and air-dried: yield 0.09 g (75%); mp 139 °C dec (Elemental Anal. Calcd for $C_{11}H_{16}N_3ORuPF_6$: C, 29.21; H, 3.57; N, 9.29. Found: C, 29.67; H, 3.73; N, 9.29).

[CpRu(CO)(CNMe)[C(NHMe)(NMe$_2$)]]PF$_6$. A solution of [CpRu(CO)(CNMe)$_2$]PF$_6$ (0.25 g, 0.63 mmol) in 100 mL of CH_3CN was treated for 45 min with dimethylamine at 0 °C. The solvents were removed, and the residue was crystallized from CH_2Cl_2 and diethyl ether at −15 °C. The white crystals were filtered and air-dried; yield 0.18 g (65%); mp 230 °C dec (Elemental Anal. Calcd for $C_{12}H_{18}N_3ORuPF_6$: C, 30.91, H, 3.89; N, 9.01. Found: C, 30.82; H, 3.89; N, 8.83).

[CpRu(CO)[C(NHMe)(NMe)C(NMe$_2$)]]PF$_6$. [CpRu(CO)(CNMe)$_2$]PF$_6$ (0.25 g, 0.63 mmol) was dissolved in 50 mL of CH_3CN. Dimethylamine was bubbled through this solution for 3 h at 0 °C. The reaction solution was transferred to a pressure bottle, and the reaction was continued at room temperature with stirring for 6 days. The solvents were then removed, and the residue was crystallized from CH_2Cl_2/diethyl ether. Off-white crystals formed and were collected on a filter and air-dried: yield 0.13 g (47%); mp 132 °C (melted with gas evolution, resolidified, and then melted again at 234 °C (melting point for [CpRu(CO)(CNMe)$_2$]PF$_3$)) (Elemental Anal. Calcd for $C_{12}H_{18}N_3ORuPF_6$: C, 30.91; H, 3.89; N, 9.01. Found; C, 30.77; H, 3.93; N, 9.29).

CpRu(CO)[C(NMe)(NMe)C(NMe$_2$)]. This compound was detected in IR and ^{1}H NMR spectra of the above reaction mixture of CpRu(CO)(CNMe)$_2^+$ with NHMe$_2$. Attempts to isolate the compound led only to recovery of the protonated chelate and were not extensively pursued.

[CpRu(CNMe)$_2$[C(NHMe)$_2$]]PF$_6$. [CpRu(CNMe)$_3$]PF$_6$ (0.26 g, 0.60 mmol) was dissolved in 50 mL of CH_3CN, and the resulting solution was treated with methylamine at 0 °C for 4 h. Removal of the solvents yielded a gray residue that was chromatographed on alumina. The product was eluted with 2% methanol in CH_2Cl_2. It was obtained as white crystals from CH_2Cl_2 by the addition of diethyl ether: yield 0.21 g (75%); mp 174.5 °C (Elemental Anal. Calcd for $C_{12}H_{19}N_4RuPF_6$: C, 30.97; H, 4.12; N, 12.04. Found: C, 31.22; H, 4.16; N, 11.96).

[CpRu(CNMe)[C(NHMe)$_2$]$_2$]PF$_6$. [CpRu(CNMe)$_3$]PF$_6$ (0.25 g, 0.6 mmol) was dissolved in 50 mL of CH_3CN, and the resulting solution was treated with methylamine at 0 °C for 4 h. The solution was then placed in a pressure bottle and allowed to stir at room temperature for 3 days. The solution was then chilled to 0 °C, the solvents were evacuated, and the residue was washed with diethyl ether and stored at −20 °C. The product was detected and characterized by its infrared and ^{1}H NMR spectra. Attempts to separate this compound from the other reaction product CpRu(CNMe)$_2$[C(NHMe)$_2$]$^+$ were unsuccessful.

[CpFe(CO)[C(NHMe)(NMe)C(NMe)]]PF$_6$. [CpFe(CO)(CNMe)$_2$]PF$_6$[15] (0.25 g, 0.67 mmol) was dissolved in 25 mL of methanol, and methylamine was bubbled through the solution at 0 °C for 2.5 h. The reaction was stoppered and allowed to stir for two more hours at which point spectroscopic data indicated that the chelate product had formed (Tables I and II). Attempts to crystallize the product, even at low temperatures, resulted in the conversion of the product to CpFe(CO)(CNMe)[C(NHMe)$_2$]$^+$.

Registry No. CpRu(CO)(CN)[C(NHMe)$_2$], 84987-34-8; CpRu(CO)(CN)[C(NHMe)(NMe$_2$)], 84987-35-9; [CpRu(CO)(CNMe)[C(NHMe)$_2$]]PF$_6$, 84987-37-1; [CpRu(CO)[C(NHMe)$_2$]$_2$]PF$_6$, 84987-39-3; [CpRu(CO)[C(NHMe)(NMe)C(NHMe)]]PF$_6$, 84987-41-7; [CpRu(CO)(CNMe)[C(NHMe)(NMe$_2$)]]PF$_6$, 84987-43-9; [CpRu(CO)[C(NHMe)(NMe)C(NMe$_2$)]]PF$_6$, 84987-45-1; CpRu(CO)[C(NMe)C(NMe$_2$)], 84987-46-2; [CpRu(CNMe)$_2$[C(NHMe)$_2$]]PF$_6$, 84987-48-4; [CpRu(CNMe)[C(NHMe)$_2$]$_2$]PF$_6$, 84987-50-8; [CpFe(CO)[C(NHMe)(NMe)C(NHMe)]]PF$_6$, 84987-52-0; CpRu(CO)(CN)(CNMe), 84987-53-1; [CpRu(CO)(CNMe)$_2$]PF$_6$, 84987-55-3; [CpRu(CNMe)$_3$]PF$_6$, 84987-57-5; [CpFe(CO)(CNMe)$_2$]PF$_6$, 70130-45-9; CpFe(CO)(CNMe)[C(NHMe)$_2$]$^+$, 52409-95-7; MeNH$_2$, 74-89-5; Me$_2$NH, 124-40-3.

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Synthesis of Organosamarium Complexes Containing Sm–C and Sm–P Bonds. Crystallographic Characterization of $[(CH_3C_5H_4)_2SmC{\equiv}CC(CH_3)_3]_2$[1]

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$[(CH_3C_5H_4)_2SmC{\equiv}CC(CH_3)_3]_2$, I, has been synthesized from $(CH_3C_5H_4)_2SmCl(THF)$ and $LiC{\equiv}CC(CH_3)_3$ in THF and characterized by spectroscopic, analytical, and crystallographic methods. I crystallizes from toluene at 0 °C in the monoclinic space group $P2_1/c$ with unit-cell dimensions a = 9.418 (3) Å, b = 17.830 (6) Å, c = 11.134 (5) Å, β = 113.10 (3)°, and Z = 2 (dimers) for D_{calcd} = 1.51 g cm^{-3}. Full-matrix least-squares refinement led to a final R value of 0.048 on the basis of 1659 observed reflections. The two $(CH_3C_5H_4)_2Sm$ units in the dimer are connected by electron-deficient alkynyl bridges that have Sm–C distances of 2.55 (1) Å and asymmetric $Sm{-}C{\equiv}C$ angles of 151 (1) and 122 (1)°. The reaction of I with $HP(C_6H_5)_2$ forms $HC{\equiv}CC(CH_3)_3$ and $(CH_3C_5H_4)_2SmP(C_6H_5)_2$, II, which has been characterized by spectroscopic and analytical methods.

Introduction

Traditionally, the two most important factors affecting the stability of organometallic complexes of the lanthanides are optimization of electrostatic interactions and saturation of the coordination sphere of the metal with bulky ligands in order to sterically block decomposition pathways.[3] A consequence of the latter feature is that the elements occurring later in the series, particularly Er, Yb, and Lu, are used more frequently in synthesis, since it is less difficult

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to sterically saturate the coordination environment of these smaller metals. For the larger, early members of the lanthanide series, even simple classes of complexes such as $(C_5H_5)_2LnCl$, are unstable with respect to disproportionation to more sterically saturated species such as $(C_5H_5)_3Ln$ and $LnCl_3$.[4] Only recently have dicyclopentadienyllanthanide halides been obtained for La, Ce, Pr, and Nd by using multiply substituted cyclopentadienyl ligands.[5-8]

Samarium has been a borderline element in terms of obtaining stable complexes by steric saturation of the metal coordination sphere. Although $(C_5H_4R)_2SmCl$ (R = H, CH_3) complexes can be obtained, syntheses of other dicyclopentadienylsamarium derivatives involving bonds such as Sm–C, Sm–P, Sm–Ge, Sm–H, etc. have been more difficult. When we initiated this research, we were aware of only two attempts to make such complexes: the synthesis of $(C_5H_5)_2SmCH_2Si(CH_3)_3$ was claimed in a 1978 review article[9] and efforts to obtain the Sm–P complex $(C_5H_5)_2SmP[C(CH_3)_3]_2$ from $(C_5H_5)_2SmCl$ and $LiP[C(CH_3)_3]_2$ reportedly did not give a purifiable product.[10,11] Since Sm(III) is one of the few lanthanides for which complexes can be readily characterized by NMR, it is unfortunate that this area has not been further developed.[12]

We report here the successful synthesis of two dicyclopentadienylsamarium complexes involving Sm–C and Sm–P bonds, $[(CH_3C_5H_4)_2SmC{\equiv}CC(CH_3)_3]_2$, I, and $(CH_3C_5H_4)_2SmP(C_6H_5)_2$, II. An X-ray crystal structure determination of I provides the first crystallographic data on noncyclopentadienyl Sm–C bonds and the second example of an asymmetric, electron-deficient alkynide bridge in a bimetallic lanthanide complex.[13]

Results and Discussion

Syntheses. Complex I was synthesized in 90% yield from $LiC{\equiv}CC(CH_3)_3$ by ionic metathesis in THF (eq 1).

$$2(CH_3C_5H_4)_2SmCl(THF) + 2LiC{\equiv}CC(CH_3)_3 \rightarrow [(CH_3C_5H_4)_2SmC{\equiv}CC(CH_3)_3]_2 + 2LiCl \quad (1)$$

This synthesis can be contrasted to that of the *cyclopentadienyl*erbium analogue $[(C_5H_5)_2ErC{\equiv}CC(CH_3)_3]_2$, III, which was obtained from $HC{\equiv}CC(CH_3)_3$ by a halide-free metalation route[13] (eq 2). The ionic metathesis

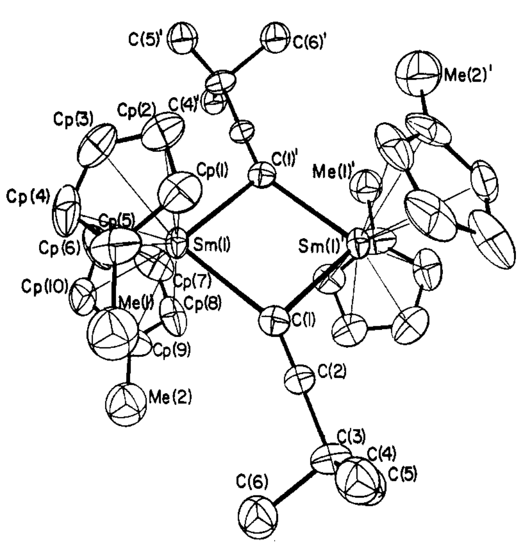

Figure 1. ORTEP plot of the molecular structure of $[(CH_3C_5H_4)_2SmC{\equiv}CC(CH_3)_3]_2$.

$$[(C_5H_5)_2ErCH_3]_2 + 2HC{\equiv}CC(CH_3)_3 \rightarrow [(C_5H_5)_2ErC{\equiv}CC(CH_3)_3]_2 + 2CH_4 \quad (2)$$

(eq 1) was not the preferred synthesis of III, because its limited solubility made it difficult to separate the metathesis byproduct LiCl. Since I is more soluble than III due to the methyl substitution on the cyclopentadienyl rings, this separation is not a problem and the ionic metathesis route could be used. Equation 2 is not currently a possible route to I, since the samarium methyl precursor has not yet been reported.

We avoided ionic metathesis routes for the synthesis of II, e.g., from $(CH_3C_5H_4)_2SmCl(THF)$ and $LiP(C_6H_5)_2$, because previously attempted syntheses of $(C_5H_5)_2SmP[C(CH_3)_3]_2$ failed by this route[10] and because preliminary reactions between $(C_5H_5)_2YCl$ and $LiP(C_6H_5)_2$ were not clean, even though a smaller, experimentally less difficult metal was used. A halide-free route to II was discovered by using $HP(C_6H_5)_2$ and I (eq 3). Since dicyclopentadienylsamarium alkyl precursors are not available, I was the choice for this metalation of $HP(C_6H_5)_2$. The fact that the alkynide is reactive enough to effect this reaction may have broader implications in organolanthanide synthesis, since both homoleptic and heteroleptic alkynide complexes of the lanthanides are readily available.[14]

$$[(CH_3C_5H_4)_2SmC{\equiv}CC(CH_3)_3]_2 + 2HP(C_6H_5)_2 \rightarrow 2(CH_3C_5H_4)_2SmP(C_6H_5)_2 + 2HC{\equiv}CC(CH_3)_3 \quad (3)$$

Characterization of $[(CH_3C_5H_4)_2SmC{\equiv}CC(CH_3)_3]_2$, I. The color, near-IR–vis spectrum and magnetic moment (1.90 μ_B) of complex I indicated it was a Sm(III) complex. The ^1H and ^{13}C NMR spectra were consistent with the presence of $CH_3C_5H_4$ and $C{\equiv}CC(CH_3)_3$ units in a 2:1 ratio. The IR spectrum of I contained a strong, sharp absorption at 2035 cm^{-1} assignable to $\nu_{C{\equiv}C}$. In comparison, $LiC{\equiv}CC(CH_3)_3$, III, and $[(CH_3C_5H_4)_2YbC{\equiv}CC(CH_3)_3]_2$[13] have $\nu_{C{\equiv}C}$ at 2025, 2050, and 2050 cm^{-1} respectively. These physical properties coupled with a complexometric metal analysis indicated an empirical formula of $(CH_3C_5H_4)_2SmC{\equiv}CC(CH_3)_3$ for I. Isopiestic molecular weight measurement in THF suggested that I exists as a monomer in

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Table I. Bond Lengths (Å) and Angles (deg) for $[(CH_3C_5H_4)_2SmC{\equiv}CC(CH_3)_3]_2$

Bond Distances

Sm(1)-Sm(1)	3.799 (1)	Sm(1)-Cp(1)	2.72 (2)
Sm(1)-Cp(2)	2.73 (2)	Sm(1)-Cp(3)	2.70 (2)
Sm(1)-Cp(4)	2.68 (2)	Sm(1)-Cp(5)	2.70 (2)
Sm(1)-Cp(6)	2.79 (3)	Sm(1)-Cp(7)	2.73 (3)
Sm(1)-Cp(8)	2.72 (2)	Sm(1)-Cp(9)	2.68 (4)
Sm(1)-Cp(10)	2.70 (3)	Sm(1)-C(1)	2.55 (1)
Sm(1)-C(1)′	2.55 (1)	Sm(1)-Ave(1)	2.71 (2)
Sm(1)-Ave(2)	2.72 (4)	Sm(1)-Cent1	2.430
Sm(1)-Cent2	2.441		

Bond Angles

C(1)-Sm(1)-C(1)	83.6 (5)	C(1)-Sm(1)-Cent1	106.6 (3)
C(1)-Sm(1)-Cent1	109.4 (3)	Cent1-Sm(1)-Cent2	128.6 (3)
C(1)-Sm(1)-Cent2	109.1 (3)	C(1)-Sm(1)-Cent2	110.0 (3)
Cp(2)-Cp(1)-Cp(5)	107 (2)	Cp(1)-Cp(2)-Cp(3)	108 (2)
Cp(2)-Cp(3)-Cp(4)	111 (3)	Cp(3)-Cp(4)-Cp(5)	106 (2)
Cp(1)-Cp(5)-Cp(4)	107 (2)	Cp(1)-Cp(5)-Me(1)	121 (2)
Cp(4)-Cp(5)-Me(1)	132 (2)	Cp(7)-Cp(6)-Cp(10)	101 (3)
Cp(6)-Cp(7)-Cp(8)	114 (3)	Cp(7)-Cp(8)-Cp(9)	106 (2)
Cp(8)-Cp(9)-Cp(10)	107 (3)	Cp(8)-Cp(9)-Me(2)	129 (2)
Cp(10)-Cp(9)-Me(2)	124 (3)	Cp(6)-Cp(10)-Cp(9)	111 (2)
Sm(1)-C(1)-Sm(1)	96.2 (5)	Sm(1)-C(1)-C(2)	151 (1)
Sm(1)′-C(1)-C(2)	112 (1)	C(1)-C(2)-C(3)	178 (1)

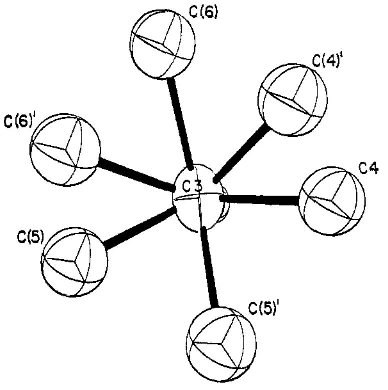

Figure 2. View of the disorder of the methyl carbon atoms of the *tert*-butyl group down the C≡C—C vector.

solution, most probably as the solvated species $(CH_3C_5H_4)_2Sm[C{\equiv}CC(CH_3)_3](THF)$, in contrast to complex III, which remains dimeric in THF. Isopiestic measurements in benzene indicate I is a dimer in this solvent, however.

Structure of I. Single crystals of I were obtained from toluene at 0 °C and were examined by X-ray diffraction methods. As shown in the ORTEP plot in Figure 1, the complex crystallizes as an alkynyl-bridged dimer, a structure which is analogous to that of III.[13] Important structural parameters are given in Table I. Disorder was observed in the *tert*-butyl part of the alkynyl ligand in I. A model in which two orientations related by a 60° rotation along the C(3)–C(2) axis were given equal weight allowed proper refinement of the structure. The two orientations superimposed along with their numbering are shown in Figure 2.

The average Sm–C distances for the carbon atoms in the two cyclopentadienyl rings of $[(CH_3C_5H_4)_2SmC{\equiv}CC(CH_3)_3]_2$ are 2.72 (4) and 2.71 (4) Å compared to values of 2.62 (2) and 2.63 (2) Å for $[(C_5H_5)_2ErC{\equiv}CC(CH_3)_3]_2$. Since Sm(III) is approximately 0.08 Å larger than Er(III),[15,16] the distances in I are within the range expected.[17] The values in I are less than the average Sm–C cyclopentadienyl distance of 2.75 Å found in the indenyl complex $Sm(C_9H_7)_3$, IV.[18] The metal to ring centroid distances are similarly related: III, 2.32, 2.34 Å; I, 2.43, 2.44 Å; IV, 2.44, 2.45, 2.48 Å.

The Sm–C(1) bond distance of 2.55 (1) Å, the first noncyclopentadienyl Sm–C distance to be reported, is also within the range expected when compared to the distances of 2.42 (2) and 2.47 (2) Å found in III plus the 0.08 Å difference in the metals' radii. The Sm–C(1)′ distance is also 2.55 (1) Å; i.e., the carbon atom of this electron-deficient alkynyl bridge is positioned symmetrically between the samarium atoms. This is not the case in III, although the difference in the two distances of 2.42 (2) and 2.47 (2) Å falls within the range frequently observed for "symmetrical" bridges.[13] (With Δ = 0.05 ± 0.03, the difference is not statistically significant but is probably real).

The alkynyl bridge in I is asymmetric, however, as evidenced by the disparity in Sm(1)–C(1)–C(2) and Sm(1)′–C(1)–C(2) angles, which are 151 (1)° and 112 (1)°, respectively. The difference in these angles, 39°, is large compared to that expected for bridging alkynyls that have no π component in bonding.[19] The extreme example of a dimer with no π component in bonding would have alkynyl bridges perpendicular to the metal metal vector and would have identical M—C≡C angles (of ~130°). The closest crystallographically characterized example of such a structure is $\{[(CH_3)_3N](CH_3)Be(C{\equiv}CCH_3)\}_2$,[21] which has Be—C≡C angles of 147° and 136°, a difference of 11°. The 39° difference in I is substantially larger and is even greater than the difference of 34° found in III.[13] The Sm(1)′–C(2) distance of 3.20 Å is too long to be involved in significant π bonding with the triple bond, however.

The methyl groups on the two cyclopentadienyl rings bound to a single metal center are approximately eclipsed with respect to each other. The methyl groups on adjacent rings on two different metals point away from each other in a "trans" orientation. This interesting disposition of methyl groups in bridged dimers has also been observed

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for $[(CH_3C_5H_4)_2TiCl]_2$,[23] $[(CH_3C_5H_4)_2ErH(THF)]_2$,[24] and $[(CH_3C_5H_4)_2YH(THF)]_2$,[24] although a different orientation is found in $[(CH_3C_5H_4)_2TiBr]_2$.[23] The asymmetry in the $C{\equiv}CC(CH_3)_3$ ligand is such that the *tert*-butyl group points away from the eclipsed methyl groups on one samarium and toward the unmethylated part of the rings on the other metal. The C(6)···Me(2) nonbonding distance of 3.79 Å is larger than necessary to avoid contact of the van der Waals radii of the attached hydrogen atoms,[25] however, and hence the bridge asymmetry in I cannot be rationalized on this basis. Furthermore, such an argument is not valid for the cyclopentadienyl complex III.

The structure of I represents a second example of an unusual, asymmetric, electron-deficient alkynyl-bridged dimer in the lanthanide series. A similar structure, postulated from electron diffraction data on $[(CH_3)_2AlC{\equiv}CCH_3]_2$, was explained in covalent terms as containing one normal Al–C single bond and one bridging C→Al dative bond involving an electron pair of the $C{\equiv}C$ multiple bond.[13,22] As more bridging organolanthanides of this type are structurally characterized, it may become necessary to use such covalent language to describe the bonding.[17]

Characterization of $(CH_3C_5H_4)_2SmP(C_6H_5)_2$, II. Complex II, the product of reaction 3, displayed a yellow color and a magnetic moment of 1.8 μ_B, both of which are characteristic of Sm(III). The IR spectrum contained an absorption at 1435 cm^{-1} characteristic of a phenyl ring attached to phosphorous.[26] No absorption characteristic of the starting materials (e.g., ν_{PH}[27] and $\nu_{C{\equiv}C}$) was observed. The ^1H NMR spectrum of II contained three singlets characteristic of $CH_3C_5H_4$, a doublet at δ 4.44, and asymmetrical triplets at δ 6.22 and 6.50. The latter three resonances are assignable to the ortho, meta, and para hydrogens, respectively, of a phenyl unit on the basis of their multiplicity and decoupling experiments. The amount these resonances shift from the normal phenyl region correlates well with the relative distance of the nuclei from the paramagnetic Sm(III) center. Phosphorus coupling was not observed presumably because of a strong interaction with the paramagnetic samarium metal center to which it is directly bound. No ^{31}P NMR signal was observed for II despite numerous attempts to locate one. ^{13}C NMR spectra of II in THF-d_8 and benzene-d_6 contained signals characteristic of $CH_3C_5H_4$ and a phenyl ring. A complete elemental analysis was obtained for II, which, taken with the above data, establishes the complex as $(CH_3C_5H_4)_2SmP(C_6H_5)_2$. Isopiestic molecular weight measurements suggested that II exists as a monomer in toluene. Single crystals of II can be grown from toluene at −10 °C, but the needlelike shape of the crystals together with the inherent absorption problems of samarium did not allow a structure solution to be obtained from the X-ray diffraction data collected.

Conclusion

The synthesis of crystalline bis(methylcyclopentadienyl)samarium alkynyl and phosphido complexes demonstrates that pure fully characterizable $(C_5H_4R)_2Sm$(non-halide) complexes are accessible by using simple cyclopentadienyl ligands. Electron-deficient alkynyl bridges appear to be available for a variety of metals in the lanthanide series and may be useful in stabilizing complexes of the more synthetically difficult metals. In addition, the alkynyl complexes may by useful synthetic precursors in organolanthanide chemistry in general when metallation reactivity is appropriate.

Experimental Section

All of the complexes described below are extremely air- and moisture-sensitive. Therefore, both the syntheses and subsequent manipulations of these compounds were conducted with rigorous exclusion of air and water by using Schlenk, vacuum line, and glovebox (Vacuum/Atmospheres HE-43 Dri Lab) techniques.

Physical Measurements. Infrared spectra were obtained as Nujol mulls on NaCl plates contained in an O-ring sealed Barnes Presslok holder by using a Perkin-Elmer 283 spectrometer. ^1H and ^{13}C NMR spectra were obtained on Bruker HX-270 and HX-90E spectrometers, respectively. Magnetic moment data were obtained by the Evans method with use of the Bruker HX-270 spectrometer.[28] Complete elemental analyses were obtained from Analytische Laboratorien, Engelskirchen, West Germany. Complexometric analyses were obtained as previously described.[13] Isopiestic molecular weight measurements were obtained by using a commercially available (SGA) Signer molecular weight apparatus to which high vacuum, greaseless Teflon stopcocks have been added. Sublimed ferrocene was used as the internal standard.

Materials. Toluene was predried with alumina, distilled from sodium, and degassed. THF was distilled from potassium benzophenone ketyl. Pentane was washed with sulfuric acid, dried over $MgSO_4$, refluxed over finely divided $LiAlH_4$, and vacuum transferred. Deuterated NMR solvents were vacuum transferred from potassium benzophenone ketyl. $HC{\equiv}CC(CH_3)_3$ (Chemical Samples Co.) was dried over molecular sieves that had been activated by heating under vacuum overnight. $HP(C_6H_5)_2$ (Strem) was used as received. Anhydrous $SmCl_3$ was prepared from the hydrate (Research Chemicals) by the method of Taylor and Carter.[29] $CH_3C_5H_4Na$ was prepared by the reaction of freshly cracked $CH_3C_5H_5$ with excess Na in THF at 0 °C. After being stirred overnight, the reaction mixture was filtered and the solvent removed from the filtrate under vacuum. The resulting product was desolvated by heating at 45 °C and 10^{-4} torr overnight.[30] $LiC{\equiv}CC(CH_3)_3$ was prepared by the reaction of n-C_4H_9Li with $HC{\equiv}CC(CH_3)_3$ in pentane. Since the specific synthesis of $(CH_3C_5H_4)_2SmCl(THF)$ has not been previously described in the literature, it is included here.

$(CH_3C_5H_4)_2SmCl(THF)$. In the glovebox, $SmCl_3$ (4.4344 g, 17.27 mmol) and $CH_3C_5H_4Na$ (3.5295 g, 34.57 mmol) were placed in a 125-mL Erlenmeyer flask containing a Teflon stirring bar. THF (90 mL) was added and the mixture stirred overnight. THF was removed by rotary evaporation, and the residue was extracted with toluene. The toluene solution was filtered through a medium porosity frit to give a clear orange solution. Removal of solvent by rotary evaporation gave orange crystals of $(CH_3C_5H_4)_2SmCl(THF)$ (3.52 g, 49%) that were washed in pentane and dried under vacuum: ^1H NMR (C_4D_8O) δ 12.25, 12.07 (s, s, $CH_3C_5\mathit{H}_4$) 3.62, 1.82 (s, s THF), −0.82 (s, $\mathit{CH}_3C_5H_4$); ^1H NMR (C_6D_6) δ 13.63 (s, $CH_3C_5\mathit{H}_4$), −0.95 (s, $\mathit{CH}_3C_5H_4$), −2.37, −4.00 (s, s, THF); $^{13}C\{^1H\}$ NMR (C_6D_6) 110.80 ($CH_3\overline{\mathit{C}(CH)_3}CH$), 106.04, 104.04 ($CH_3\overline{C\mathit{C}H\mathit{C}H\mathit{C}H}$), 66.43, 22.70 (THF), 19.41 ($\mathit{C}H_3C_5H_4$); IR (cm^{-1}) 1020 (m), 1015 (m), 930 (w), 825 (m), 750 (s). Anal. Calcd for $SmC_{16}H_{22}O$: Sm. 36.14. Found: Sm, 36.8.

$[(CH_3C_5H_4)_2SmC{\equiv}CC(CH_3)_3]_2$. $LiC{\equiv}CC(CH_3)_3$ (0.9360 g, 10.62 mmol) was added as a solid to $(CH_3C_5H_4)_2SmCl(THF)$ (4.4044 g, 10.57 mmol) in THF (80 mL) in a 125-mL Erlenmeyer flask containing a Teflon-coated stirring bar. The reaction mixture was stirred overnight; the solvent was removed by rotary evap-

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oration, and the residue was extracted with toluene. The extract was filtered through a fine porosity frit to give an orange filtrate. Removal of solvent by rotary evaporation yielded an orange product that was washed with pentane and dried under vacuum to yield I as a free-flowing yellow powder (3.764 g, 90%): ^{1}H NMR (C_6D_6) δ 13.96 (s, 4, $CH_3C_5\mathit{H}_4$), 12.19 (s, 4, $CH_3C_5\mathit{H}_4$), –0.17 (s, 6, $C\mathit{H}_3C_5H_4$), –2.67 (s, 9, $C{\equiv}CC(C\mathit{H}_3)_3$); $^{13}C\{^1H\}$ NMR (C_6D_6, ppm) 121.37 ($CH_3\overline{\mathit{C}(CH)_3C}H$), 113.03, 112.52 ($CH_3\overline{C\mathit{C}HCHC\mathit{H}C}H$), 23.89 ($\mathit{C}H_3C_5H_4$), 19.93 ($\mathit{C}(CH_3)_3$), 18.66 ($C(\mathit{C}H_3)_3$); IR (cm^{-1}) 3075 (w), 2275 (w), 2035 (s), 1675 (w), 1570 (w), 1360 (s), 1235 (s), 1200 (m), 1160 (m), 1085 (m), 1060 (s), 1040 (s), 1025 (s), 930 (s), 850 (w), 820 (s), 750 (s), 700 (w), 620 (w); magnetic susceptibility (299 K, cgs) $10^6\chi_g = 3.84$; $\mu_{eff} = 1.9\ \mu_B$; isopiestic molecular weight, calcd for $(CH_3C_5H_4)_2Sm[C{\equiv}CC(CH_3)_3](THF)$ 462, found in THF 465 ± 80, calcd for $[(CH_3C_5H_4)_2SmC{\equiv}CC(CH_3)_3]_2$ 780, found in C_6H_6 870 ± 80; near-IR–vis [0.024 M in toluene, λ_{max}, nm (ϵ)] 1570 (13), 1540 (10), 1520 (7), 1490 (8, sh), 1470 (16), 1420 (3), 1380 (11), 1290 (5), 1250 (11), 1230 (11), 1100 (3), 1090 (9), 1980 (5), 960 (2). Yellow rectangular prisms of I suitable for X-ray diffraction can be grown from toluene at 0 °C. Anal. Calcd for $SmC_{18}H_{23}$: Sm, 38.60. Found: Sm, 37.7.

$(CH_3C_5H_4)_2SmP(C_6H_5)_2$. In the glovebox, $[(CH_3C_5H_4)_2SmC{\equiv}CC(CH_3)_3]_2$ (2.6328 g, 3.38 mmol) and toluene (40 mL) were placed in a 100-mL Schlenk flask containing a Teflon-coated magnetic stirring bar. The flask was removed from the glovebox and attached to a double manifold. $HP(C_6H_5)_2$ (1.18 mL, 6.82 mmol) was added by syringe, and the reaction was stirred for 1 week forming an orange solution and a precipitate. The reaction mixture was filtered by using a coarse Schlenk filter, and the solvent was removed from the resulting filtrate to form an orange oil. Pentane was condensed onto the oil, and the mixture was shaken vigorously. This mixture was filtered to give an orange solid and a yellow filtrate containing excess $HP(C_6H_5)_2$. The orange solid was taken into the glovebox and washed with pentane to give another yellow filtrate. Extraction of the solid with toluene gave a solution that formed orange crystals upon rotary evaporation. The crystals were washed with pentane and reextracted with toluene, as described above, giving analytically pure $(CH_3C_5H_4)_2SmP(C_6H_5)_2$ (1.3409 g, 40%): ^{1}H NMR (C_6D_6) δ 14.62, 14.25 (s, s, $CH_3C_5\mathit{H}_4$), 6.50 (t, $J = 8.3$ Hz, C_6H_5, para H), 6.22 (t, $J = 5.8$ Hz, $C_6\mathit{H}_5$, meta H) 4.44 (d, $J = 4.2$ Hz, $C_6\mathit{H}_5$, ortho H), –1.23 ($C\mathit{H}_3C_5H_4$); double irradiation at δ 6.50 changes the δ 6.22 signal to a doublet ($J = 11.7$ Hz); irradiation at δ 6.22 changes both δ 6.50 and δ 4.44 signals to singlets; irradiation at δ 4.44 changes the δ 6.22 signal to a doublet ($J = 11.7$ Hz); $^{13}C\{^1H\}$ NMR (C_4D_8O, ppm) 134.69, 129.30, 120.33 (C_6H_5) 106.33, 103.98, ($CH_3\mathit{C}_5H_4$), 22.74 ($\mathit{C}H_3C_5H_4$); $^{13}C\{^1H\}$ NMR (C_6D_6, ppm) 128.62, 127.60, 124.16 (C_6H_5), 111.02, 105.68, 103.77, ($CH_3\mathit{C}_5H_4$), 23.26 ($\mathit{C}H_3C_5H_4$); ^{31}P NMR (toluene-d_8, –40 °C); no signal could be found over a range of 270 ppm on either side of H_3PO_4; IR (cm^{-1}) 1570 (w), 1435 (m, sh), 1240 (m), 1160 (w), 1100 (w), 1070 (m), 1040 (s), 1030 (s), 1020 (s), 995 (w), 970 (w), 930 (m), 910 (sh, 850 (w), 835 (s), 820 (m), 790 (w), 740 (br), 695 (s), 690 (s); magnetic susceptibility (299 K, cgs) $10^6\chi_g = 2.63$; $\mu_{eff} = 1.8\ \mu_B$; isopiestic molecular weight, calcd for $(CH_3C_5H_4)_2SmP(C_6H_5)_2$ 494, found in toluene 420 ± 80. Yellow needles of II can be grown from toluene at –10 °C. Anal. Calcd for $SmC_{24}H_{24}P$: Sm, 30.45; C, 58.30; H, 4.90; P, 6.27. Found: Sm, 30.21; C, 58.59; H, 5.00; P, 6.14.

X-ray Data Collection, Structure Determination, and Refinement for $[(CH_3C_5H_4)_2SmC{\equiv}CC(CH_3)_3]_2$. A single crystal of I suitable for X-ray analysis was sealed in a thin-walled capillary prior to data collection. Final lattice parameters as determined from 15 high-angle reflections ($\theta > 20°$) centered on an Enraf-Nonius CAD-4 diffractometer are given in Table II. Intensity data were collected in a manner similar to that previously described.[31] A summary of data collection parameters is given in Table II. The intensities were corrected for Lorentz and polarization effects. A ψ scan was performed in preparation for an empirical absorption correction, but the results showed it to be unnecessary.

The space group was uniquely defined as $P2_1/c$ by systematic absences. The samarium atom was located on a Patterson map, and the subsequent calculation of the difference Fourier map led to the location of all the non-hydrogen atoms. Conversion to anisotropic temperature factors and refinement led to $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o| = 0.068$. At this point problems were noted with the methyl carbon atoms of the butyl group: the thermal ellipsoids were not realistic and the bond angles did not make chemical sense. Removal of three atoms followed by the calculation of a difference Fourier map revealed six peaks of equal height. Inclusion of each at an occupancy factor of 0.5 and further refinement afforded final values of $R_1 = 0.048$ and $R_2 = \{\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2\}^{1/2} = 0.050$. (Thermal parameters and bond lengths and angles related to the methyl carbon atoms of the butyl groups were quite reasonable). Hydrogen atoms were not located. The largest parameter shifts in the final cycle of refinement were less than 0.02 of their estimated standard derivations. The final difference Fourier showed no feature greater than 0.4 e/Å^3. Unit weights were used at all stages; no systematic variation of $w(|F_o| - |F_c|)^2$ vs. $|F_o|$ or $(\sin\theta)/\lambda$ was noted. The function $w(|F_o| - |F_c|)^2$ was minimized.[32] Neutral atom scattering factors were taken

Table II. Crystal Data and Summary of Intensity Data Collection and Structure Refinement

compd	$[(CH_3C_5H_4)_2SmC{\equiv}CC(CH_3)_3]_2$
M_r	389.7
space group	$P2_1/c$
cell const	
a, Å	9.418 (3)
b, Å	17.830 (6)
c, Å	11.134 (5)
β, deg	113.10 (3)
cell vol, Å^3	1719.8
molecules/unit cell	2 (dimers)
ρ(calcd), g cm^{-3}	1.51
μ(calcd), cm^{-1}	34.6
radiatn	Mo Kα
max cryst dimens, mm	0.20 × 0.30 × 0.45
scan width	0.80 + 0.20 tan θ
std reflctns	400, 080, 004
decay of stds	±3%
reflectns measd	2818
2θ range, deg	0–50
obsd reflctns, $I \geq 3\sigma(I)$	1659
no. of parameters varied	172
GOF	2.57
R	0.048
R_w	0.050

Table III. Final Fractional Coordinates for $[(CH_3C_5H_4)_2SmC{\equiv}CC(CH_3)_3]_2$

atom	x/a	y/b	z/c	U(eqv), Å^2
Sm(1)	0.09458 (8)	0.06992 (4)	0.13697 (7)	0.069
C(1)	–0.058 (1)	–0.0524 (8)	0.100 (1)	0.077
C(2)	–0.124 (1)	–0.0994 (7)	0.136 (1)	0.067
C(3)	–0.202 (2)	–0.1560 (8)	0.185 (1)	0.091
Cp(1)	0.338 (2)	–0.025 (1)	0.247 (2)	0.106
Cp(2)	0.392 (2)	0.030 (2)	0.187 (2)	0.121
Cp(3)	0.401 (2)	0.097 (2)	0.252 (3)	0.125
Cp(4)	0.353 (2)	0.088 (2)	0.353 (3)	0.120
Cp(5)	0.314 (2)	0.010 (2)	0.353 (2)	0.123
Cp(6)	0.033 (3)	0.222 (2)	0.156 (3)	0.180
Cp(7)	–0.097 (4)	0.190 (2)	0.048 (3)	0.184
Cp(8)	–0.181 (2)	0.138 (2)	0.087 (3)	0.129
Cp(9)	–0.109 (3)	0.132 (1)	0.221 (3)	0.159
Cp(10)	0.022 (3)	0.183 (1)	0.263 (3)	0.137
C(4)	–0.093 (4)	–0.220 (2)	0.253 (3)	(iso)
C(5)	–0.368 (4)	–0.166 (2)	0.091 (3)	(iso)
C(6)	–0.225 (4)	–0.117 (2)	0.309 (3)	(iso)
C(4)′	–0.106 (4)	–0.179 (2)	0.322 (3)	(iso)
C(5)′	–0.236 (4)	–0.227 (2)	0.092 (4)	(iso)
C(6)′	–0.359 (4)	–0.126 (2)	0.175 (3)	(iso)
Me(1)	0.253 (3)	–0.035 (1)	0.440 (2)	(iso)
Me(2)	–0.156 (3)	0.092 (1)	0.307 (3)	(iso)

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from Cromer and Waber[33] for Sm and C. The scattering for Sm was corrected for the real and imaginary components of anomalous dispersion by using the table of Cromer and Liberman.[34] The final fractional coordinates are given in Table III. The final values of the thermal parameters are given in the supplementary material.

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Registry No. I, 84642-15-9; II, 84642-16-0; $LiC{\equiv}CC(CH_3)_3$, 37892-71-0; $(CH_3C_5H_4)_2SmCl(THF)$, 84623-27-8; $HP(C_6H_5)_2$, 829-85-6; $HC{\equiv}CC(CH_3)_3$, 917-92-0; $SmCl_3$, 10361-82-7; $CH_3C_5H_4Na$, 55562-83-9; THF, 109-99-9.

Supplementary Material Available: Listings of structure factor amplitudes, anisotropic thermal parameters, and complete bond length and angle information (12 pages). Ordering information is given on any current masthead page.

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Structure of the Hydrogenation Catalyst $[(P\frown P)Rh(NBD)]ClO_4$, $P\frown P = (\eta^5\text{-}[(CH_3)_3C]_2PC_5H_4)_2Fe$, and Some Comparative Rate Studies

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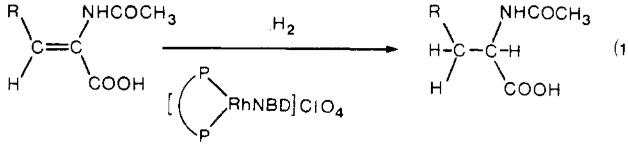
The structure of the hydrogenation catalyst precursor $[(P\frown P)Rh(NBD)]ClO_4$ $[P\frown P = (\eta^5\text{-}[(CH_3)_3C]_2PC_5H_4)_2Fe$; NBD = norbornadiene] has been determined. The cationic moiety finds Rh in a very distorted "square-planar" environment coordinated to the double bonds of the norbornadiene ligand at distances of 2.181 (5) and 2.161 (5) Å and the phosphorus atoms of the bidentate chelating phosphine ligand at distances of 2.466 (1) and 2.458 (1) Å. Relative rate studies, employing the aforementioned catalyst precursor and also the related precursor where $P\frown P = (\eta^5\text{-}[(C_6H_5)_2PC_5H_4]_2Fe)$, have been performed for the hydrogenation reactions of (acylamino)acrylic, (acylamino)cinnamic, itaconic, and methylcinnamic acids in methanol and/or ethanol. The results of these experiments, together with related work previously reported, are discussed and rationalized in terms of the steric and electronic effects exerted by the substituents attached to the chelating bis(phosphine) ligands.

Most studies of homogeneous catalysis by metal complexes have used tertiary phosphines such as triphenylphosphine or bis(tertiary phosphines) such as 1,2-bis(diphenylphosphino)ethane as ligands. With appropriate synthetic ingenuity similar optically active ligands can be isolated as one or the other enantiomer and complexes of these have been studied with respect to their ability to catalyze asymmetric reactions. In particular notable success has been achieved in the asymmetric hydrogenation of amino acid precursors such as α-(acylamino)cinnamic acid using cationic rhodium(I) complexes of optically active chelating bis(tertiary phosphines) as catalyst precursors:[1] for example, eq 1, R = C_6H_5 and $P\frown P$ = $(C_6H_5)_2PCH(CH_3)CH(CH_3)P(C_6H_5)_2$, chiraphos, where the optical yield is nearly 100%.[2]



(1)

The almost universal use of ligands with arylphosphorus moieties in reaction such as (1) has resulted in much attention being focused on the aryl rings with respect to their involvement in the discrimination step. Thus heavy emphasis has been placed on the idea that the incoming prochiral substrate "sees" a chiral array of aryl rings (propellors) held by a fixed complex-ring conformation.[3,4] Binding of one face or the other of the substrate gives a pair of diastereomeric intermediates in equilibrium that are hydrogenated at different rates to afford the mixture of enantiomeric products. These ideas have been elegantly elaborated by the groups of Halpern and Bosnich and co-workers,[4-7] who also point out that the rate or hydrogenation of the diastereomers 1 will be governed by the stability of the *cis*-dihydride intermediate 2: see eq 2 where $P\frown P$ is optically active and $=\frown O$ (where O is gen-

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