Anal. Calcd. for C₂₅H₄₄P₂ClYb:
C, 48.8; H, 7.21; P, 10.07; Cl, 5.77. Found: C, 48.6; H, 7.06; P,
9.88; Cl, 5.54. IR data: 2718 w, 1292 m, 1276 w, 1149 m, 1087 w,
1014 m, 943 s, 908 s, 880 w, 830 w, 799 w, 759 m, 723 m, 709 w, 699 w,
683 w, 615 w, 590 w, 372 m, 298 s, 248 s cm⁻¹.

Iodobis(pentamethylcyclopentadienyl)tetrahydrofuranytterbium(III),
Yb(C₅Me₅)₂I(thf)

The complex Yb(C₅Me₅)₂(thf) (0.58 g, 1.12 mmol) in toluene
(25 mL) was added to silver iodide (0.27 g, 1.15 mmol) and the mixture
stirred for 14 h. The violet solution was filtered, concentrated to
ca. 8 mL under reduced pressure, and cooled (-10°C). The violet
crystals were isolated in 60 percent yield (0.43 g). When heated in a
sealed capillary, the compound decomposes (turns grey) at ca. 130°C.
Anal. Calcd. for C₂₄H₃₈OIYb: C, 44.9; H, 5.96. Found: C, 45.1;
H, 6.10. IR data: 2723 w, 1344 m, 1248 w, 1178 w, 1039 w sh, 1012 s,
956 w, 926 w, 914 w sh, 860 s, 841 w sh, 730 m, 697 w, 676 w, 595 m,
467 w, 388 m, 308 s cm⁻¹.
Reaction of silver trifluoroacetate with Yb(C₅Me₅)₂(OEt₂)

Silver trifluoroacetate (0.24 g, 1.1 mmol) in toluene (40 mL) was added to Yb(C₅Me₅)₂(OEt₂) (0.57 g, 1.1 mmol) in 15 mL of toluene. The resulting purple solution was stirred for 6 h, filtered and concentrated to ca. 30 mL under reduced pressure. Cooling (-10°C) gave violet crystals of [Yb(C₅Me₅)₂O₂CCF₃]₂, identified by its m.p. and infrared spectrum, in 68 percent yield.

Reaction of Iodine with Eu(C₅Me₅)₂(thf)OEt₂

Iodine (0.13 g, 0.51 mmol) in diethyl ether (20 mL) was added to Eu(C₅Me₅)₂(thf)(OEt₂) (0.60 g, 1.06 mmol) in diethyl ether (30 mL), resulting in a red solution with a grey precipitate. After stirring for 10 h, the volatile material was removed under reduced pressure, and the residue washed with pentane. The solid was crystallized from tetrahydrofuran (ca. 8 mL, -10°C). The isolated crystals (m.p. > 300°C) were white. The yield of EuI₂(thf)₂ was 23 percent (0.13 g). Anal. Calcd. for C₆H₁₆I₂O₂Eu: C, 17.5; H, 2.91; I, 46.2. Found: C, 17.3; H, 2.98; I, 44.9. IR data: 1339 w, 1293 w, 1028 s, 917 m, 870 s, 671 m cm⁻¹.

Reaction of allylbromide with Eu(C₅Me₅)₂(thf)(OEt₂)

A diethyl ether solution (10 mL) of allyl bromide (0.19 g, 1.6 mmol) was added to a cooled (0°C) solution of Eu(C₅Me₅)₂(thf)(OEt₂) (0.89 g, 1.6 mmol). A blue solution developed after ca. 1 min. The solution was allowed to warm to room temperature, and a yellow solid began to precipitate, leaving a red solution. After stirring 6 h, the Eu(C₅Me₅)₂(thf)(OEt₂) starting material was isolated from the diethyl ether solution in 43 percent yield (identified by m.p. and
i.r.). The yellow solid was washed with diethyl ether (40 mL), and
tetrahydrofuran was added (15 mL). The yellow solid was only slightly
soluble in the tetrahydrofuran. The solvent was removed, and an
infrared spectrum of the residue showed only bands due to tetrahydro-
furan (1030 and 872 cm\(^{-1}\)). Characterization of this material was not
pursued further.

**Reaction of trimethylchlorosilane with Eu(C\(_5\)Me\(_5\))\(_2\)(thf)(OEt\(_2\))**

Addition of trimethylchlorosilane (0.14 g, 1.3 mmol) to
Eu(C\(_5\)Me\(_5\))\(_2\)(thf)(OEt\(_2\)) (0.75 g, 1.3 mmol) in diethyl ether (30
mL) resulted in precipitation of a yellow-green solid after 7 h. The
Eu(C\(_5\)Me\(_5\))\(_2\)(thf)(OEt\(_2\)) starting material was isolated from the
diethyl ether solution in 45 percent yield. The yellow-green solid,
which was insoluble in tetrahydrofuran and pyridine, showed only
coordinated tetrahydrofuran in its infrared spectrum (1028 and 881
cm\(^{-1}\)).

**Reaction of silver trifluoroacetate with Eu(C\(_5\)Me\(_5\))\(_2\)(thf)(OEt\(_2\))**

The addition of silver trifluoroacetate (0.35 g, 1.6 mmol) in
toluene (30 mL) to Eu(C\(_5\)Me\(_5\))\(_2\)(thf)(OEt\(_2\)) (0.91 g, 1.16 mmol)
in toluene (30 mL) resulted in a brown suspension. The suspension was
stirred for 10 h, then the solvent was removed under reduced pressure.
The residue was extracted with tetrahydrofuran (60 mL). After con-
centration of the tetrahydrofuran solution to 10 mL, diethyl ether (3
mL) was added and the solution cooled to \(-70^\circ\text{C}\). Yellow microcrystals
(0.32 g) were isolated and dried in vacuo (m.p. > 300°C). Anal. C,
29.9; H, 3.15. Eu(U\(_2\)CCF\(_3\))\(_2\)(thf) requires C, 29.4; H, 3.29. IR
data: 3104 w, 1661 s, 1189 s, 1133 s, 1032 m, 880 m, 839 m, 797 m,
720 s, 602 w, 519 w, 270 s cm\(^{-1}\).
Reaction of chloroform with $\text{Eu}(\text{C}_5\text{Me}_5)_2(\text{thf})(\text{OEt}_2)$

Chloroform (1 mL, an excess) was added to a cooled (0°C) diethyl ether (25 mL) solution of $\text{Eu}(\text{C}_5\text{Me}_5)_2(\text{thf})(\text{OEt}_2)$ (0.64 g, 1.1 mmol). The blue solution was stirred for 25 min., and the volatile material was removed at 0°C. The blue residue was extracted with pentane (25 mL). The pentane solution was concentrated to ca. 8 mL under reduced pressure and cooled (-70°C) to give blue prisms (ca. 40 mg) that contained chloride (AgNO$_3$ test). IR data: 2722 w, 1209 w, 1110 w sh, 1096 m, 1063 s, 1012 w, 876 m, 840 w cm$^{-1}$. Nothing further was done to characterize this substance.

Reaction of europium trichloride with $\text{Eu}(\text{C}_5\text{Me}_5)_2(\text{thf})(\text{OEt}_2)$

The addition of $\text{Eu}(\text{C}_5\text{Me}_5)_2(\text{thf})(\text{OEt}_2)$ (0.67 g, 1.12 mmol) in tetrahydrofuran (50 mL) to $\text{EuCl}_3$ (0.30 g, 1.2 mmol) resulted in a blue solution that quickly began to deposit a green precipitate. IR of green precipitate: 2720 w, 1260 m, 1062 w, 1032 s, 970 w, 912 w, 878 s, 800 m, 627 w cm$^{-1}$. This substance was not further characterized.

Pentamethylyclopentadienyltris(tetrahydrofuran)europium(II) hexafluorophosphate, $[\text{Eu}(\text{C}_5\text{Me}_5)(\text{thf})_3][\text{PF}_6]$.

To solid ferrocinium hexafluorophosphate (0.77 g, 2.3 mmol), cooled to 0°C, was added $\text{Eu}(\text{C}_5\text{Me}_5)_2(\text{thf})(\text{OEt}_2)$ (1.32 g, 2.3 mmol) in diethyl ether (40 mL). After warming to room temperature, the solution was stirred for 10 h, resulting in an orange solution and a pale green precipitate. Ferrocene, identified by its m.p. and infrared spectrum, was crystallized from the diethyl ether solution. The green solid was washed with pentane (2 x 40 mL), and dissolved in tetrahydrofuran (20
mL). Concentration of the tetrahydrofuran solution to ca. 3 mL and cooling (-10°C) led to crystallization of large green prisms (m.p.=108-110°C) in 39 percent yield (0.58 g). The effective magnetic moment (5-40K) was 7.52 B.M., with C = 7.02. Anal. Calcd. for

C_{22}H_{42}PF_6O_3Eu: C, 40.7; H, 6.06; P, 4.78. Found: C, 40.3;
H, 6.04; P, 4.74. IR data: 2724 w, 1346 w, 1299 w, 1178 m, 1038 s,
873 s, 840 s, 734 s, 668 m, 560 s, 478 w cm\(^{-1}\).

**Bis(pentamethylcyclopentadienyl)tetracarbonylcobaltate(tetrahydrofuran)ytterbium(III), [(C_{5}Me_{5})_{2}Yb(thf)][Co(CO)\(_4\)]**

The divalent Yb(C_{5}Me_{5})_{2}(OEt_{2}) (1.12 g, 2.16 mmol) in toluene (15 mL) was added to octacarbonyldicobalt (0.37 g, 1.08 mmol) in toluene (10 mL). The solution was stirred for 36 h, resulting in precipitation of a blue solid. After removing the toluene, the blue solid was dissolved in tetrahydrofuran (30 mL) and filtered. The tetrahydrofuran solution was concentrated to 10 mL. Addition of pentane (20 mL) and cooling (-10°C) gave blue prisms (m.p. > 300°C) in 74 percent yield (1.10 g). \(^1\)H NMR (26°C, d\(_8\)-PhMe): \(\delta 8.36, s, v_{1/2} = 43\) Hz. The effective magnetic moment, determined by Evans' method in benzene at 30°C, was 4.1 B.M. Anal. Calcd. for

C_{28}H_{38}O_{5}CoYb: C, 49.0; H, 5.58. Found: C, 47.3; H, 5.39. IR
data: 3496 w, 2731 w, 2023 s, 1973 w, 1939 s, 1917 s, 1823 w, 1798 m
sh, 1761 s, 1318 w, 1300 w, 1251 w, 1179 w, 1060 w, 1041 w, 1010 s,
959 w, 828 w, 917 w, 858 s, 676 w, 563 s, 526 s, 511 s, 439 m, 380 m,
320 s cm\(^{-1}\).
Bis[bis(pentamethylcyclopentadienyl)ytterbium(III)] pentacarbonyl-
molybdate, \([\text{Yb}(\text{C}_5\text{Me}_5)_2]_2[\text{Mo}(\text{CO})_5]\)

A toluene (60 mL) solution of \(\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)\) (0.70 g, 1.35 mmol) was added to molybdenum hexacarbonyl (0.18 g, 0.68 mmol), and the solution was stirred for 36 h. The toluene was removed under reduced pressure, and the red residue dissolved in tetrahydrofuran (30 mL). Filtration, concentration to ca. 8 mL and cooling (-10°C) caused crystallization of red needles (m.p. > 310°C) in 41 percent yield (0.62 g). The compound was hydrolyzed in benzene. Analysis of the benzene extract by \(^1\text{H} N\text{MR}\) showed resonances due to \(\text{C}_5\text{Me}_5\text{H}\) only.

Anal. Calcd. for \(\text{C}_{45}\text{H}_{60}\text{O}_5\text{MoYb}\): C, 48.1; H, 5.38. Found: C, 48.4; H, 5.64. IR data: 2723 w, 2008 m, 1991 w, 1920 s, 1902 s, 1882 s, 1632 s, 1414 m, 1136 s, 1063 w, 998 s, 843 s, 667 m, 609 w, 562 w, 537 m, 468 w, 404 w, 372 m, 311 m cm\(^{-1}\).

Bis[bis(pentamethylcyclopentadienyl)tetrahydrofuran ytterbium(III)]
tetracarbonylferrate, \([\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{thf})]_2[\text{Fe}(\text{CO})_4]\)

Iron pentacarbonyl (0.21 g, 1.1 mmol) in toluene (10 mL) was cooled to 0°C, and \(\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)\) (1.11 g, 2.14 mmol) in toluene (20 mL) was added. A purple solid separated from solution after 1 h of stirring. Toluene was filtered from the solid, which was washed with more toluene (2 x 20 mL). The infrared spectrum of the blue solid contained peaks at 2018 w, 1981 w, 1752 m sh, 1710 s br and 1609 s br cm\(^{-1}\). The compound was dissolved in tetrahydrofuran (25 mL). This solution was filtered, concentrated to ca. 8 mL, and diethyl ether (20 mL) was added. Cooling (-10°C) afforded blue microcrystals in 72
percent yield (0.95 g). The $^1$H NMR spectrum (26°C, d$_8$-thf) con-
tained a peak ($v_{1/2} = 144$ Hz) at $s$ 9.52. Hydrolysis of the compound
in benzene gave a 2:1 mixture of C$_5$Me$_5$H and tetrahydrofuran (by
$^1$H NMR). Anal. Calcd. for C$_{52}$H$_{76}$O$_6$FeYb$_2$: C, 52.1; H, 6.39.
Found: C, 51.6; H, 6.42. IR data: 2720 w, 2004 w, 1980 w, 1961 w,
1928 s, 1922 s, 1753 m sh, 1741 s, 1711 s, 1648 m sh, 1608 s br, 1162
w, 1059 w, 1008 m, 856 m, 798 w, 653 m, 568 s, 551 s, 382 m, 310 s
cm$^{-1}$. The compound reacts with triphenylchlorosilane (two molar
equivalents) in tetrahydrofuran to generate Fe(CO)$_4$(SnPh$_3$)$_2$ and
Yb(C$_5$Me$_5$)$_2$Cl(thf) (by IR).

**Bis[bis(pentamethylylcyclopentadienyl)ytterbium(III)] undecacarbonyl-
triferrate, [Yb(C$_5$Me$_5$)$_2$][Fe$_3$(CO)$_{11}$]**

The compound Yb(C$_5$Me$_5$)$_2$(OEt$_2$) (0.77 g, 1.49 mmol) in
toluene (30 mL) was added to Fe$_3$(CO)$_{12}$ (0.37 g, 0.73 mmol) in
toluene (10 mL). After stirring for 48 h, the resulting solution was
filtered, evaporated to ca. 15 mL and cooled (-70°C) to obtain dark
violet prisms (m.p. = 307-310°C). Overall yield was 55 percent
(1.13 g). $^1$H NMR (26°C, d$_8$-PhMe): $s$ 6.11 ($v_{1/2} = 130$ Hz) and
8.09 ($v_{1/2} = 130$ Hz). The effective magnetic moment (5-60K) was
3.91 B.M. per ytterbium. The compound follows Curie behavior over this
temperature range. Anal. Calcd. for C$_{51}$H$_{71}$O$_{11}$Fe$_3$Yb$_2$: C,
44.6; H, 5.21. Found: C, 44.8; H, 4.63. IR data: 3260 w, 3100 w,
2722 wm 2048 w, 1998 s, 1973 s, 1667 w, 1604 s br, 1261 m, 1098 m br,
1020 m, 800 m, 727 m, 692 w, 658 m, 612 w sh, 598 m sh, 580 s, 493 w,
451 s, 393 m, 310 s cm$^{-1}$. 

Chapter 2 References


11. As measured on the JEOL FX90-Q on an authentic sample of tri(n-butyl)phosphine.

CHAPTER 3

DIVALENT BIS(TRIMETHYLSILYL)AMIDO LANTHANIDE COMPLEXES

Bis(trimethyldisilylamido) Europium(II) Complexes

The reaction scheme initially devised for the preparation of bis(trimethyldisilylamido) derivatives of europium(II) and ytterbium(II) involved preparation of the trivalent mono-chloro compounds \( \text{Ln}[\text{N(SiMe}_3\text{)}_2]_2\text{Cl} \), followed by reduction with sodium naphthalene:

\[
2\text{Ln}[\text{N(SiMe}_3\text{)}_2]_3 + \text{LnCl}_3 \rightarrow 3\text{Ln}[\text{N(SiMe}_3\text{)}_2]_2\text{Cl} \\
\text{Ln}[\text{N(SiMe}_3\text{)}_2]_2\text{Cl} + \text{NaNaph} \rightarrow \text{Ln}[\text{N(SiMe}_3\text{)}_2]_2 + \text{NaCl} + \text{Naph}
\]

Numerous attempts to prepare the mono-chloro species by the methods used to obtain \( \text{Cp}_2\text{LnCl} \) resulted in crystallization of the \( \text{Ln}[\text{N(SiMe}_3\text{)}_2]_3 \) starting material (see Experimental Section). It seems likely, however, that the mono-chloro derivative of europium exists, at least to some degree in solution, since europium tri-chloride, which is only sparingly soluble in tetrahydrofuran, dissolves in the presence of \( \text{Eu}[\text{N(SiMe}_3\text{)}_2]_3 \). Confirmation of this hypothesis was shown by the \textit{in situ} reduction with sodium naphthalene giving small yields (ca. 10 percent) of \( \text{Eu}[\text{N(SiMe}_3\text{)}_2]_2(\text{thf})_2 \).

A much improved synthesis of this europium(II) complex, as well as its 1,2-dimethoxyethane (dme) analogue utilizes europium diiodide:

\[
\text{EuI}_2 + 2\text{NaN(SiMe}_3\text{)}_2 \rightarrow \text{Eu}[\text{N(SiMe}_3\text{)}_2]_2L_2 \quad \text{L = thf or dme}
\]
The yields from this reaction are much improved, 60-80 percent. The yellow \( \text{Eu}[\text{N(SiMe}_3\text{)}_2]_2(\text{thf})_2 \) and \( \text{Eu}[\text{N(SiMe}_3\text{)}_2]_2(\text{dme})_2 \) represent the first pentane-soluble derivatives of a divalent lanthanide. The tetrahydrofuran in \( \text{Eu}[\text{N(SiMe}_3\text{)}_2]_2(\text{thf})_2 \) can be displaced by bipyridine, yielding yellow \( \text{Eu}[\text{N(SiMe}_3\text{)}_2]_2(\text{bipy}) \).

The 1,2-dimethoxyethane complex follows Curie behavior, \( \chi_m = CT^{-1} \), from 5 to 45 K with \( C = 8.82 \) and \( \mu_{\text{eff}} = 8.43 \) B.M. The magnetic moment is similar to that found for the isoelectronic gadolinium(III) compound \( \text{Gd}[\text{N(SiMe}_3\text{)}_2]_3 \) (7.75 B.M. at 98K) [1], and is consistent with an \( ^8S_{7/2} \) ground state.

As further characterization, a single-crystal X-ray structure determination was performed on \( \text{Eu}[\text{N(SiMe}_3\text{)}_2]_2(\text{dme})_2 \) [2]. The compound crystallizes in space group C2/c, with \( Z = 4 \). An ORTEP drawing, as viewed down the crystallographic two-fold axis, is shown in Figure 1. The carbon atoms in the ethylene units of the 1,2-dimethoxyethane ligands are disordered between the two positions shown in Figures 1 and 2. It is not apparent whether this disorder is static or dynamic, but the two structures represent two different puckered conformations for the five-membered chelate rings.

Figure 3 is a stereochemical view of the coordination geometry about the six-coordinate europium(II) ion. The coordination polyhedron cannot be described by a simple regular geometric figure. The two bulky silylamine groups are surprisingly close to one another, resulting in a \( N-\text{Eu}-N \) angle of only 134.5°. Keper has shown, from points-on-a-sphere repulsion energy calculations, that for six-coordinate
Figure 1. ORTEP drawing of Eu[N(SiMe$_3$)$_2$]$_2$(dme)$_2$ as viewed down the twofold axis.
Figure 2. ORTEP drawing of Eu[N(SiMe$_3$)$_2$](dme)$_2$ showing the molecule in the other configuration due to disorder in C(9) and C(10).
Figure 3. ORTEP view of the coordination sphere about europium in $\text{Eu}[\text{N(SiMe}_3\text{)}_2]_2(\text{dme})_2$. 
complexes of the type $M(bidentate)_2(unidentate)_2$, the unidentate ligands are pulled together when the bidentate ligands have small normalized bites [3]. Kepert defines the normalized bite of a chelating ligand as the distance between donor atoms in the chelate group divided by the metal-donor atom distance. It is the bidentate nature of the 1,2-dimethoxyethane ligands that prevents the two silylamide groups from repelling each other to a greater extent. The normalized bite of the 1,2-dimethoxyethane ligands in this complex is among the smallest known, 0.98. Clearly, repulsive interactions between coordinated atoms are more important in defining this detail of the structure than the overall steric bulk of the ligands.

Bond angles and distances in the planar bis(trimethylsilyl)amide ligands are comparable to those found in other structures [4–8]. The europium(II)-nitrogen bond distance is 2.53 Å, the first such bond length determined, whereas the europium(III)-nitrogen bond length in $\text{Eu}[\text{N(SiMe}_3)_2]_3$ is 2.26 Å. The difference of 0.27 Å is due mostly to the change in bond length with oxidation state, estimated as 0.23 Å from the ionic radii listed by Shannon [9]. The europium(II)-oxygen bond lengths in this structure are 2.638 and 2.756 Å, and Kepert has shown that such a difference may accompany the bending distortion discussed above. These europium(II)-oxygen distances are in good agreement with those reported in the $\text{EuCl}_2 \cdot 2\text{H}_2\text{O}$ structure [10], which range from 2.69 to 2.74 Å.

The reaction of europium diiodide with two molar equivalents of sodium bis(trimethylsilyl)amide in diethyl ether does not lead to a
Figure 4. ORTEP view of first NaEu[N(SiMe$_3$)$_2$)$_3$ molecule.
Figure 5. ORTEP view of second NaEu[N(SiMe$_3$)$_2$)$_3$ molecule.
Figure 6. Some bond distances in the molecule NaEu[N(SiMe$_3$)$_2$]$_3$. 
Figure 7. Some bond angles calculated for NaEu[N(SiMe$_3$)$_2$]$_3$. 
complex with coordinated ether, but to the anionic NaEu\([N(SiMe_3)_2]_3\) complex. This yellow, crystalline material is soluble in diethyl ether, pentane and toluene, from which it may be crystallized. The isolation of this compound from diethyl ether solutions suggests that the bis(trimethylsilyl)amide anion is a better base toward \(\text{Eu}[N(SiMe_3)_2]_2\) than diethyl ether, though a weaker base than tetrahydrofuran or 1,2-dimethoxyethane.

The compound that crystallizes from pentane or diethyl ether exhibits physical properties that differ somewhat from the product that is obtained from toluene (see Experimental Section). The two species probably differ only in assuming a different space group upon crystallization, as the unit cell volume of the product crystallized from pentane (3454 Å\(^3\)) is nearly one-half the unit cell volume of the compound crystallized from toluene (6996 Å\(^3\)). Numerous attempts were made to collect suitable X-ray data with crystals obtained by slow cooling of a pentane solution. Although consistent problems with twinning prohibited collection of a full data set, unit cell parameters were obtained (\(a = 9.90, b = 12.35\) and \(c = 28.85\) Å; \(\alpha = 99.5^\circ\), \(\beta = 91.8^\circ\) and \(\gamma = 95.8^\circ\)), along with determination of the space group (P\(\overline{1}\)) [11].

Fortunately, crystals of NaEu\([N(SiMe_3)_2]_3\) obtained from toluene were of good quality (space group P\(2_1/n\), \(Z = 8\)) [12]. There are two crystallographically unique molecules in the unit cell; ORTEP drawings for both are presented in Figures 4 and 5. Bond distances and angles, presented in figures 6 and 7, reveal some rather peculiar
structural features. The sodium atom is bonded to two bis(trimethylsilyl)amido groups, with the two nitrogen atoms bridging sodium and europium, giving the nitrogens a pseudotetrahedral environment. The third silylamide ligand is planar at the nitrogen atom. This accounts for the two $\nu$(NSi$_2$) stretching frequencies observed at 1240 and 1206 cm$^{-1}$ in the infrared spectrum. Correspondingly, the four-coordinate nitrogen atoms are further from europium (2.55 and 2.54 Å) than the three-coordinate nitrogen atom (2.46 Å). The NaN$_2$EuN coordination plane is very close to planar, resulting in N-Eu-N angles that sum to $359^\circ$.

A most surprising feature of the structure are the four short europium-carbon(methyl) contacts (3.07, 3.12, 3.25 and 3.44 Å) shown as dotted lines in Figure 5. Since the van der Waals radius of a methyl group is 2.0 Å [13], and the atomic radius of europium 2.42 Å (as calculated from europium metal [14]), it appears that these distances represent bonding interactions. These interactions would seem to arise from donation of electron density from the methyl groups to the electropositive and coordinatively unsaturated europium metal center. If the methyl groups are acting as ligands in this fashion, the effective ionic radius of the europium(II) center should reflect this. The effective ionic radius of a bis(trimethylsilyl)amide ligand, 1.47(3) Å, is well established from a number of X-ray structure determinations [15]. Subtracting this value from the one europium-(three coordinate)nitrogen bond distance, one obtains 0.99 Å for the ionic radius of the europium(II) ion. Shannon [9] suggests a value of
1.20 Å for the ionic radius of seven-coordinate europium(II). A value for the ionic radius of europium(II) in three-coordination can be calculated from the equation:

\[
\frac{R_{II}}{R_I} = \left(\frac{\text{CN}_{II}}{\text{CN}_I}\right)^{1/(n-1)}
\]

where \( R \) is the interionic distance and \( \text{CN} \) is the coordination number of the complex [15]. Using a Born exponent \( (n) \) of 12, and the six-coordinate interionic distance of 2.53 Å obtained from the structure of \( \text{Eu}[\text{N(SiMe}_3)_2](\text{dme})_2 \), an interionic distance of 2.38 Å, or an effective europium(II) radius of 0.91 Å, is obtained. The observed europium(II) ionic radius therefore lies between the values expected for three- and seven-coordinate europium(II), suggesting that the methyl groups do play a role in determining the ionic radius of europium.

It is of interest to determine the type of interaction that gives rise to the small europium-carbon separations, particularly in light of recent interest in hydrocarbon activation by transition metals [16-19]. Previous examples of bonding between trivalent lanthanides and formally neutral hydrocarbon fragments have been structurally characterized. In the compound \([\text{Nd(C}_5\text{H}_4\text{Me})_3]_4\), in which each neodymium atom is pentahapto-bound to three monomethylcyclopentadienyl ligands, the tetramer is formed by monohapto interactions between the metal atom and a \( \text{C}_5\text{H}_4\text{Me} \) ligand from another \( \text{Nd(C}_5\text{H}_4\text{Me})_3 \) fragment [20]. The latter neodymium-carbon separations are 2.98 and
2.99 Å. Similarly, SmCp₃ [21] and the polymeric ScCp₃ [22] exhibit this secondary, metal–n¹-C₅H₅ interaction.

It is not clear from these examples, or from the structure of NaEu[N(SiMe₃)₂]₃, whether the metal atoms are interacting through a hydrogen atom or directly with the carbon atom. This question has been addressed for the isostructural, methyl-bridged dimers [Cp₂MMMe]₂ (M = Yb or Y) in which direct, back-side interactions of the metals with the methyl carbon atom was differentiated from M⋯H-C(H₂)-M bonding by location of the hydrogen atoms in the crystal structure of the yttrium compound [23]. The structure shows all three hydrogens of the methyl groups to be pointed away from, and not interacting with, the metal atoms. Although the hydrogen atoms in Cp₂Yb(μ-Me)₂AlMe₂ [24] were not located, the bridge-bonding appears to be similar to that observed in [Cp₂MMMe]₂ (M = Yb or Y); the bridging angles at the methyl carbon atoms are 87° in [Cp₂YbMe]₂, 88° in [Cp₂YMe]₂ and 83 and 78° in Cp₂Yb(μ-Me)₂AlMe₂. The crystal structure of [AlMe₃]₃, in which the hydrogen atoms were located, also shows direct metal–carbon interactions, and an Al–C(methyl)–Al bond angle of 76° [25].

This latter observation, i.e., that M–Me–M' angles appear to be constrained to ca. 80°, suggests a possible bonding model for NaEu[N(SiMe₃)₂]₃. The observed Eu–C(methyl)–Si angles are 78, 80, 82 and 82°, implying that the europium–methyl interactions can be viewed in terms of methyl groups that asymmetrically bridge the more electropositive europium and silicon atoms. This view of the structure
is consistent with expected charge distributions in the molecule, and
with direct europium-carbon, rather than europium-hydrogen
interactions:

\[
\begin{array}{c}
\text{N} \\
\text{S}^-
\end{array}
\quad
\begin{array}{c}
\text{S}^+ \\
\text{Eu} \\
\text{Si} \\
\text{S}^- \\
\text{C} \\
\text{S}^- \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{S}^+ \\
\text{S}^+ \\
\text{S}^+
\end{array}
\]

The methyl groups, being bound to the electropositive silicon
atoms, are rather carbanionic in character. Furthermore, considering
the bonding between europium and its ligands to be highly ionic, the
silylamide group probably carries close to a full negative charge,
which may be partially delocalized onto the methyl carbon atoms.
Therefore, one can view the europium-carbon attraction as being highly
electrostatic in nature.

This model for the metal-carbon interaction in NaEu[N(SiMe₃)₂]₃
may help shed light on the role of uranium(IV) in activating the methyl
groups of a bis(trimethylsilyl)amide ligand. The uranium(IV) compound
[(Me₃Si)₂U]₃UX (X = H or Me) has been shown to give rise to the
heteroatom metallocycle
\[(\text{Me}_3\text{Si})_2\text{N}_2\text{UN}(\text{SiMe}_3)\text{SiMe}_2\text{CH}_2\] via the reactions:

\[\text{[(Me}_3\text{Si})_2\text{N}_2\text{U}]\rightarrow\text{[(Me}_3\text{Si})_2\text{N}_2\text{UN}(\text{SiMe}_3)\text{SiMe}_2\text{CH}_2 + \text{H}_2}\]

\[\text{[(Me}_3\text{Si})_2\text{N}_2\text{Um}] \rightarrow \text{[(Me}_3\text{Si})_2\text{N}_2\text{UN}(\text{SiMe}_3)\text{SiMe}_2\text{CH}_2 + \text{MeH}\]

This transformation appears to proceed without a change in oxidation state of the metal, since metallocycle formation is also observed in analogous thorium(IV), zirconium(IV), and hafnium(IV) systems [26,29], for which an oxidative addition process is highly unlikely. A metal-carbon interaction of the type observed in NaEu[(SiMe)_3]_2 could lead to a concerted elimination of methane (or hydrogen), if analogous bond polarizations are induced:
A possible confirmation of this scheme would be reaction of the NaEu[N(SiMe₃)₂]₃ compound with a methyl carbanion source (a strong base), such as methyl lithium, to yield methane and a metallocycle of the type Li\{[(Me₃Si)₂N]EuN(SiMe₃)SiMe₂CH₂\}.

Bis(trimethylsilyl)amido Ytterbium(II) Complexes

The reactions between ytterbium diiodide and sodium bis(trimethylsilyl)amide in ether solvents are not as straightforward as the analogous europium reactions. The product obtained from the reaction of ytterbium diiodide and two molar equivalents of bis(trimethylsilyl)amide in 1,2-dimethoxyethane, after extraction and crystallization with toluene, is the blue Yb[N(SiMe₃)₂]₂(dme)₂. This compound gives a red pentane solution, from which the red Yb[N(SiMe₃)₂]₂(dme) can be crystallized. These results suggest the solvent-dependent equilibrium:

\[
\text{Yb[N(SiMe₃)₂]₂(dme)₂} \quad \rightleftharpoons \quad \text{Yb[N(SiMe₃)₂]₂(dme)} + \text{dme}
\]

The crystallization of a mono(dme) complex from pentane, rather than a bis(dme) complex, as is the case with the europium(II) silylamide, is a reflection of the smaller ionic radius of ytterbium(II) in six-coordination (1.02 vs. 1.17 Å for europium(II) [9]). In the mass spectrum, molecular ions were observed for both Yb[N(SiMe₃)₂]₂(dme)₂ and Yb[N(SiMe₃)₂]₂(dme).
The divalent Yb[N(SiMe$_3$)$_2$]$_2$(dme)$_2$ can be oxidized to the yellow, trivalent Yb[N(SiMe$_3$)$_2$]$_2$I(dme) by reaction with silver iodide in toluene. This reaction therefore represents the only known route to a bis(silylamide)monohalide derivative of a lanthanide. In an attempt to prepare a bis(silylamide)methyl complex of ytterbium(III), methyl lithium was added to a pentane solution of Yb[N(SiMe$_3$)$_2$]$_2$I(dme). Unfortunately, the only product isolated from this reaction was LiN(SiMe$_3$)$_2$.

A bis(diethyl ether) complex, Yb[N(SiMe$_3$)$_2$]$_2$(OEt$_2$)$_2$, can be obtained by the reaction of ytterbium diiodide with one or two equivalents of sodium bis(trimethylsilyl)amide, followed by crystallization from diethyl ether. This is in contrast to the analogous reaction between europium diiodide and sodium bis(trimethylsilyl)amide, from which only NaEu[N(SiMe$_3$)$_2$]$_3$ was obtained from diethyl ether. As the Lewis acidity of Yb[N(SiMe$_3$)$_2$]$_2$ is probably very similar to that of Eu[N(SiMe$_3$)$_2$]$_2$, this difference most likely reflects the smaller ionic radius of ytterbium(II).

The Yb[N(SiMe$_3$)$_2$]$_2$(OEt$_2$)$_2$ is thermochroic, being yellow at -70°C and orange at room temperature. The bonding between the ytterbium and the diethyl ether ligands is strong enough for observation of the parent ion (as an M-3 peak) in the mass spectrum. The mono(diethyl ether) complex is observed as an M-1 peak (567), and as is typical, the base-free ion appears as an M-1 peak (493). The coordinated diethyl ether seems to dissociate readily in aliphatic or aromatic hydrocarbons, in which Yb[(N(SiMe$_3$)$_2$]$_2$(OEt$_2$)$_2$
produces a red solution, since the diethyl ether is easily removed from
the complex by heating to 80°C in toluene.

When the residue from the reaction between ytterbium diiodide and
bis(trimethylsilyl)amide is extracted with toluene, the red sodium salt
NaYb[N(SiMe₃)₂]₃ is obtained. This is possibly due to the
tendency of coordinated diethyl ether to dissociate from
Yb[N(SiMe₃)₂]₂(OEt₂)₂ in toluene, producing the coordinative
unsaturated Yb[N(SiMe₃)₂]₂, which, in the presence of
sodium iodide, disproportionates to NaYb[N(SiMe₃)₂]₃ and YbI₂.
The sodium salt NaYb[N(SiMe₃)₂]₃ is more readily crystallized
from pentane, from which well-formed needles are obtained. The
compound is not isostructural with NaEu[N(SiMe₃)₂]₃, but crystal-
izes in space group Pbca, with Z = 8 [11]. The unit cell volume
(7174 Å³), however, closely resembles that of the europium analogue
(6996 Å³). Refinement of X-ray data for a crystal structure
determination is now in progress [30].

A tetrahydrofuran complex, obtained by reaction of ytterbium
diiodide and sodium bis(trimethylsilyl)amide in tetrahydrofuran, or by
addition of tetrahydrofuran to Yb[N(SiMe₃)₂]₂(OEt₂)₂, proved
somewhat difficult to characterize rigorously. From elemental analyses
and ¹H NMR integrated intensities, the stoichiometry of the compound
appeared to correspond approximately to Yb[N(SiMe₃)₂]₂(tnf)₂.₅,
though the stoichiometry varied slightly from sample to sample.
This orange complex did not give a tetrahydrofuran complex in the mass
spectrum, the highest mass peak observed corresponding to
Yb[N(SiMe₃)₂]₂.
The nitrile t-BuCN readily displaces diethyl ether from Yb[N(SiMe₃)₂]₂(0Et₂)₂. The dark red complex obtained, Yb[N(SiMe₃)₂]₂(NC Bu⁺)₃, has a ν(C≡N) stretching frequency of 2254 cm⁻¹ in its infrared spectrum.

The diethyl ether complex also reacts with phenylacetylene to yield the known divalent phenylacetylide Yb(C≡CPh)₂ [31].

**Phosphine Complexes**

The 4f-metals behave as rather hard Lewis acids in coordination complexes. Much of the organometallic chemistry of these metals is strongly influenced by strong bonding to Lewis bases, many times with bases that are generally involved in the preparative chemistry, such as solvent molecules and halide ions. Lanthanide complexes are also known to form a variety of donor complexes with, for example, ethers, amines, cyanides and isocyanides. In spite of this, only one example of a lanthanide phosphine coordination complex, the black YbCp₃(PPH₃), has been claimed [32]. This raises a question as to whether phosphines can function as good donor ligands to the lanthanides.

Based on the reported heats of formation for donor complexes of the hard Lewis acids H⁺ [33], BMe₃ [34] and GaMe₃ [35], it seemed that phosphine coordination to a lanthanide might not only be energetically feasible, but just as favorable as coordination of nitrogen or oxygen bases (see Table I). It has recently been shown that phosphine complexes of the tervalent actinide metals can be readily prepared [36]. Therefore, it seemed reasonable to expect to observe lanthanide phosphine complexes as stable, isolable species.
Table I. Thermochemical data for formation of some acid-base complexes.

Basicity Towards $H^+$ (gas phase) [33]

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<thead>
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<th>$\Delta H$ (kcal mol$^{-1}$)</th>
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<tr>
<td>$Me_3N$</td>
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<tr>
<td>$Me_3P$</td>
<td>223</td>
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<tr>
<td>$Et_2O$</td>
<td>197</td>
</tr>
<tr>
<td>THF</td>
<td>196</td>
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</table>

$MMe_3 + L \rightleftharpoons MMMe_3 \cdot L$ (gas phase) [34,35]

<table>
<thead>
<tr>
<th>M</th>
<th>L</th>
<th>$\Delta H$ (kcal mol$^{-1}$)</th>
</tr>
</thead>
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</tr>
<tr>
<td></td>
<td>$Me_3P$</td>
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</tr>
<tr>
<td>Ga</td>
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<td>0</td>
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<td></td>
<td>$Me_3P$</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>$Et_2O$</td>
<td>10</td>
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</table>
The preparation of pentane-soluble complexes of Ln[N(SiMe$_3$)$_2$]$_2$ \((\text{Ln} = \text{Eu or Yb})\) with the relatively weak donor ligands N(SiMe$_3$)$_2$ and OEt$_2$ would appear to offer potential routes to phosphine complexes of Ln[N(SiMe$_3$)$_2$]$_2$ via displacement reactions.

This is indeed the case, as sodium bis(trimethylsilyl)amide is readily displaced from the complex NaEu[N(SiMe$_3$)$_2$]$_3$ by 1,2-dimethylphosphinoethane (dmpe) or tri(n-butyl)phosphine in pentane to yield the orange complexes Eu[N(SiMe$_3$)$_2$]$_2$(dmpe)$_{1.5}$ and Eu[N(SiMe$_3$)$_2$]$_2$(PBU$_3$)$_2$, respectively. The presence of the phosphine ligands in these complexes was confirmed by hydrolysis experiments, in which the free phosphines generated were identified by their $^1$H and $^{31}$P{$_1^1$H} NMR spectra. The complex Eu[N(SiMe$_3$)$_2$]$_2$(PBU$_3$)$_2$ has an effective magnetic moment of 7.4 B.M. at 30°C in benzene, as determined by Evans' method. The species Eu[N(SiMe$_3$)$_2$]$_2$(dmpe)$_{1.5}$ was observed in the mass spectrum of Eu[N(SiMe$_3$)$_2$]$_2$(dmpe)$_{1.5}$ (at m/e = 623). The bis[tri(n-butyl)phosphine] complex did not give a molecular ion in the mass spectrum.

The diethyl ether complex, Yb[N(SiMe$_3$)$_2$]$_2$(OEt$_2$)$_2$, also serves as a useful starting material for the preparation of phosphine coordination complexes. Reaction with 1,2-dimethylphosphinoethane in pentane produces the purple Yb[N(SiMe$_3$)$_2$]$_2$(dmpe). This compound exhibits normal, diamagnetic shifts in the $^1$H and $^{13}$C{$_1^1$H} NMR spectra. The $^{31}$P{$_1^1$H} NMR spectrum contains a single resonance due to coordinated dmpe, at $\delta$ -40.9. The coordination chemical shift is therefore 8.5 ppm downfield from the free ligand [37]. A molecular ion, at m/e 644, was observed in the mass spectrum.
A crystal structure of this compound has been determined [12]. An ORTEP view of $\text{Yb}[N(SiMe_3)_2]_2(dmpe)$, which crystallizes in space group $F2\bar{1}d$, with $Z = 8$, is shown in Figure 8. The two silylamine ligands are related by a twofold axis that passes through the Cl-Cl bond and ytterbium. Figures 9 and 10 present some of the distances and angles, respectively, observed in the molecule.

As in $\text{NaEu}[N(SiMe_3)_2]_2$, short metal-carbon(methyl) contacts (3.04 Å) are observed. A number of the observed structural parameters in the silylamine ligand reflect distortions that result from the interaction. The $\text{Si}1$-$\text{C}5$ distance of 1.90 Å has been lengthened relative to the other $\text{Si}1$-$\text{C}$(methyl) distances of 1.86 and 1.87 Å. Likewise, the $\text{N}$-$\text{Si}1$ distance (1.69 Å) is greater than the $\text{N}$-$\text{Si}2$ distance (1.67 Å). Constriction of the $\text{Yb}$-$\text{N}$-$\text{Si}1$ and $\text{N}$-$\text{Si}1$-$\text{C}5$ angles is also apparent. Constraint of the thermal motion in $\text{C}5$ has allowed location of the hydrogen atoms in the $\text{C}5$ methyl groups. These hydrogens are seen to assume nearly tetrahedral positions about the carbon atom, and do not appear to be interacting with the ytterbium atom. This is consistent with a direct ytterbium-carbon interaction.

Phosphine coordination complexes are also formed by the reaction of $\text{Yb}[N(SiMe_3)_2]_2(\text{JEt}_2)_2$ with 1,2-dimethylphosphinomethane (dmpm) and tri(n-butyl)phosphine. The red $\text{Yb}[N(SiMe_3)_2]_2(dmpm)_2$ complex gives a temperature independent (-40 to +25°C) shift in the $\text{^31P\{^1H\}}$ NMR spectrum of $\delta = 44.7$, corresponding to a downfield shift of 11.0 ppm from that of the free ligand [38]. The $\text{^31P\{^1H\}}$ NMR spectrum of brown-red $\text{Yb}[N(SiMe_3)_2]_2(\text{PBu}^n_3)_2$ in $d_6$-benzene contains a resonance at $\delta = 29.6$, coincident with the
Figure 8. An ORTEP drawing of Yb[N(SiMe₃)₂]₂(dmpe).
Figure 9. Some bond distances in the complex Yb[N(SiMe$_3$)$_2$]$_2$(dmpe).
Figure 10. Some bond angles in the complex Yb[N(SiMe$_3$)$_2$]$_2$(dmpe).
Table II. Some physical properties of the Ln[N(SiMe₃)₂]₂-phosphine complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Color</th>
<th>m.p., °C</th>
<th>3¹P{¹H}a</th>
<th>Δb</th>
</tr>
</thead>
<tbody>
<tr>
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<td>94-95</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Eu[N(SiMe₃)₂]₂(PBu₃)₂</td>
<td>orange</td>
<td>48-49</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Yb[N(SiMe₃)₂]₂(dmpe)</td>
<td>purple</td>
<td>195-197</td>
<td>-40.9</td>
<td>8.5</td>
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<tr>
<td>Yb[N(SiMe₃)₂]₂(dmpm)₂</td>
<td>red</td>
<td>60-61</td>
<td>-44.7</td>
<td>11.0</td>
</tr>
<tr>
<td>Yb[N(SiMe₃)₂]₂(PBu₃)₂</td>
<td>brown-red</td>
<td>46-48</td>
<td>-29.6</td>
<td>0</td>
</tr>
<tr>
<td>Yb[N(SiMe₃)₂]₂(diphos)</td>
<td>red</td>
<td>206-209</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

a  All values in ppm (δ) vs. 85 percent H₃PO₄  
b  Downfield shift in ppm from free ligand value.
chemical shift observed for free tri(n-butyl)phosphine [39]. This latter observation suggests a very weak interaction between tri(n-butyl)phosphine and the Yb[N(SiMe₃)₂]₂ fragment, or an extensive dissociation of the phosphine in solution.

The chelating phosphine 1,2-diphenylphosphinoethane (diphos) reacts with the sodium salt NaYb[N(SiMe₃)₂]₃ in pentane to precipitate the red Yb[N(SiMe₃)₂]₂(diphos), which is only sparingly soluble in aromatic hydrocarbons. Some physical properties of the phosphine complexes reported here are listed in Table II.
Chapter 3 References


18. Tulip, T., personal communication.


CHAPTER 4

TRIVALENT PENTAMETHYLCYCLOPENTADIENYL LANTHANIDE COMPLEXES

As a result of difficulties encountered in trying to prepare the monochlorobisamide species, Ln[N(SiMe₃)₂]₂Cl, pentamethylcyclopentadienide (C₅Me₅), another sterically demanding ligand, was used. The known chemistry of this ligand with other large metals suggests that only two C₅Me₅ units can be substituted about the metal atom. Therefore, preparation of (C₅Me₅)₂LnCl derivatives appeared to be straightforward. In the analogous bis(cyclopentadienyl) compounds ([C₅H₅]₂Ln(μ-Cl)]₂ in benzene and (C₅H₅)₂LnCl(thf) in tetrahydrofuran), the metal is formally eight-coordinate, being bound to two cyclopentadienyl groups (three coordinate ligands) and two other donor ligands.

Ytterbium trichloride reacts with two equivalents of LiC₅Me₅ in tetrahydrofuran, and after crystallization from diethyl ether, violet [Li(OEt₂)₂][(C₅Me₅)₂YbCl₂] is obtained as the only product. Though species analogous to the bis(cyclopentadienyl) compounds are not obtained, the coordination number of eight is maintained. Presumably, the steric bulk of the C₅Me₅ ligands prevents formation of the chloro-bridged dimer. The diethyl ether in this anionic complex can be displaced by N,N,N',N'-tetramethylethylenediamine, giving [Li(tmed)][(C₅Me₅)₂YbCl₂]. Anionic complexes of samarium and neodymium, [Li(tmed)][(C₅Me₅)₂SmCl₂], [Li(OEt₂)₂][(C₅Me₅)₂NdCl₂] and [Li(tmed)₂][(C₅Me₅)₂NdCl₂] were prepared in a similar manner.
The solid-state structure of \([\text{Li(\text{OEt}_2)_2}][\text{(C}_5\text{Me}_5)_2\text{YbCl}_2] \)\^[2\] shows the diethyl ether ligands coordinated to lithium with the chlorides bridging ytterbium and lithium. This structure, which is also exhibited by the anionic complexes \([\text{Li(\text{OEt}_2)_2}][\text{(C}_5\text{Me}_5)_2\text{YbI}_2] \) and \([\text{Li(\text{OEt}_2)_2}][\text{(C}_5\text{H}_4\text{SiMePh}_2)_2\text{YbCl}_2] \)\^[2\], is probably maintained in all the above ionic species, except \([\text{Li(tmed)_2}][\text{(C}_5\text{Me}_5)_2\text{NdCl}_2] \). The stoichiometry of this compound suggests separated ion pairs, as in \([\text{n-Bu}_4\text{N}][\text{(C}_5\text{Me}_5)_2\text{YbCl}_2] \) (see below). This difference in structure probably reflects subtle changes in coordination energies and/or lattice energies in going from samarium and ytterbium to the larger neodymium ion.

Isolation of anionic organometallic species has precedent in lanthanide chemistry; other examples include \([\text{Li(thf)_2}][\text{Yb(C}_5\text{H}_4\text{SiMe}_3)_2\text{Cl}_2] \), \([\text{Li(thf)_4}][\text{Yb(CH(SiMe}_3)_2\text{Cl}_2] \) and \([\text{Li(thf)_4}][\text{Yb(CH}_2\text{SiMe}_3)_4] \), reported by Lappert et. al. \^[3\]. Factors that influence relative stabilities for the neutral and anionic complexes are not clear \^[3\], but the stability of the anionic derivatives is most likely related to the strong affinity of these hard metal acids for high coordination numbers and hard donor ligands. By forming organolithium adducts, these metals are therefore able to stabilize species that can be considered as intermediates in alkyl-halide exchange reactions \^[2\].

In an attempt to destabilize the anionic structure, \(\text{NaC}_5\text{Me}_5\) was used as a reagent. Two equivalents of \(\text{NaC}_5\text{Me}_5\) react with \(\text{YbCl}_3\) to give two products, the anionic \([\text{Na(\text{OEt}_2)_2}][\text{(C}_5\text{Me}_5)_2\text{YbCl}_2] \) (33 percent) and \((\text{C}_5\text{Me}_5)_2\text{YbCl}(\text{thf}) \) (42 percent), isolated by fractional crystallization from diethyl ether. Thus, elimination of \(\text{NaCl}\) is more facile than \(\text{LiCl}\) elimination under similar conditions.
When extraction and crystallization are carried out with toluene, 
\((C_5\text{Me}_5)_2\text{YbCl}(\text{thf})\) is obtained as the only product. The 
coordinated tetrahydrofuran in this molecule is readily identified by 
infrared absorptions at 1014 and 862 cm\(^{-1}\). The \((C_5\text{Me}_5)_2\text{YbCl}(\text{thf})\) 
was prepared independently from the divalent \(\text{Yb}(C_5\text{Me}_5)_2(\text{thf})\) and 
\(\text{CH}_2\text{Cl}_2\) or \(\text{YbCl}_3\) (see Chapter 6). It can also be prepared from 
\((C_5\text{Me}_5)_2\text{YbCl}_2\text{AlCl}_2\) and tetrahydrofuran [2].

The salt \([\text{Na}(\text{OEt}_2)_2][(C_5\text{Me}_5)_2\text{YbCl}_2]\) yields the complex
\([\text{Na}(\text{tmed})][(C_5\text{Me}_5)_2\text{YbCl}_2]\) upon reaction with
\(\text{N,N,N',N'-tetramethylethylendiamine}\). Data for a crystal structure
determination were collected on crystals of this complex, but it could
not be refined properly [4]. A disorder in the hydrocarbon ligands
allowed only the heavy atoms (Yb, Cl and Na) to be located. These
atoms form the bridged structure I (Figure 1), analogous to
\([\text{Li}(\text{OEt}_2)_2][(C_5\text{Me}_5)_2\text{YbCl}_2]\). The magnetic susceptibility
of \([\text{Na}(\text{OEt}_2)_2][(C_5\text{Me}_5)_2\text{YbCl}_2]\) follows Curie-Weiss behavior
from 4 to 45 K, the effective magnetic moment being 3.91 B.M.
\((\Theta = -3.7 K \text{ and } C = 1.90); \) the magnetic moment of
\((C_5\text{Me}_5)_2\text{YbCl}(\text{thf})\) at 28°C (Evans' method) is 4.20 B.M.

The \([\text{Na}(\text{OEt}_2)_2][(C_5\text{Me}_5)_2\text{YbCl}_2]\) can be converted
quantitatively to the neutral, trivalent, tetrahydrofuran complex by
stirring it in toluene with a small amount of tetrahydrofuran present.
This observation suggests that in the reaction of \(\text{NaC}_5\text{Me}_5\) with
\(\text{YbCl}_3\), the salt \([\text{Na}(\text{thf})_2][(C_5\text{Me}_5)_2\text{YbCl}_2]\) is formed
initially, which then eliminates \(\text{NaCl}\) in solvents less polar than
Figure 1. Structure of $[\text{Na(tmed)}][\text{C}_5\text{Me}_5]_2\text{YbCl}_2$.
\[ \text{I} \]

Diagram of a chemical compound with labels Yb, Cl, Na, Me₂, and N.
tetrahydrofuran. The analogous lithium salts appear to be much more stable with respect to loss of LiCl, since they do not undergo this disproportionation in toluene-tetrahydrofuran mixtures.

Attempts to obtain the base-free species, \((\text{C}_5\text{Me}_5)_2\text{YbCl}\), by sublimation of the tetrahydrofuran or anionic complexes failed (see Experimental Section). However, \((\text{C}_5\text{Me}_5)_2\text{YbCl}\) is observed as the highest mass peak in the mass spectrum of \((\text{C}_5\text{Me}_5)_2\text{YbCl}(\text{thf})\). The tetrahydrofuran in this complex may be displaced by nitrogen bases; pyridine and diethyl amine yield \((\text{C}_5\text{Me}_5)_2\text{YbCl}(\text{py})\) and \((\text{C}_5\text{Me}_5)_2\text{YbCl}(\text{NHe}\text{t}_2)\), respectively. However, diisopropyl amine does not displace tetrahydrofuran from \((\text{C}_5\text{Me}_5)_2\text{YbCl}(\text{thf})\).

Crystals of \((\text{C}_5\text{Me}_5)_2\text{YbCl}(\text{thf})\) were unsuitable for a single-crystal X-ray analysis due to twinning, and \((\text{C}_5\text{Me}_5)_2\text{YbCl}(\text{py})\) appeared to have a stacking disorder [4].

The reaction between neodymium trichloride and two equivalents of NaC\(_5\)Me\(_5\) in tetrahydrofuran also yields two products after crystallization from diethyl ether, blue \([\text{Na(OEt}_2]_2[(\text{C}_5\text{Me}_5)_2\text{NdCl}_2]\) and green \((\text{C}_5\text{Me}_5)_2\text{NdCl}(\text{thf})\). The latter complex has the same infrared spectrum as \((\text{C}_5\text{Me}_5)_2\text{YbCl}(\text{thf})\). The \((\text{C}_5\text{Me}_5)_2\text{NdCl}(\text{thf})\) is obtained as the only product if extraction and crystallization are carried out with pentane. The only product isolated from samarium trichloride and NaC\(_5\)Me\(_5\) under similar conditions was \([\text{Na(OEt}_2]_2[(\text{C}_5\text{Me}_5)_2\text{SmCl}_2]\). The sodium salts of neodymium and samarium, which give identical infrared spectra, differ from \([\text{Na(OEt}_2]_2[(\text{C}_5\text{Me}_5)_2\text{YbCl}_2]\) in containing less diethyl ether and in not eliminating NaCl upon stirring in toluene in the presence
of tetrahydrofuran. The tmed complex $[\text{Na(tmed)}][(C_5\text{Me}_5)_2\text{SmCl}_2]$, however, does appear to be isostructural with the ytterbium analogue (by ir).

The mono-ring complex, $[\text{Na(OEt}_2)_2][(C_5\text{Me}_5)_2\text{NdCl}_3]$, which is simply a $\text{NaC}_5\text{Me}_5(\text{OEt}_2)_2$-adduct of $\text{NdCl}_3$, can be isolated from one molar equivalent of $\text{NaC}_5\text{Me}_5$ and $\text{NdCl}_3$ in tetrahydrofuran, followed by crystallization from diethyl ether. All the above chloride species and some of their physical properties are listed in Table 1.

It was of interest to explore the utility of the $[(C_5\text{Me}_5)_2\text{YbCl}_2]^-$ and $(C_5\text{Me}_5)_2\text{YbCl(thf)}$ species as starting materials for the preparation of more reactive $(C_5\text{Me}_5)_2\text{YbX}$ ($X = \text{alkyl, hydride, borohydride, amide, etc.}$) derivatives. The neutral, base-free systems are of interest, since these coordinatively unsaturated species are expected to exhibit an extensive reaction chemistry and to lead to compounds of unusual structural types. These compounds might also serve as routes to base-free divalent compounds, if reduction in a non-coordinating solvent can be effected. However, the lanthanide metals in these systems are quite tenacious in maintaining an eight-coordinate environment.

Watson has shown that reactions of $[(C_5\text{Me}_5)_2\text{YbCl}_2]^-$ with $\text{MeLi}$ lead to $[(C_5\text{Me}_5)_2\text{Yb(Me)Cl}]^-$, $[(C_5\text{Me}_5)_2\text{YbMe}_2]^-$, and $(C_5\text{Me}_5)_2\text{YbMe(thf)}$, depending upon reaction conditions [5]. The Grignard reagent, $\text{PhMgBr}$, reacts with $(C_5\text{Me}_5)_2\text{YbCl(py)}$ to give $(C_5\text{Me}_5)_2\text{YbClBrMgPh(py)}$. This compound probably has a
<table>
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<td>[Li(OEt₂)₂][([C₅Me₅]₂NdCl₂)</td>
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<tr>
<td>(C₅Me₅)₂NdCl(thf)</td>
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<td>221-223</td>
<td>violet</td>
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<tr>
<td>(C₅Me₅)₂YbCl(NH₂Et₂)</td>
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<td>purple</td>
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structure similar to 1, with the halide ligands bridging the ytterbium and magnesium atoms. Reaction of \([n-\text{Bu}_4\text{N}][\text{BH}_4]\) with 
\([\text{Li}(\text{OEt}_2)_2][(\text{C}_5\text{Me}_5)_2\text{YbCl}_2]\) in toluene did not lead to a borohydride derivative, but to \([n-\text{Bu}_4\text{N}][(\text{C}_5\text{Me}_5)_2\text{YbCl}_2]\), the stoichiometry of which can be derived from the \(^1\text{H}\) NMR spectrum. Broadened, shifted singlets were observed at \(6.10\) \((8\text{H})\), \(6.75\) \((8\text{H})\), \(4.45\) \((8\text{H})\), \(3.52\) \((30\text{H})\) and \(2.85\) \((12\text{H})\) (Figure 2).

The simplest approach to preparing neutral, seven-coordinate \((\text{C}_5\text{Me}_5)_2\text{LnX}\) is to incorporate an \(X\) group that is bulky enough to prevent coordination of another base. The silylamides 
\((\text{C}_5\text{Me}_5)_2\text{LnN(\text{SiMe}_3}_2)\), where \(\text{Ln}\) is Nd or Yb, have been prepared from \([\text{Li}(\text{OEt}_2)_2][(\text{C}_5\text{Me}_5)_2\text{NdCl}_2]\) and \((\text{C}_5\text{Me}_5)_2\text{YbCl(py)}\), respectively, with sodium bis(trimethylsilyl)amide. These compounds have infrared spectra identical to the related monomeric uranium(III) derivative, \((\text{C}_5\text{Me}_5)_2\text{UN(\text{SiMe}_3}_2\) [6]. In an attempt to prepare the base-free divalent compound, \(\text{Yb}(\text{C}_5\text{Me}_5)_2\), \((\text{C}_5\text{Me}_5)_2\text{YbN(\text{SiMe}_3}_2\) was refluxed with sodium amalgam in toluene, but no reduction was observed. In an attempt to prepare the amide complex 
\((\text{C}_5\text{Me}_5)_2\text{YbNET}_2\), \([\text{Li}(\text{OEt}_2)_2][(\text{C}_5\text{Me}_5)_2\text{YbCl}_2]\) was reacted with \(\text{LiNET}_2\) in diethyl ether. A small amount of insoluble material was formed, and most of the \([\text{Li}(\text{OEt}_2)_2][(\text{C}_5\text{Me}_5)_2\text{YbCl}_2]\) remained unreacted (see Experimental Section).

Use of chelating, four-electron donor ligands could yield neutral, base-free complexes which are still eight-coordinate. Such compounds might then be useful in preparing base-free divalent complexes by
Figure 2. $^1\text{H}$ NMR spectrum of $[\text{n-Bu}_4\text{N}][\text{(C}_5\text{Me}_5)_2\text{YbCl}_2]$.
reduction in a non-coordinating solvent. Since carboxylate (RCO$_2^-$) ligands have been effectively utilized as leaving groups in transition metal chemistry, they seemed ideally suited. Another chelating ligand, diethylidithiocarbamate (Et$_2$NCS$^-$) is electronically similar, but contains the softer sulfur atoms as donors. Derivatives of both of these ligands were prepared as shown:

$$\text{NaO}_2\text{CR} \xrightarrow{\text{[Na(OEt$_2$)$_2$][C$_5$Me$_5$)$_2$YbCl$_2$]} \quad \begin{array}{c} \text{R = CF$_3$ or CMe$_3$} \\ \text{NaS$_2$CNET$_2$} \end{array} \xrightarrow{\text{[C$_5$Me$_5$)$_2$Yb(S$_2$CNET$_2$)}}$$

The analogous neodymium dithiocarbamate, (C$_5$Me$_5$)$_2$Nd(S$_2$CNET$_2$), was prepared similarly. The physical properties of these compounds are described in the experimental section.

Because two donor atoms are present, RCO$_2^-$ and Et$_2$NCS$^-$ yield ether-free complexes. Unfortunately the ytterbium(III) species could not be reduced with sodium-amalgam in refluxing toluene. Dubec has reported (C$_5$H$_5$)$_2$Ln(O$_2$CR) derivatives [1], which are dimeric in solution, with bridging carboxylates. The (C$_5$Me$_5$)$_2$Yb(O$_2$CMe$_3$) gives dimeric fragments in the mass spectrum, suggesting that it is associated in a similar fashion.

The similarity in the magnetic behavior of (C$_5$Me$_5$)$_2$Yb(O$_2$CMe$_3$) and (C$_5$Me$_5$)$_2$Yb(S$_2$CNET$_2$) at low temperature suggests that the magnetic properties of the ytterbium ions in these complexes are not greatly effected by the change from carboxylate to dithiocarbamate
ligand. The effective magnetic moments (5-45K) of 3.29 and 3.39 B.M., respectively, are close in value to those of other ytterbium(III) complexes in this temperature range (cf. Yb[N(SiMe₃)₂]₃, 3.10 B.M. and [(C₅H₅)₃Yb]₂(pyrazine) [7], 3.48 B.M.).

Figure 3, which shows the ¹H NMR spectrum of (C₅Me₅)₂Yb(S₂CNET₂), illustrates the usefulness of NMR data in characterizing these paramagnetic complexes. Though proton-proton coupling is lost due to line broadening, the integrated intensities confirm the stoichiometry of the complex.

Because little is known about the properties of sulfur-based ligands in molecular lanthanide systems, an X-ray crystal structure determination of (C₅Me₅)₂Yb(S₂CNET₂) was also undertaken [8]. Crystal structures have appeared for Na[La(S₂CNET₂)₄] [9] and Ln[S₂P(C₆H₁₁)₂]₃, where Ln is Sm, Pr, Dy and Lu [10,11].

Figure 4 shows the ytterbium atom bonded to two pentamethylcyclopentadienyl rings and to the two sulfur atoms of the diethylthiocarbamate ligand. The diethylthiocarbamate ligand is disordered; the atoms N, C(12A), C(13A), C(12B), and C(13B) are in general positions with half of the molecules in the conformation shown, and half in the conformation that would result from a 180° rotation about the two-fold axis. The (C₅Me₅)₂Yb fragment has perfect C₂ symmetry.

The ytterbium-carbon distances average 2.63 ± 0.03 Å and the ytterbium-sulfur distance is 2.70 Å. The metal atom is 2.33 Å from the mean plane defined by the C(1)-C(5) ring. The five methyl carbon atoms of the C₅Me₅ group are all bent out of the mean plane away from
Figure 3. $^1$H NMR spectrum of $(C_5Me_5)_2Yb(S_2CNMe_2)$. 
$(C_5\text{Me}_5)_2Yb(S_2\text{CNEt}_2)$
Figure 4. ORTEP drawing of \((\text{C}_5\text{Me}_5)_2\text{Yb(S}_2\text{CNEt}_2)\).
ytterbium; the distances from the planes for these methyl carbon atoms are 0.18, 0.19, 0.07 and 0.34 Å for atoms C(6)-C(10). The pentamethylcyclopentadienyl rings are in a staggered conformation with respect to each other (see Figure 5).
Figure 5. ORTEP view of \((C_5Me_5)_2 Yb(S_2CNEt_2)\) down the ring center-ring center vector.
Chapter 4 References


CHAPTER 5
DIVALENT PENTAMETHYLCYCLOPENTADIENYL LANTHANIDE COMPLEXES

Ether Complexes

In contrast to the trichlorides of neodymium, samarium and ytterbium, europium trichloride does not yield a trivalent compound upon reaction with two equivalents of NaC\textsubscript{5}Me\textsubscript{5} in tetrahydrofuran. The product isolated after crystallization from toluene is the red, divalent Eu(C\textsubscript{5}Me\textsubscript{5})\textsubscript{2}(thf). Thus, NaC\textsubscript{5}Me\textsubscript{5} appears to be a reducing agent towards EuCl\textsubscript{3}. In support of this, reaction of EuCl\textsubscript{3} with three equivalents of NaC\textsubscript{5}Me\textsubscript{5} in tetrahydrofuran generates the europium(II) compound in higher yield (65-70 percent). The reduction of europium(III) to europium(II) by the C\textsubscript{5}Me\textsubscript{5}\textsuperscript{−} anion is not all that surprising, considering the small Eu(III)/Eu(II) reduction potential (ca. -0.4 V, as estimated from spectroscopic data [1]). The less reducing parent anion, C\textsubscript{5}H\textsubscript{5}\textsuperscript{−}, is known to reduce Ta(V) to Ta(IV) [2], Ti(IV) to Ti(III) [3] and Re(V) to Re(III) [4].

It is interesting to note that the tris(cyclopentadienyl) compound EuCp\textsubscript{3} was not reported in the original description of other tris-(cyclopentadienyl)lanthanide complexes, which were purified by sublimation [5]. The apparent decomposition of this compound upon attempted vacuum sublimation is most likely related to the stability of the divalent oxidation state. This compound was later isolated as a mono-tetrahydrofuranate adduct by crystallization from tetrahydrofuran [6]. The tris(monomethylcyclopentadienyl) complex, Eu(C\textsubscript{5}H\textsubscript{4}Me\textsubscript{3})(thf), is also readily prepared [7].
These observations suggest an increase in the reducing power of the cyclopentadienyl group upon substitution of hydrogens for electron-donating methyl groups. The He(I) and He(II) photoelectron spectra of substituted ferrocenes shows that this inductive effect of the methyl groups causes the first ionization energy from the ligand to drop by ca. 0.2 eV in going from Fe(n-C$_5$H$_5$)$_2$ to Fe(n-C$_5$H$_4$Me)$_2$, and by ca. 1.0 eV in going from Fe(n-C$_5$H$_5$)$_2$ to Fe(n-C$_5$Me$_5$)$_2$ [8].

The divalent complex Eu(C$_5$Me$_5$)$_2$(thf) is quite soluble in aromatic hydrocarbons and sparingly soluble in aliphatic hydrocarbons. From diethyl ether, it crystallizes with one molar equivalent of diethyl ether to give Eu(C$_5$Me$_5$)$_2$(thf)(OEt)$_2$. The diethyl ether can be removed by recrystallization from toluene, suggesting that it is weakly bound or simply present as solvent of crystallization.

The oxidation state of europium was confirmed by a low temperature magnetic susceptibility study, which shows that Eu(C$_5$Me$_5$)$_2$(thf)(OEt)$_2$ follows Curie behavior from 5-50K, with $\mu_{\text{eff}} = 7.99$ B.M. and $C = 7.91$. This magnetic behavior is that expected for the $^8S_{7/2}$ ground state term of 4f$^7$ ions [9].

The related ytterbium(II) complex, Yb(C$_5$Me$_5$)$_2$(thf), can be obtained from ytterbium dichloride and two molar equivalents of NaC$_5$Me$_5$ in refluxing tetrahydrofuran. This complex is red and diamagnetic, as expected for a closed-shell 4f$^{14}$ electron configuration ($^1S_0$). Accordingly, normal, diamagnetic $^1H$ and $^{13}C$($^1H$) nuclear magnetic resonance parameters are observed. The proton chemical shift attributed to the C$_5$Me$_5$ ligand is temperature
dependent, ranging from 1.98 ppm at 80°C to 2.18 ppm at -50°C. The
tetrahydrofuran resonances are also temperature dependent. Between
+80 and -50°C the center of the multiplet due to the α-protons ranges
from 4.02 to 3.30 ppm, and those due to the β-protons range from 1.81
to 1.32 ppm.

The \( ^{13}C\{1\}^{1}H \) NMR resonances for the \( C_5Me_5 \) ligand of some
divalent ytterbium compounds are listed in Table I, along with those
of other diamagnetic pentamethylcyclopentadienyl complexes. It is to
be noted that the observed shifts of the ytterbium(II) derivatives are
comparable to those observed in compounds of the more electropositive
metals.

A good correlation between aromatic carbon-13 chemical shifts and
electron populations in aromatic systems has been established [10,11].
An increase in the π-electron density at a carbon atom will result in
a downfield shift of that carbon atom, by ca. 180 ppm per unit charge
density for benzene rings [12]. Therefore, the observed shifts of the
\( C_5Me_5 \) ring carbons may be a measure of the amount of electron
density that a \( C_5Me_5 \) ring is donating to a metal. Such a correla-
tion has been attempted for carbon-13 shifts in cyclooctatetraene
derivatives of thorium [13]. It appears that more charge density is
localized on the \( C_5Me_5 \) rings for the early transition metals than
for ytterbium(II), despite the strongly reducing character of
ytterbium(II) (vide infra). Also, it appears that the \( C_5Me_5 \) anion
donates more electron density to the later transition metals than to
ytterbium(II).
Table I. $^{13}\text{C}^{1\text{H}}$ NMR data for diamagnetic C$_5$Me$_5$ Compounds.$^a$

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ring C</th>
<th>Methyl C</th>
<th>Solvent</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na[(C$_5$Me$_5$)$_2$Mn]</td>
<td>72</td>
<td>8.5</td>
<td>d$_8$-tnf</td>
<td>b</td>
</tr>
<tr>
<td>(C$_5$Me$_5$)$_2$Fe</td>
<td>78</td>
<td>9.6</td>
<td>d$_6$-PnH</td>
<td>b</td>
</tr>
<tr>
<td>[(C$_5$Me$_5$)$_2$Co]PF$_6$</td>
<td>93</td>
<td>6.3</td>
<td>d$_6$-Me$_2$CO</td>
<td>b</td>
</tr>
<tr>
<td>(C$_5$Me$_5$)$_2$Rh(S$_2$CNMe)$_2$</td>
<td>97</td>
<td>9.3</td>
<td>CDCl$_3$</td>
<td>c</td>
</tr>
<tr>
<td>[Rh$_4$H$_4$(C$_5$Me$_5$)$_4$]$_2$</td>
<td>102</td>
<td>12.1</td>
<td>d$_6$-Me$_2$CO</td>
<td>d</td>
</tr>
<tr>
<td>[(C$_5$Me$_5$)$_2$V(CO)$_2$]PF$_6$</td>
<td>107</td>
<td>9.3</td>
<td>d$_6$-Me$_2$CO</td>
<td>b</td>
</tr>
<tr>
<td>(C$_5$Me$_5$)$_2$Yb(thf)</td>
<td>111</td>
<td>11.5</td>
<td>d$_8$-PhMe</td>
<td>this work</td>
</tr>
<tr>
<td>(C$_5$Me$_5$)$_2$Yb(MeOC$_2$H$_3$)</td>
<td>112</td>
<td>11.5</td>
<td>d$_6$-PhH</td>
<td>this work</td>
</tr>
<tr>
<td>(C$_5$Me$_5$)$_2$Yb(dmpm)</td>
<td>112</td>
<td>12.0</td>
<td>d$_6$-PhH</td>
<td>this work</td>
</tr>
<tr>
<td>(C$_5$Me$_5$)Ta(CHCMe$_3$)(CH$_2$CMe$_3$)$_2$</td>
<td>114</td>
<td>12.1</td>
<td>d$_6$-PhH</td>
<td>e</td>
</tr>
<tr>
<td>(C$_5$Me$_5$)$_2$Zr(H)(OCHNbcP$_2$)</td>
<td>116</td>
<td>7.8</td>
<td>d$_6$-PhH</td>
<td>f</td>
</tr>
<tr>
<td>(C$_5$Me$_5$)$_2$TiMe$_2$</td>
<td>119</td>
<td>17.8</td>
<td>d$_8$-PhMe</td>
<td>g</td>
</tr>
<tr>
<td>(C$_5$Me$_5$)Ta(CH$_2$CMe$_3$)$_2$Cl$_2$</td>
<td>124</td>
<td>12.8</td>
<td>d$_6$-PhH</td>
<td>e</td>
</tr>
</tbody>
</table>

$^a$ All values in ppm (δ) vs. tetramethysilane.


The Yb(C$_5$Me$_5$)$_2$(thf) forms a hemi-toluene solvate, Yb(C$_5$Me$_5$)$_2$(thf) 1/2PhMe, upon crystallization from toluene. Crystals of this compound are monoclinic (P2$_1$/n) with Z = 4 [14]. An ORTEP diagram (Figure 1) shows the ytterbium atom bonded to two n$_5$C$_5$Me$_5$ ligands and the oxygen atom of tetrahydrofuran. The Yb(C$_5$Me$_5$)$_2$(thf) molecule has approximate C$_2$ symmetry about the ytterbium-oxygen bond. The toluene molecules are disordered between two positions in the lattice [14].

The coordination about ytterbium is very close to planar, with a C$_5$Me$_5$ centroid-Yb-C$_5$Me$_5$ centroid angle of 143.5(3)$^\circ$ and centroid-Yb-0 angles of 107.73(3)$^\circ$ and 108.8(3)$^\circ$. The close approach of the C$_5$Me$_5$ rings results in severe displacements of methyl carbons C9, C16, and C17 from the planes of their respective C$_5$ rings (0.18, 0.14 and 0.21 Å, respectively). Other methyl carbon displacements range from 0.03 to 0.11 Å. Figure 2 is a projection of the two C$_5$Me$_5$ rings down the ring centroid-ring centroid vector, showing the staggered conformation of the rings.

The average ytterbium-carbon bond length (2.66 ± 0.02 Å) less the ionic radius of ytterbium(II) in seven coordination (counting C$_5$Me$_5$ as a three-coordinate ligand) of 1.08 Å [15] yields 1.58 Å for the effective ionic radius of the pentamethycyclopentadienide group. This value is similar to those observed for other lanthanide and actinide cyclopentadienide compounds (1.64 ± 0.04 Å) in which the metal-ring bonding is considered to be primarily ionic [16]. The ytterbium-oxygen distance, 2.412(5) Å, less the ytterbium(II) ionic radius gives 1.33 Å as the ionic radius of a three-coordinate oxygen atom. A value of 1.36 Å has been suggested by Shannon [15].
Figure 1. ORTEP diagram of Yb(C₅Me₅)₂(thf).
Figure 2. A view of \((C_5Me_5)_2Yb(thf)\) down the ring centroid-ring centroid vector, showing the staggered conformation of the \(C_5Me_5\) rings.
Under less forcing conditions one can obtain the diethyl ether complex \( \text{Yb(C}_5\text{Me}_5\text{)}_2(\text{OEt}_2) \) by the room temperature reaction of ytterbium diiodide and two equivalents of \( \text{NaC}_5\text{Me}_5 \) in diethyl ether. This complex is bright green and diamagnetic. The red europium(II) analogue, \( \text{Eu(C}_5\text{Me}_5\text{)}_2(\text{OEt}_2) \), can be prepared in a similar manner.

The crystal structure of \( \text{Yb(C}_5\text{Me}_5\text{)}_2(\text{OEt}_2) \) [17], by Watson and Harlow, shows the low-valent, coordinatively-unsaturated ytterbium center interacting with the methyl groups of the diethyl ether ligand. This interaction, which is most likely analogous to the metal-carbon interactions observed in \( \text{Yb}[\text{N(SiMe}_3\text{)}_2]_2(\text{dmpe}) \) and \( \text{NaEu}[\text{N(SiMe}_3\text{)}_2]_2 \), results in rather short ytterbium-methyl carbon contacts as shown:
This unusual bonding mode for diethyl ether may be responsible for the
dramatic difference in color between Yb(C₅Me₅)₂(thf) (red) and
Yb(C₅Me₅)₂(OEt₂) (green).

Tetrahydrofuran is a better base towards Yb(C₅Me₅)₂ than
diethyl ether, since tetrahydrofuran displaces diethyl ether almost
quantitatively from Yb(C₅Me₅)₂(OEt₂). Some lability of the
tetrahydrofuran ligand can be observed in the presence of excess
diethyl ether, since upon recrystallization of Yb(C₅Me₅)₂(thf)
from diethyl ether, small yields (ca. 10 percent) of
Yb(C₅Me₅)₂(OEt₂) are obtained.

Attempts to remove the ether ligands from the above compounds to
give the base-free complex have failed. The Eu(C₅Me₅)₂(thf)
compound gives small amounts of an orange sublimate at ca. 145°C and
10⁻² mm Hg. This impure orange sublimate could not be purified by
fractional crystallization. The Yb(C₅Me₅)₂(thf) compound gave
an orange sublimate at 125°C/10⁻² mm Hg in ca. 40 percent yield.
This material, which was impure (m.p. 122-140°C), gave peaks in the
infrared spectrum at 3692 and 3648 cm⁻¹ (possibly due to an –OH
group); the presence of tetrahydrofuran was indicated by absorptions
at 1020 and 890 cm⁻¹. The same material, which could not be fully
characterized due to the small quantity obtained, is also formed by
refluxing Yb(C₅Me₅)₂(thf) in p-xylene. The diethyl ether
complex, Yb(C₅Me₅)₂(OEt₂), decomposes without subliming at ca.
120°C and 10⁻² mm Hg. The fact that the bis(cyclopentadienyl)
complexes of europium(II) and ytterbium(II) can be sublimed under
vacuum at 400-420°C [18] suggests that the $C_5\text{Me}_5$ derivatives, which have a lower coordination number and a more electron-rich metal, have a lower energy decomposition pathway, possibly via reaction with the ether ligands.

Apparently, reactions of the tetrahydrofuran compounds with Lewis acids do not result in simple transfer of the tetrahydrofuran ligand to the added Lewis acids. The reaction of $\text{Yb}(C_5\text{Me}_5)_2(\text{thf})$ with $\text{AlCl}_3$ or $\text{BBr}_3$ gave a red solid (containing halide) that was insoluble in pentane, toluene and diethyl ether. A mixture of products that could not be purified was obtained by the reaction of $\text{Eu}(C_5\text{Me}_5)_2(\text{thf})$ with $\text{AlMe}_3$.

A methyl vinyl ether complex, $\text{Yb}(C_5\text{Me}_5)_2(\text{MeOC}_2\text{H}_3)$ was prepared from $\text{YbI}_2$, $\text{NaC}_5\text{Me}_5$ and methyl vinyl ether in toluene. The green color of this compound suggests a ytterbium-carbon interaction of the type observed for $\text{Yb}(C_5\text{Me}_5)_2(\text{OEt}_2)$. Methyl vinyl ether appears to be a better donor than diethyl ether toward $\text{Yb}(C_5\text{Me}_5)_2$, since $\text{Yb}(C_5\text{Me}_5)_2(\text{MeOC}_2\text{H}_3)$ can be crystallized unchanged from diethyl ether. Methyl vinyl ether is displaced, however, by tetrahydrofuran and pyridine.

Addition of $\text{OPPh}_3$ to $\text{Yb}(C_5\text{Me}_5)_2(\text{OEt}_2)$ in diethyl ether, followed by crystallization of the precipitate from tetrahydrofuran-dietynyl ether gives purple $\text{Yb}(C_5\text{Me}_5)_2(\text{thf})(\text{OPPh}_3)$. The tetrahydrofuran is lost in the mass spectrometer, since only $\text{Yb}(C_5\text{Me}_5)_2(\text{OPPh}_3)$ was observed in the mass spectrum.
The preparation of these coordination complexes establishes the utility of the bulky C₅Me₅ ligand in preparing a new class of monomeric, hydrocarbon-soluble divalent complexes. Though the divalent ionic radii are greater than the trivalent radii for a given coordination number, the divalent C₅Me₅ compounds often form seven-coordinate complexes, in contrast to the trivalent C₅Me₅ derivatives, which are typically eight-coordinate. This suggests that the lower oxidation state results in a softer, more electron-rich metal center that may exhibit reaction chemistry that has not been observed in lanthanide systems. We are now in a position to study the chemistry of these reduced metal species in non-coordinating hydrocarbon solvents.

**Amine Complexes**

Aromatic amines displace tetrahydrofuran or diethyl ether from the europium(II) and ytterbium(II) complexes to yield the eight-coordinate compounds listed in Table II. These compounds are very intensely colored, and except for Yb(C₅Me₅)₂(bipy), are only sparingly soluble in non-coordinating hydrocarbons. Solution properties are therefore difficult to study. However, normal, diamagnetic ¹H NMR shifts are observed for Yb(C₅Me₅)₂(py)₂ and Yb(C₅Me₅)₂(p-Me₂NC₅H₅)₂ at room temperature.

Diamagnetic NMR shifts are not observed for Yb(C₅Me₅)₂(bipy). The resonance for the C₅Me₅ protons in the ¹H NMR spectrum was shifted ca. 2 ppm downfield to δ 4.11 (J₁/₂ = 9 Hz). The proton chemical shifts for the bipyridine ligand could not be assigned, but broadened peaks were observed at δ 25.62, 5.24 and -13.11. The two...
<table>
<thead>
<tr>
<th>Compound</th>
<th>Color</th>
<th>Melting Point</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu(C₅Me₅)₂(bipy)</td>
<td>brown</td>
<td>&gt; 300°C</td>
</tr>
<tr>
<td>Yb(C₅Me₅)₂(bipy)</td>
<td>brown</td>
<td>&gt; 300°C</td>
</tr>
<tr>
<td>Yb(C₅Me₅)₂(py)₂</td>
<td>green</td>
<td>208-210°C</td>
</tr>
<tr>
<td>Yb(C₅Me₅)₂(p-Me₂NC₅H₅N)₂</td>
<td>blue</td>
<td>241-242°C</td>
</tr>
</tbody>
</table>
resonances due to the C₅Me₅ group were the only resonances observed in the ¹³C{¹H} spectrum. The ring and methyl carbon resonances, which were assigned from the coupled spectrum, were shifted upfield to -42.2 and -3.35 ppm, respectively.

These NMR data suggest that Yb(C₅Me₅)₂(bipy) is paramagnetic. This is substantiated by the effective magnetic moment, 2.4 B.M. (30°C, C₆H₆), measured by the Evans method. This moment is much lower than the value of ca. 4.5 B.M. expected for ytterbium(III) at 30°C [9]. The most straightforward explanation for the magnetic behavior is that the reducing ytterbium(II) ion has transferred some electron density to the π-system of the bipyridine ligand. If bipy accepts an electron to generate the bipy radical anion, bipy⁻, two unpaired electrons would result—one on the metal (now ytterbium(III), r¹³) and one on bipy. The two unpaired electrons must then be interacting antiferromagnetically, since the observed moment is much less than that expected for two unpaired electrons. This type of intramolecular antiferromagnetic exchange has been postulated for the compounds Yb(bipy)₄ (μₑff = 2.79 B.M. at 34°C), Yb(o-phen)₄ (μₑff = 2.78 B.M. at 34°C) and Eu(bipy)₄ (μₑff = 5.74 B.M. at 34°C) [19]. As with these binary compounds, a simple bonding explanation for Yb(C₅Me₅)₂(bipy) is not possible, since the valence 4f electrons are well-shielded from ligand orbitals by the 5S²5p⁶ shell. It is difficult to ascertain whether promotion of a 4f electron to a 5d orbital to generate a more covalent bonding interaction with the unpaired bipy electron is energetically feasible. A similar situation exists for Cp₂Ti(bipy),
in which weak paramagnetism can be explained in terms of a thermally accessible triplet system, \( \text{Cp}_2\text{Ti(III)(bipy)} \) [20]. This triplet state lies just above a singlet ground state in energy, so that both states contribute to observed magnetic moments at temperatures above -196°C. Values reported for the reduction of free bipyridine range from -1.30 to -1.87 V, depending on the solvent [25]. Since the oxidation potential of Yb(II) is only about 1.1 V, it appears as though coordination of bipyridine to the Yb(II) ion must promote the electron transfer.

The low-temperature susceptibility data for \( \text{Yb(C}_5\text{Me}_5\text{)}_2\text{(bipy)} \), \( \text{Yb(C}_5\text{Me}_5\text{)}_2\text{(py)}_2 \) and \( \text{Yb(C}_5\text{Me}_5\text{)}_2\text{(p-Me}_2\text{NC}_5\text{H}_5\text{N)}_2 \), plotted as \( \mu_{\text{eff}} \) vs. temperature, are presented in Figure 3. All three compounds show very weak paramagnetism, with effective magnetic moments ranging from 0.56 to 0.98 B.M. for \( \text{Yb(C}_5\text{Me}_5\text{)}_2\text{(bipy)} \), 0.45 to 0.53 B.M. for \( \text{Yb(C}_5\text{Me}_5\text{)}_2\text{(py)}_2 \) and 0.57 to 0.69 B.M. for \( \text{Yb(C}_5\text{Me}_5\text{)}_2\text{(p-Me}_2\text{NC}_5\text{H}_5\text{N)}_2 \). Unfortunately, the errors in these values are very large (25-50 percent), since the values measured approach the sensitivity of the magnetometer. Therefore, the observed magnetic behavior might be due to small amounts of trivalent impurities. However, this seems unlikely, since the \( \text{Yb(C}_5\text{Me}_5\text{)}_2\text{(thf)} \) complex, of comparable air-sensitivity, showed the expected negative values for diamagnetism over the same temperature range, when manipulations and measurements were conducted in a similar manner. The europium(II) complex \( \text{Eu(C}_5\text{Me}_5\text{)}_2\text{(bipy)} \) shows perfectly normal magnetic behavior from 5-600K, following Curie behavior with an effective moment of 7.73 B.M. (C = 7.41).
Figure 3. Effective magnetic moments as a function of temperature for $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{bipy})$, $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{py})_2$ and $\text{Yb}(\text{C}_5\text{Me}_5)_2^-$ $(\text{p-Me}_2\text{NC}_5\text{H}_5\text{N})_2$. 
A more complete description of the electronic structure of these aromatic amine coordination complexes must wait for more detailed measurements of their electronic properties. Of most importance are a more accurate $\mu_{\text{eff}}$ vs. temperature study over a wide temperature range, epr investigations and a single crystal X-ray structure determination. These studies are now in progress [21].

Whatever is responsible for the observed moments, it seems clear that the ytterbium(II) center is pushing electron density onto the heterocycle, nitrogen ligand. This raises the possibility of interactions of the base-free complex, Yb(C$_5$Me$_5$)$_2$, with softer ligands giving weaker donor but stronger acceptor properties (i.e., CO, olefins and acetylenes), and, in light of the tendency of ytterbium(II) to coordinate hydrocarbons, the potential use of Yb(C$_5$Me$_5$)$_2$ in activating such ligands. The Yb(C$_5$Me$_5$)$_2$ unit seems to be exhibiting dual properties in terms of its electron affinity. It is clearly quite electron-donating toward some substrates, as will be discussed further in Chapter 6, and in this sense electron rich. However, its strong affinity for hard Lewis bases, such as diethyl ether and tetrahydrofuran, make it appear electron poor, and willing to accept electron density.

An X-ray structure has been determined for Yb(C$_5$Me$_5$)$_2$(py)$_2$ [22]. This compound crystallizes from toluene as well-separated monomeric units in the monoclinic system $P2_1/\alpha$, with $Z = 4$. Figure 4 shows the distorted tetrahedral array of the ligands about ytterbium, with approximate $C_2$ symmetry. The angles about the coordination sphere are: N(1)-Yb-N(2) = $122.5(2)^\circ$, N(1)-Yb-C$_5$Me$_5$ centroid(1) =
Figure 4. ORTEP view of Yb(C₅Me₅)₂(py).
103.6(2)°, N(1)-Yb-C₅Me₅ centroid(2) = 111.5(3)° and centroid(1)-Yb-centroid(2) = 107.7(3)°.

The average ytterbium-carbon distance is 2.74 ± 0.04 Å, somewhat longer than the corresponding distance in Yb(C₅Me₅)₂(thf) (2.66 ± 0.02 Å) due to the increase in coordination number. The Yb-N(1) and Yb-N(2) distances are 2.586(7) and 2.544(6) Å, respectively. If one subtracts the ionic radius of eight-coordinate ytterbium(II), 1.14 Å [15], from the Yb-N distances, one obtains 1.45 and 1.40 Å for the ionic radii of the pyridine nitrogen atoms. A value of 1.40 Å can be calculated from the structure of the eight-coordinate bis(pyridine) tris(2,2,6,6-tetramethylheptane-3,5-dionato) europium(III) [23]. The bond distances therefore reflect ionic coordination about a ytterbium(II) center. Bond distances within the pyridine and C₅Me₅ rings are also normal.

The displacements of the methyl carbon atoms from the planes of their respective C₅ rings are greater than in Yb(C₅Me₅)₂(thf), ranging from 0.13 to 0.31 Å. This is a result of more steric crowding in Yb(C₅Me₅)₂(py)₂, which has a higher coordination number. A view of the staggered C₅Me₅ rings is shown in Figure 5.

Phosphine Complexes

In toluene, the divalent Ln(C₅Me₅)₂(OEt₂) species do not form isolable phosphine coordination complexes with the monodentate phosphines PMe₃ or P(n-Bu)₃, or with the bidentate 1,2-diphenylphosphinoethane. The chelating phosphines 1,2-dimethylphosphinoethane (dmpe) and 1,2-dimethylphosphinomethane (dmpm), however, do give isolable complexes. Reaction of the diethyl ether complexes with one
Figure 5. View of $\text{Yb(}C_5\text{Me}_5\text{)}_2(\text{py})_2$ down the centers of the $C_5\text{Me}_5$ rings.
molar equivalent of dmpe in toluene results in precipitation of an insoluble substance having the stoichiometry Ln(\text{C}_5\text{Me}_5)_2(\text{dmpe}), where Ln = Eu or Yb. Hydrolysis of the europium derivative in benzene gives a 2:1 mixture of pentamethylocyclopentadiene and dmpe (by \textsuperscript{1}H NMR). The \textsuperscript{31}P\{\textsuperscript{1}H\} NMR spectrum of the hydrolysate shows that free dmpe is the only phosphine-containing product. The europium and ytterbium compounds have identical infrared spectra and similar melting points, suggesting similar structures. Their exceedingly low solubilities in hydrocarbons indicates a polymeric structure such as:

The dmpe complexes are slightly soluble in diethyl ether, from which microcrystalline samples may be obtained. Addition of tetrahydrofuran results in immediate formation of the Ln(\text{C}_5\text{Me}_5)_2(\text{thf}).

Addition of cmpm to Ln(\text{C}_5\text{Me}_5)_2(\text{UEt}_2) (Ln = Eu, Yb) in toluene results in formation of the red Eu(\text{C}_5\text{Me}_5)_2(dmpm) or the dark green Yb(\text{C}_5\text{Me}_5)_2(dmpm). These complexes appear to be isostructural since they have superimposable infrareds and indentical melting points. They are soluble in toluene, from which they can be
crystallized, though attempts to crystallize the dmppm complexes from diethyl ether yielded only the diethyl ether complexes. Therefore, in the presence of excess ether, the dmppm ligand is completely exchanged.

Normal, diamagnetic chemical shifts are observed in the $^1H$, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra of Yb(C$_5$Me$_5$)$_2$(dmppm).

Coordination of dmppm to ytterbium results in a downfield shift of ca. 16 ppm in the $^{31}P\{^1H\}$ NMR spectrum, from $\delta - 55.7$ [24] for the free ligand to $\delta - 39.6$. None of the chelating phosphine complexes of Eu(C$_5$Me$_5$)$_2$ or Yb(C$_5$Me$_5$)$_2$ gave molecular ions in their mass spectra.

In forming coordination complexes with the divalent Ln(C$_5$Me$_5$)$_2$ (Ln = Eu, Yb), chelating alkyl phosphines appear to act as better bases toward Ln(C$_5$Me$_5$)$_2$ than does diethyl ether. In contrast to the divalent Ln[N(SiMe$_3$)$_2$]$_2$ units, the Ln(C$_5$Me$_5$)$_2$ do not form complexes with P(n-Bu)$_3$ from their diethyl ether complexes. Ligand exchange reactions indicate the following ordering of basicities toward Yb(C$_5$Me$_5$)$_2$: bipyridine, pyridine > tetrahydrofuran > methyl vinyl ether, dmpe, dmppm > diethyl ether.

Chapter 5 References


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CHAPTER 6

REACTION CHEMISTRY OF THE DIVALENT PENTAMETHYLCYCLOPENTADIENYL LANTHANIDES

Reactions with Lewis and Protic Acids

Having prepared toluene-soluble, monomeric derivatives of ytterbium(II) and europium(II), we could begin to explore the simple reaction chemistry of these low-valent compounds. In toluene, the ytterbium(II) diethyl ether complex, Yb(C₅Me₅)₂(OEt₂), does not react with the unsaturated molecules carbon monoxide (15 atm), propene (2 atm) or diphenylacetylene (1:1 in refluxing toluene). There is also no observable reaction between Yb(C₅Me₅)₂(OEt₂) and D₂ (16 atm) in toluene. This may mean that these molecules simply do not compete well with diethyl ether for a coordination site at ytterbium. As we have seen, tri(n-butyl)phosphine, a stronger donor than carbon monoxide, an olefin or an alkyne, does not displace diethyl ether from Yb(C₅Me₅)₂(OEt₂) (see Chapter 5).

The ether complex Yb(C₅Me₅)₂(OEt₂) reacts with sodium bis(trimethylsilyl)amide to form a simple coordination complex, [Na(OEt₂)][Yb(C₅Me₅)₂N(SiMe₃)₂], after crystallization from diethyl ether. This green sodium salt is completely insoluble in toluene, but can be crystallized from diethyl ether. The presence of only one molar equivalent of diethyl ether suggests that the sodium ion may be coordinated to the nitrogen atom of the N(SiMe₃)₂ ligand and/or a methyl group (cf. NaEu[N(SiMe₃)₂]₃, Chapter 3). The amine,HN(SiMe₃)₂, does not react with Yb(C₅Me₅)₂(OEt₂) in tetrahydrofuran nor in refluxing toluene.
Dornberger, et. al. have shown that one cyclopentadienyl ligand can be removed from YbCp₃ and SmCp₃ by protonation with NH₄Cl to yield the chloro-species YbCp₂Cl and SmCp₂Cl, respectively [1]. Fischer and Bielany have shown that this type of reaction is more general in using a variety of protic acids HX to obtain the mixed-ligand species [Cp₃-nLnXₙ]ᵢ [2]. Of particular interest are reactions in which the acids used were weaker than cyclopentadiene (pKa ≈ 15). Thus, ammonia (pKa ≈ 33) was used to obtain [Cp₂YbNH₂]ₓ, and terminal alkynes (pKa ≈ 20-21) yielded [Cp₂LnC₂R]ₓ. The latter reaction seems to contradict the claims that SmCp₃ only catalyzes the trimerization of phenylacetylene [3], and that NdCp₃ induces a small paramagnetic shift in the ¹H NMR spectrum of phenylacetylene due to formation of the adduct Cp₃Nd·HC₂Ph [4].

Since the inductive effect of the methyl groups should increase the basicity of the pentamethylcyclopentadienide anion relative to that of the cyclopentadienide anion, it appeared that protonation of the C₅Me₅ ligands in lanthanide compounds would be even more favorable. Upon reaction of Yb(C₅Me₅)₂(thf) with one molar equivalent of NH₄Cl in tetrahydrofuran, a yellow solid precipitated, which gave an elemental analysis consistent with the formulation YbCl₂(thf)₂. Only absorptions due to tetrahydrofuran were observed in the infrared spectrum. The known mono-tetrahydrofuran complex YbCl₂(thf) is also yellow [5]. The Yb(C₅Me₅)₂(thf) starting material was isolated from the tetrahydrofuran solution. The yields of YbCl₂(thf)₂ and starting material indicate that the NH₄Cl reacted with only one-half
an equivalent of $\text{Yb}(C_5\text{Me}_5)_2(\text{thf})$. Some unsuccessful reactions of $\text{Yb}(C_5\text{Me}_5)_2(\text{OEt}_2)$ and $\text{Eu}(C_5\text{Me}_5)_2(\text{thf})$ with organic acids are described in the experimental section (Chapter 2).

One molar equivalent of phenylacetylene reacts with the ether complex $\text{Yb}(C_5\text{Me}_5)_2(\text{OEt}_2)$ to give a red, pentane-soluble compound of stoichiometry $[\text{Yb}(C_5\text{Me}_5)C_2\text{Ph}]_x$. The presence of the alkynyl ligand is indicated by an infrared absorption, $v(\text{C=Cr})$, at 2040 cm$^{-1}$. This compound is undoubtedly associated since the mass spectrum contains peaks due to $\text{Yb}_2(C_5\text{Me}_5)_3(C_2\text{Ph})_2$, $\text{Yb}_2(C_5\text{Me}_5)_2(C_2\text{Ph})$, $\text{Yb}_2(C_5\text{Me}_5)(C_2\text{Ph})_2$, $\text{Yb}_2(C_5\text{Me}_5)(C_2\text{Ph})$ and $\text{Yb}(C_5\text{Me}_5)(C_2\text{Ph})$ ions.

The $^1\text{H NMR}$ spectrum of $[\text{Yb}(C_5\text{Me}_5)(C_2\text{Ph})]_x$ also shows the presence of $C_5\text{Me}_5$ and phenylacetylide in a 1:1 molar ratio. However, the resonances have been shifted downfield and broadened (see Experimental Section), implying the presence of a paramagnetic molecule. It is very difficult to rationalize this observation, except to suggest the presence of another small-mass ligand that could account for a trivalent oxidation state, such as hydrogen or oxygen. However, this would seem to be inconsistent with the mass spectral results. Clearly further work is required to clarify the molecular structure of this unusual complex.

It is interesting that this compound is isolated ether-free. The alkynyl ligand, which probably bridges ytterbium centers through one carbon atom, or in a $\sigma-\pi$ fashion (cf. $[\text{CuC}_2\text{Ph}]_x$ [6]), is a better donor ligand than diethyl ether. A more dramatic example of the base strength of an alkynyl group as a ligand toward ytterbium(II) is found
in the base-free \([\text{Yb(C}_2\text{Ph})_2]_x\), which can be crystallized from
tetrahydrofuran [7]. We have seen that neutral, \(sp^3\)-hybridized
carbon atoms can serve as donor ligands to divalent europium and
ytterbium (Chapters 3 and 5). It is not surprising, then, that the
more electronegative \(sp\)-hybridized carbon atoms will form stronger
bonds to a lanthanide metal. The compounds \(\text{Cp}_2\text{LnC}_2\text{R} (\text{Ln} = \text{Gd, Ho, Er and Yb [8]; R} = \text{Ph and Ln} = \text{Er; R} = \text{Ph and t-Bu [9]})\) and
\(\text{CpHo(C}_2\text{Ph}) [8],\) are probably associated as well. The mode of bridge-
bonding in all of the above lanthanide alkynyl complexes is similar,
since the \(\nu(\text{C} \equiv \text{C})\) stretching frequencies fall in the same region,
2040-2050 \(\text{cm}^{-1}\).

Reactions with Oxidizing Agents

In dichloromethane, the divalent compound \(\text{Yb(C}_5\text{Me}_5)_2(\text{thf})\) is
readily oxidized to the mono-chloro species \(\text{Yb(C}_5\text{Me}_5)_2\text{Cl(\text{thf})}\).Formally, this reaction represents transfer of a chlorine radical,
\(\text{Cl}^\cdot\), from dichloromethane to ytterbium(II) in a one-electron
oxidative addition. In contrast, the europium(II) compound
\(\text{Eu(C}_5\text{Me}_5)_2(\text{thf})\) does not react with dichloromethane. This is
consistent with the greater stability of the divalent oxidation state
for europium.

A more convenient route to the mono-chloro species
\(\text{Yb(C}_5\text{Me}_5)_2\text{Cl(\text{thf})}\) is by reaction of \(\text{Yb(C}_5\text{Me}_5)_2(\text{thf})\) with
one molar equivalent of ytterbium trichloride in toluene. This type
of reaction has also provided a route to a trivalent complex of
1,2-dimethylphosphinomethane, \(\text{Yb(C}_5\text{Me}_5)_2\text{Cl(dmpm)}\), by the reaction
of \(\text{Yb(C}_5\text{Me}_5)_2(\text{dmpm})\) with \(\text{YbCl}_3\) in toluene. This purple,
crystalline compound has an effective magnetic moment of 4.4 B.M. (by Evans' method). It is of interest to determine the mode of coordination of dmpm to the Yb(C₅Me₅)₂Cl unit, as the nine-coordinate complex would seem to be severely sterically hindered. A single-crystal X-ray diffraction study is in progress [10].

If general, one-electron oxidative additions to ytterbium(II) could provide routes to numerous trivalent derivatives. It is reasonable to expect formation of ytterbium-carbon bonds by oxidative addition of an organic radical to ytterbium(II). However, the compounds HCP₃ and HgPh₂, both potential sources of radicals, did not react with Yb(C₅Me₅)₂(OEt₂) in refluxing toluene.

One-electron oxidative additions can also be carried out with silver(I) salts. In toluene, silver iodide reacts with Yb(C₅Me₅)₂(thf) to give the purple, mono-iodo complex Yb(C₅Me₅)₂I(thf). The infrared spectrum of this compound is identical to that for Yb(C₅Me₅)₂Cl(thf), except for the presence of a metal-chlorine stretching frequency at 253 cm⁻¹ in the spectrum of the latter compound.

Adding one molar equivalent of silver trifluoroacetate in toluene to Yb(C₅Me₅)₂(OEt₂) generates the trivalent [Yb(C₅Me₅)₂(O₂CCF₃)]₂, which was also prepared from [Yb(C₅Me₅)₂Cl₂]⁻ and NaO₂CCF₃ (see Chapter 4).

A one-electron oxidation of Yb(C₅Me₅)₂(dme) to the cationic complex [Yb(C₅Me₅)₂(dme)][PF₆] with [FeCp₂][PF₆] has been reported by Watson [11].
Attempts to oxidize the divalent $\text{Eu}(\text{C}_5\text{Me}_5)_2(\text{thf})$ did not lead to isolation of a trivalent product, but to loss of the $\text{C}_5\text{Me}_5$ rings. Reaction of $\text{Eu}(\text{C}_5\text{Me}_5)_2(\text{thf})(\text{OEt}_2)$ with one-half molar equivalent of $\text{I}_2$ in diethyl ether led to isolation of $\text{EuI}_2(\text{thf})_2$ after crystallization from tetrahydrofuran. Allyl bromide or trimethylchlorosilane (one molar equivalent) react with $\text{Eu}(\text{C}_5\text{Me}_5)_2(\text{thf})(\text{OEt}_2)$ to generate yellow insoluble precipitates. The reaction with allyl bromide proceeded through a blue species (in diethyl ether) that persisted for approximately 20 minutes at room temperature. Approximately one-half of the $\text{Eu}(\text{C}_5\text{Me}_5)_2(\text{thf})(\text{OEt}_2)$ starting material was isolated from these reaction mixtures. The yellow precipitates show only bands due to tetrahydrofuran in the infrared spectrum, and contain halide ($\text{AgNO}_3$ test). Therefore, they are most likely $\text{EuBr}_2(\text{thf})_x$ and $\text{EuCl}_2(\text{thf})_x$, respectively.

In a similar fashion, silver trifluoroacetate (one molar equivalent) reacts with $\text{Eu}(\text{C}_5\text{Me}_5)_2(\text{thf})(\text{OEt}_2)$ to give a tetrahydrofuran-soluble product that contains no $\text{C}_5\text{Me}_5$ ligands (by infrared spectroscopy), and gives an elemental analysis consistent with $\text{Eu}(\text{CO}_2\text{CCF}_3)_2(\text{thf})_2$.

The 1:1 reactions of $\text{Eu}(\text{C}_5\text{Me}_5)_2(\text{thf})(\text{OEt}_2)$ with $\text{CHCl}_3$ or $\text{EuCl}_3$ led to blue solutions which deposited green, insoluble solids after approximately 5 minutes. If the reaction with $\text{CHCl}_3$ is carried out at $0^\circ\text{C}$ for 10 minutes, a blue solid may be isolated by removal of the diethyl ether solvent under reduced pressure. Minute quantities of this blue compound were crystallized from pentane at $-10^\circ\text{C}$. The
blue prisms contained chlorine (by AgNO\textsubscript{3} test). Unfortunately, the small quantities isolated precludes proper characterization.

The blue species that results from attempted oxidation of Eu(C\textsubscript{5}Me\textsubscript{5})\textsubscript{2}(thf)(OEt\textsubscript{2}) appear to be rather unstable compounds, possibly a divalent Eu(C\textsubscript{5}Me\textsubscript{5})Cl or a trivalent Eu(C\textsubscript{5}Me\textsubscript{5})\textsubscript{2}Cl species, which disproportionate or decomposes to other products. Since the only products isolated from these attempted oxidations are divalent, it would appear that the europium(III) oxidation state is unstable in the presence of the pentamethycyclopentadienide anion. In support of this, a mono-ring derivative of stoichiometry [Eu(C\textsubscript{5}Me\textsubscript{5})(thf)\textsubscript{3}][PF\textsubscript{6}] can be obtained from the reaction of Eu(C\textsubscript{5}Me\textsubscript{5})\textsubscript{2}(thf)(OEt\textsubscript{2}) with [FeCp\textsubscript{2}][PF\textsubscript{6}]. Therefore, rather than oxidize the divalent metal species to a trivalent compound, as in the case for ytterbium, an electron is transferred from the C\textsubscript{5}Me\textsubscript{5} anion to [FeCp\textsubscript{2}][PF\textsubscript{6}], generating ferrocene. The oxidation state of [Eu(C\textsubscript{5}Me\textsubscript{5})(thf)\textsubscript{3}][PF\textsubscript{6}] was established by a low-temperature (5-40 K) magnetic susceptibility study, which showed the compound to have an effective magnetic moment of 7.52 B.M., with C = 7.02.

Reactions with Transition Metal Carbonyl Compounds

The observation that Yb(C\textsubscript{5}Me\textsubscript{5})\textsubscript{2}(thf) is readily oxidized to the trivalent species Yb(C\textsubscript{5}Me\textsubscript{5})\textsubscript{2}Cl(thf) suggested that the divalent metalloccene might be able to reduce low-valent transition metal compounds. Zero-valent, transition metal carbonyl compounds, being readily available, were therefore chosen as substrates. These compounds seemed to offer the possibility of reaction with the zero-valent metal center and/or a carbonyl ligand.
By varying reaction stoichiometries, it was discovered that \( \text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}) \) reacted with \( \text{Co}_2(\text{CO})_8 \) in a 2:1 molar ratio, generating a blue solid that could be crystallized from tetrahydrofuran/pentane mixtures as well-formed prisms. This compound is paramagnetic (\( \mu_{\text{eff}} = 4.1 \) B.M. at 30°C in benzene, by Evans' method), indicating an oxidation from ytterbium(II) to ytterbium(III). The \( ^1\text{H} \) NMR spectrum showed a broad singlet (\( \nu_{1/2} = 43 \) Hz) at \( \delta 8.36 \) due to \( \text{C}_5\text{Me}_5 \) protons. The elemental analysis was consistent with the formulation \([\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{tnf})][\text{Co}(\text{CO})_4] \), implying that the Co-Co bond had been broken by a one-electron reduction from Co(0) to Co(-I). The tetracarbonylcobaltate anion can also be generated using sodium amalgam [12] or thallium metal [13] as the reducing agent. The infrared spectrum (\( \nu(\text{CO}) = 2023 \) s, 1973 w, 1939 s, 1917 s, 1823 w, 1708 w sn, and 1761 s cm\(^{-1}\)) shows significantly lowered carbonyl stretching frequencies relative to \([\text{Et}_3\text{NH}][\text{Co}(\text{CO})_4] \) [14], which could indicate isocarbonyl bonding.

In order to elucidate the structure of this novel compound, a single crystal X-ray study was undertaken [15]. Crystals of \([\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{tnf})][\text{Co}(\text{CO})_4] \) are triclinic, \( \text{P}\overline{1} \), with \( Z = 2 \). Two views of the compound (Figures 1 and 2) show the presence of a Yb-O-C-Co isocarbonyl linkage (\( <\text{Yb}-\text{O}(1)-\text{C}(21) = 163.0(2)^\circ \) and \( <\text{Co}-\text{C}(21)-\text{O}(1) = 177.8(2)^\circ \)). There is a significant difference (0.05 Å) between the average C-O(terminal) bond length (1.14 ± 0.02 Å) and the C-O(iso) bond length of 1.133(3) Å. This, in addition to the lowered carbonyl stretching frequencies, implies a weakening of the
Figure 1. ORTEP drawing of \([\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{thf})][\text{Co(CO)}_4]\).
Figure 2. View of $[\text{Yb(C}_5\text{Me}_5)_2(\text{thf})][\text{Co(CO)}_4]$ through the $\text{C}_5\text{Me}_5$ ring centers.
C-O bond upon coordination of the Lewis acid center Yb(C₅Me₅)₂(thf)+. Such carbonyl 'activation' in transition metal compounds has been extensively investigated by Shriver, who has utilized group IIIA Lewis acids [16]. In concert with a lengthening of the C-O(iso) bond, the Co-C(iso) bond appears to be strengthened by this interaction; the difference between the average Co-C(terminal) bond length (1.77 ± 0.03 Å) and the Co-C(iso) bond length (1.699(3) Å) is 0.07 Å.

The ytterbium-oxygen(thf) bond (2.335(2) Å) is longer than that of the ytterbium-oxygen(CO) bond of 2.258(2) Å. This may be ascribed to the different coordination number (hybridization) of the two different types of oxygen atoms.

The average ytterbium-carbon bond length of 2.596(2) Å is similar to that found in the trivalent species (C₅Me₅)₂Yb(S₂CNEt₂) (2.63(3) Å) of identical coordination number but significantly shorter than that found in the divalent species, (C₅Me₅)₂Yb(py)₂ (2.742(7) Å) of the same coordination number. These bond length changes are consistent with the view that the ytterbium atom in [(C₅Me₅)₂Yb(thf)][Co(CO)₄] is trivalent, since Shannon suggests that the ionic radius of ytterbium(III) is ca. 0.16 Å smaller than that of ytterbium(III) [17].

The ytterbium atom is displaced 2.312(1) Å from the C(1)-C(5) ring plane, and 2.294(1) Å from the C(11)-C(15) ring plane. The displacements of the methyl carbons from their respective C₅ ring planes range from 0.31(2) to 0.66(4) Å away from ytterbium.

Other Lewis acid-transition metal isocarbonyl linkages have been structurally characterized, including [Mg(py)₄][CpMo(CO)₃]₂ [18],
\[(\text{CO})_2\text{Co}_3\text{CO}]_{2}[\text{CpTiCo(CO)}_4] \] [19] and \[[\text{CpFe(CO)Et}_3]_2\] \[20\]. However, \[[\text{Yb(}C_5\text{Me}_5)_2(\text{thf})][\text{Co(CO)}_4] \] is the first structurally characterized example of a lanthanide metal serving as the Lewis acid in an isocarbonyl linkage. The compound SmCp\(_3\) has been shown to induce a shift of the carbonyl stretching frequencies in various binary transition metal carbonyls to lower frequency \[21\]. Crease and Legzdins \[4\] have reported the 2:1 adducts \((\text{MeC}_5\text{H}_4)\text{Mn(CO)}_3(\text{LnCp}_3)_2\), where Ln is Sm, Yb or Nd.

When crystallized from toluene, \[[\text{Yb(}C_5\text{Me}_5)_2(\text{thf})][\text{Co(CO)}_4] \] loosens tetrahydrofuran to produce \[[\text{Yb(}C_5\text{Me}_5)_2][\text{Co(CO)}_4] \) \((\nu(\text{CO}): 2038 \text{ m, } 1974 \text{ m, } 1962 \text{ w sh, } 1870 \text{ s, } 1788 \text{ s, and } 1739 \text{ s cm}^{-1}\)\). This implies that a second carbonyl ligand can readily displace tetrahydrofuran from the coordination sphere of ytterbium. This compound, as well as its thf complex, exhibit more carbonyl stretching bands than would be predicted for the lowest possible point group symmetries. A possible explanation for this observation is the existence of more than one isomer, or partial loss of thf (in nujol) in the case of the thf complex. However, note that this phenomenon is also observed for the other ytterbium-transition metal carbonyl complexes described here.

Because crystallographic and infrared data suggested an activation of the isocarbonyl C-O bond, \[[\text{Yb(}C_5\text{Me}_5)_2(\text{thf})][\text{Co(CO)}_4] \] was exposed to hydrogen (18 atm) for 24 h in both toluene and tetrahydrofuran. However, only starting material was recovered from the reaction solutions. The reactivity of this isocarbonyl toward electrophiles and nucleophiles are of interest, but such reactions were not investigated.
Other transition metal carbonyl anions are also readily prepared from $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$. Molybdenum hexacarbonyl reacts with two molar equivalents of the divalent ytterbium compound to yield $[\text{Yb}(\text{C}_5\text{Me}_5)_2]_2[\text{Mo}(\text{CO})_5]$. This compound can be crystallized from tetrahydrofuran without incorporation of tetrahydrofuran as a ligand, presumably because two isocarbonyl linkages per ytterbium are formed in a chelating fashion. Sodium [22] and lithium [23] salts of $\text{Mo}(\text{CO})_5^{2-}$ have also been reported. The carbonyl stretching frequencies in $[\text{Yb}(\text{C}_5\text{Me}_5)_2]_2[\text{Mo}(\text{CO})_5]$ are observed at 2009, 1920, 1903, 1882, 1632 and 1414(? cm$^{-1}$). No reaction was observed between the divalent $\text{Eu}(\text{C}_5\text{Me}_5)_2(\text{thf})$ and $\text{Mo}(\text{CO})_6$ in toluene after 48 h.

In a similar fashion, $[\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{thf})]_2[\text{Fe}(\text{CO})_4]$ can be prepared by reaction of $\text{Fe}(\text{CO})_5$ and two molar equivalents of $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ in toluene, followed by crystallization from tetrahydrofuran. Carbonyl stretching frequencies are observed at 2004 w, 1980 w, 1961 w, 1928 s, 1922 m, 1753 m sh, 1741 s, 1711 s, 1648 m sh and 1608 s br cm$^{-1}$. This blue, paramagnetic compound gives a single, broad resonance ($v_{1/2} = 144$ Hz) in the $^1\text{H}$ NMR spectrum at $\delta 9.52$. Reaction of $[\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{thf})]_2[\text{Fe}(\text{CO})_4]$ with two molar equivalents of $\text{SnPh}_3\text{Cl}$ in tetrahydrofuran gives the known compound $\text{Fe}(\text{CO})_4(\text{SnPh}_3)_2$ [24], and $\text{Yb}(\text{C}_5\text{Me}_5)_2\text{Cl}(\text{thf})$.

The $\text{Fe}_3(\text{CO})_{12}$ cluster may also be reduced by $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$. Reaction of two equivalents of $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ with $\text{Fe}_3(\text{CO})_{12}$ in toluene, or stoichiometric amounts of $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ and $\text{Fe}_2(\text{CO})_9$
in toluene results in a dark red solution, from which violet prisms of 
\([\text{Yb}(\text{C}_5\text{Me}_5)_2][\text{Fe}_3(\text{CO})_{11}]\) can be crystallized. The infrared spectrum shows carbonyl stretching frequencies at 2048 w, 1998 s, 1973 s, 1667 w and 1604 s br cm\(^{-1}\). The complex is paramagnetic (\(\mu_{\text{eff}} = 3.91\) B.M. per ytterbium; 5-60 K), and has two resonances (\(v_{1/2} = 130\) Hz) in the \(^1\text{H}\) NMR spectrum at \(6.809\) and \(6.11\) for the inequivalent \(\text{C}_5\text{Me}_5\) rings.

The structure was determined from an X-ray crystallographic study [25]. Of the three discrete molecules in the unit cell, two are well ordered and related by inversion (Figure 3), while the third is disordered about the center of inversion. The molecule possesses approximate \(C_{2v}\) symmetry about the \(\text{Fe}(1)-\text{C}(1)\) vector.

The two \(\text{Fe}-\text{Fe}\) distances of 2.524(1) and 2.538(1) Å are essentially identical, as are the four \(\text{Yb}-\text{O}\) distances [average 2.243(5) Å]. The average \(\text{Yb}-\text{C}\) bond length [2.573(13) Å] compares favorably with those observed in related eight-coordinate ytterbium(III) species (see below).

The \(\text{Fe}(2)-\text{Fe}(1)-\text{Fe}(3)\) angle is 161.8°; there is no direct interaction between \(\text{Fe}(2)\) and \(\text{Fe}(3)\). The two planes defined by the carbonyls bound to \(\text{Yb}(1)\) and \(\text{Yb}(2)\) are inclined with respect to each other with a dihedral angle of 168.1°, and bend away from the unique carbonyl ligand bonded to \(\text{Fe}(1)\). Thus, the overall shape of the cluster might be described as an inverted umbrella, the handle being the unique carbonyl bound to \(\text{Fe}(1)\). The least-squares plane defined by the bridging carbonyl carbons \(\text{C}(2), \text{C}(3), \text{C}(4)\) and \(\text{C}(5)\) is 0.36 Å below \(\text{Fe}(1)\) and above \(\text{Yb}(1)\) and \(\text{Yb}(2)\) by 0.50 and 0.48 Å, respectively.
Figure 3. ORTEP view of ordered $[\text{Yb(C}_5\text{Me}_5)_2][\text{Fe}_3(\text{CO})_{11}]$ molecule.
Figure 4. ORTEP view of disordered [Yb(C₅Me₅)₂][Fe₃(CO)₁₁] molecule. Oxygen atoms bonded to C25P and C26P were not located.
The terminal Fe(2) and Fe(3) atoms are slightly below this plane (by 0.06 and 0.02 Å, respectively).

Although the Fe-Fe distances are similar to those found in the triiron clusters \([\text{Fe}_3(\text{CO})_{11}]^{2-}\) [26], \([\text{Fe}_3(\text{CO})_{11}]^\text{H}^-\) [27] and \(\text{Fe}_3(\text{CO})_{12}\) [28], the familiar triangular arrangement of iron atoms is not observed. The preferred triangular geometry of the \([\text{Fe}_3(\text{CO})_{11}]^{2-}\) cluster is clearly perturbed by the presence of the \((\text{C}_5\text{Me}_5)_2\text{Yb}(\text{III})\) units, which have forced two more carbonyls into bridging positions. It is well known that bridging CO's are better than terminal CO's as \(\sigma\)-donors to hard Lewis acids and that certain Lewis acids can induce terminal-to-bridge CO shifts [29-31]. In order to act as chelating groups to both \((\text{C}_5\text{Me}_5)_2\text{Yb}(\text{III})\) units, in which eight-coordination is favored, the \([\text{Fe}_3(\text{CO})_{11}]^{-2}\) cluster distorts by breaking an Fe-Fe bond. This process would not require much energetically, as Fe-Fe bond strengths in carbonyl clusters have been estimated as being ca. 19 kcal/mole [32]. Although the open structure of the Fe\(_3\) cluster core is not typical, the \([\text{Fe}_3(\text{CO})_{11}]^{2-}\) portion of the compound is electron precise, with 48 electrons.

It is not clear now or why \(\text{Fe}_2(\text{CO})_9\) can also be used to generate \([\text{Yb(}C_5\text{Me}_5)_2][\text{Fe}_3(\text{CO})_{11}]\), but this reaction seems to imply that the product is a particularly stable ytterbium-iron isocarbonyl species. This stability may be due to the ability of \([\text{Fe}_3(\text{CO})_{11}]^{2-}\) to form chelate rings to two ytterbiums simultaneously. The resulting 'opened' cluster would seem to have a rich
reaction chemistry. However, toluene solutions of the $[\text{Yb(C}_5\text{Me}_5)_2][\text{Fe}_3(\text{CO})_{11}]$ cluster did not react with $\text{H}_2$ or $\text{CO}$ at 18 atm during a 24 h period.

**Summary of Crystallographic Data**

Bonding of the cyclopentadienyl group and its substituted analogues to $f$-block metals is thought to be predominantly ionic, i.e., there is very little electron exchange between the metal atom and the organic ligand. A structural criterion has been advanced by Raymond that is remarkably accurate in predicting $f$-metal to carbon bond lengths, given the simplicity and therefore utility of the model [33]. The fundamental principle of the model is that metal-carbon bond lengths are a sensitive function of the oxidation state and coordination number of a given metal ion. Subtraction of the ionic radius of a metal atom, which is a function of the oxidation state and coordination number, from the observed metal-carbon bond length gives the effective ionic radius of a cyclopentadienyl group. Though ligand-ligand repulsions also play a role in determining the metal-carbon bond length, for the $f$-block metals, the effective ionic radius of the cyclopentadienyl ligand is observed to be fairly constant, $1.64 \pm 0.04$ Å. Thus, it may be said that the bonding in these organometallic molecules is largely ionic.

In the course of these investigations into the chemistry of pentamethylcyclopentadienyl derivatives of the lanthanide metals, a number of compounds whose structures can be used to test this model have been prepared. Using the ionic radii tabulated by Shannon [17],
one can estimate the effective ionic radius of the $C_5Me_5$ ligand in
the bis(pentamethylcyclopentadienyl)ytterbium complexes that have been
structurally characterized. As shown in Table 1, these radii are
consistent with the value suggested by Raymond for predominantly ionic
bonding, $1.64 \pm 0.04$ Å. Based on these structural data alone, the
bonding in ytterbium(II) and ytterbium(III) pentamethylcyclopentadienyl
complexes appears to be largely ionic.
Table 1. Effective Ionic Radii (Å) of $C_5Me_5^-$ in Ytterbium Compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>M-C Bond Length, Å</th>
<th>Metal Ion Radius, Å</th>
<th>Effective $C_5Me_5^-$ Radius, Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Yb(C_5Me_5)_2(py)_2$</td>
<td>2.74(4)</td>
<td>1.14</td>
<td>1.60</td>
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<tr>
<td>$Yb(C_5Me_5)_2(thf)$</td>
<td>2.66(2)</td>
<td>1.08</td>
<td>1.58</td>
</tr>
<tr>
<td>$Yb(C_5Me_5)_2(S_2CHET_2)$</td>
<td>2.63(3)</td>
<td>0.985</td>
<td>1.64</td>
</tr>
<tr>
<td>$[Yb(C_5Me_5)_2(thf)][Co(CO)_4]$</td>
<td>2.596(2)</td>
<td>0.985</td>
<td>1.61</td>
</tr>
<tr>
<td>$[Yb(C_5Me_5)_2]_2[Fe_3(CO)_11]$</td>
<td>2.57(1)</td>
<td>0.985</td>
<td>1.59</td>
</tr>
<tr>
<td>$[Li(OEt)_2][(C_5Me_5)_2YbCl_2]$ [34]</td>
<td>2.611(4)</td>
<td>0.985</td>
<td>1.63</td>
</tr>
<tr>
<td>$Yb(C_5Me_5)_2AlCl_4$ [34]</td>
<td>2.584(5)</td>
<td>0.985</td>
<td>1.60</td>
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</table>
Chapter 6 References


