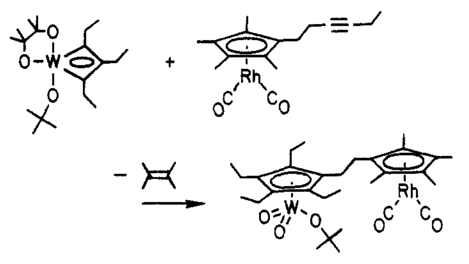

(5)

6

^{13}C NMR spectrum in the cyclopentadienyl carbon signal region shows signals for one η^5-C_5R_4R'-type ring bound to W and one η^5-C_5R_4R'-type ring bound to Rh (Figure 1d). The highest mass pattern in the FD mass spectrum of 6 is found around 744, the mass expected for 6 (^{184}W) minus one carbonyl ligand. The IR spectrum of 6 is a composite of that of 1 and that of 5, suggesting that there is little or no interaction between the two ends of the molecule.

No peralkylated cyclopentadienyl system linked by two carbon atoms is known. The compounds reported here, especially heterobimetallic 6, are not likely to be preparable by traditional techniques. We will be attempting to prepare other heterobimetallic linked cyclopentadienyl systems via approaches analogous to that shown in eq 5 and will be exploring the fundamental chemistry of such species.

Acknowledgment. This work has been supported by the Director, Office of Basic Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division, of the U.S. Department of Energy under Contract DE-AC02-78ER04949-A003. We also thank the Biomedical Research Support Shared Instrumentation Grant Program, Division of Research Resources, for funds to purchase the X-ray diffraction equipment under NIH Grant S10RR02243-01 and the Canadian government for an NSERC postdoctoral fellowship to S.A.M.

Supplementary Material Available: Description of crystallography, crystal data, final positional and thermal parameters, selected interatomic distances, atom labeling scheme, and final observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page.

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(15) The group notation is being changed in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is being eliminated because of wide confusion. Group I becomes groups 1 and 11, group II becomes groups 2 and 12, group III becomes groups 3 and 13, etc.

Preparation, Structure, and Reactivity of $[Fe\{CH(PPh_2)_3\}(C_5H_5)][PF_6]$, a Monometallic, η^3 Complex of Tris(diphenylphosphino)methane

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Summary: Ultraviolet irradiation of $[Fe(p\text{-xylene})(Cp)][PF_6]$ and tris(diphenylphosphino)methane (tppm) gives $[Fe\{HC(PPh_2)_3\}(Cp)][PF_6]$ in 96% yield. Crystal structure analysis (R = 6.2%) shows that all three phosphorus atoms are coordinated to the iron atom, providing the first example of η^3 coordination of tppm on a single metal. There is considerable strain in the tricyclic system, with all three P-C-P angles less than 90°. One Fe-P bond is easily opened by refluxing acetonitrile, giving $[Fe(MeCN)(\eta^2\text{-tppm})(Cp)][PF_6]$.

Tris(diphenylphosphino)methane (tppm)[1] has received considerable attention as a ligand for transition metals.[2] In particular, tppm has been shown to promote "spontaneous self-assembly" of the metal cluster $[Ni_3(\mu_3\text{-tppm})(CO)_6]$ from $Ni(CO)_4$.[2a] In other studies, η^1, η^2, η^2-μ, and η^3-μ_3 coordination, and rearrangement, have been demonstrated,[2] but in no case has tppm been found with all three phosphorus atoms coordinated to a single transition-metal center. We report the first instance of tppm acting as a η^3 ligand.

Ultraviolet irradiation[3] of a mixture of $[Fe(p\text{-xylene})(Cp)][PF_6]$[4] (418 mg, 1.12 mmol) and tppm (671 mg, 1.18 mmol) in ~80 mL of dichloromethane for 8 h, followed by filtration, evaporation to ~10 mL in vacuo, and slow addition of ~15 mL of ethyl ether gives $[Fe\{HC(PPh_2)_3\}(Cp)][PF_6]$[4] (I, 903 mg, 96% yield) as orange crystals. Spectroscopic characterization[5] suggested that η^3 coordination of tppm had occurred, but the shift of the cyclopentadienyl protons in the ^{1}H NMR spectrum of I was δ 5.60, at anomalously low field. Ordinarily, phosphine substituents cause an upfield shift of the cyclopentadienyl resonance in $[FeL_3(Cp)]^+$: e.g., $[Fe(\eta^1\text{-dppm})(CO)_2(Cp)]^+$ (dppm = bis(diphenylphosphino)methane), δ 5.52,[6] $[Fe(\eta^2\text{-dppm})(CO)(Cp)]^+$, δ 5.25,[6] $[Fe(\eta^1\text{-dppm})(\eta^2\text{-dppm})(Cp)]^+$, δ 4.76,[7] $Fe\{\eta^3\text{-MeC}(CH_2PPh_2)_3\}(Cp)]^+$, δ 5.06,[8a] and $[Fe\{\eta^3\text{-PhP}(CH_2CH_2PPh_2)_2\}(Cp)]^+$, δ 4.23.[8b] In order to confirm η^3 coordination of tppm in I and to gain some insight into this NMR anomaly, a crystal structure analysis of I was carried out.[9]

Single crystals of I were obtained by slow evaporation of a dichloromethane solution of I with a stream of ethyl ether-saturated nitrogen. An ORTEP[10] plot of the resulting structure is shown in Figure 1, and selected bond lengths

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(5) ^{1}H NMR ($(CD_3)_2CO$, 90 MHz) δ 7.7–6.9 (30 H, m, Ph), (1 H, q, $^2J_{P-H}$ = ~5 Hz, CH), 5.60 (5 H, q, $^3J_{P-H}$ = 1.6 Hz, Cp); ^{31}P NMR ($(CD_3)_2CO$, 80.96 MHz) δ_P 30.05 (3 P, s, Fe–P), –142.21 (1 H, sept, J = 708 Hz, PF_6^-).

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Table I. Selected Bond Lengths (Å) and Angles (deg) (with Esds) for $[Fe\{HC(PPh_2)_3\}(Cp)][PF_6]\cdot{}^1/_2CH_2Cl_2$

Bond Lengths

Fe-P1	2.212 (2)	P1-C21	1.827 (6)
Fe-P2	2.222 (2)	P2-C1	1.874 (6)
Fe-P3	2.219 (2)	P2-C31	1.839 (6)
Fe-CPO[a]	1.719 (6)	P2-C41	1.828 (6)
Fe-CPOA[a]	1.706 (6)	P3-C1	1.875 (6)
P1-C1	1.885 (6)	P3-C51	1.821 (6)
P1-C11	1.814 (6)	P3-C61	1.822 (6)
		C1-H1[b]	1.008 (5)
		P4-F[c]	1.53 (3)

Bond Angles

P1-Fe-P2	72.48 (6)	P3-Fe-CPOA[a]	138.3 (1)
P1-Fe-P3	71.90 (6)	P1-C1-P2	88.4 (2)
P1-Fe-CPO[a]	136.2 (1)	P1-C1-P3	87.6 (2)
P1-Fe-CPOA[a]	137.8 (1)	P2-C1-P3	88.3 (2)
P2-Fe-P3	72.03 (6)	Fe-P1-C1	83.8 (2)
P2-Fe-CPO[a]	137.2 (1)	Fe-P2-C1	83.7 (2)
P2-Fe-CPOA[a]	135.4 (1)	Fe-P3-C1	83.8 (2)
P3-Fe-CPO[a]	138.0 (1)		

[a] CPO and CPOA are the centroids of the cyclopentadienyl groups CPO and CPA, respectively. [b] H1 was located in a difference Fourier but was not refined. [c] Average of six P-F distances.

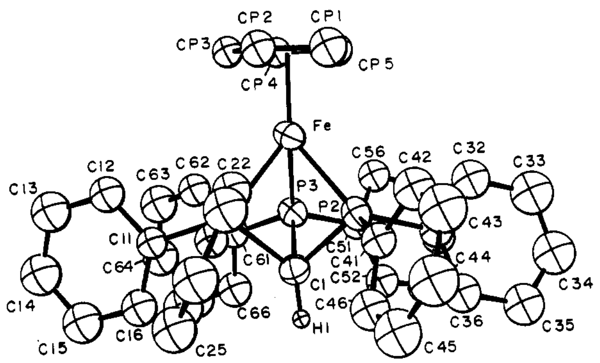

Figure 1. An ORTEP[10] plot of the $[Fe\{HC(PPh_2)_3\}(Cp)]^+$ cation, showing 50% probability ellipsoids. Hydrogen atoms, except for H1, are omitted for clarity. H1 is arbitrarily scaled. Only one of the two half-occupied cyclopentadienyl groups is shown. Phenyl carbons are numbered sequentially.

and angles are presented in Table I. The $[Fe\{HC(PPh_2)_3\}(Cp)]^+$ cation indeed contains a η^3-tppm ligand, and there is evidence for considerable strain in this ferratriphosphabicyclo[1.1.1]pentane system. The Fe–P bond lengths are about the same as those found in the structure of $[Fe(CO)(dppm)(Cp)][BPh_4]$ (II), 2.226 (6) and 2.198 (6) Å.[11] The P–C1 bonds are barely longer than those in II, 1.84 (2) and 1.86 (2) Å, and slightly longer than the P–phenyl distances in I itself. The nonbonded Fe–C1 distance in I is 2.746 (5) Å, which is ca. 0.6 Å longer than a typical Fe–C bond (2.0–2.2 Å)[12] but is about the same as the fractional Fe–C2 bonds in $[\{Fe(CO)_2(Cp)\}_2(\eta^3\text{-}\mu\text{-}CH_2CHCH_2)]^+$ (2.59 and 2.72 Å).[13] The major distortions in I are angular. The P–Fe–P angles are smaller than that angle in II, 74.6 (2)°. The most remarkable distortion is that *all of the P–C1–P angles are less than 90°*. Thus, one can consider carbon C1 to be using primarily p orbitals to form three bonds to phosphorus, leaving an orbital rich in s character to bond to H1. The P1–P2–P3 plane is parallel to the cyclopentadienyl plane (~1.8° angle). A possible explanation of the anomalous cyclopentadienyl NMR shift of I is found in the orientations of the six phenyl rings. All six rings are "stacked" about the equator of the cation, such that adjacent phenyl rings on different phosphorus atoms are approximately parallel[2h] (the interplanar angles are as follows: Ph1–Ph6 = 24.4°, Ph2–Ph4 = 19.4°, and Ph3–Ph5 = 25.0°, where PhN is the plane consisting of atoms CN1–CN6). The planes of the phenyl rings are approximately perpendicular to the cyclopentadienyl plane (angles range from 72.9° (Ph6) to 114.7° (Ph2), averaging 89.3°). The collective ring currents of the stacked phenyl rings are probably responsible for the anomalous deshielding of the cyclopentadienyl protons.[14]

Refluxing acetonitrile reacts rapidly with I, displacing one arm of the tppm ligand to quantitatively produce $[Fe(MeCN)(\eta^2\text{-tppm})(Cp)][PF_6]$ (III).[15] The reaction is stereospecific, producing only one of the two possible isomers (exo or endo at C1). The acetonitrile ligand of II exchanges with CD_3CN at room temperature, with a half-life of about 35 min as followed by proton NMR. The photoreaction of $[Fe(p\text{-xylene})(Cp)][PF_6]$ with tppm in acetonitrile[3e] produces the *same* isomer of III. This result confirms that the simultaneous availability of three coordination sites, in the absence of any other potential ligands, is essential for the formation of a η^3-tppm complex. The sequential reaction of $FeCl_2$ with tppm, TlCp, and NH_4PF_6, a method which successfully produces $[Fe\{\eta^3\text{-}PhP(CH_2CH_2PPh_2)_2\}(Cp)][PF_6]$,[8c] does *not* give I.

Although the methinyl (H1) proton in I should be fairly acidic, attempts to deprotonate I using $Na[N(SiMe_3)_2]$, $KOCMe_3$, KH, and *n*-BuLi have thus far led mainly to recovered starting material, with some decomposition, despite the facile deprotonation of $[Fe(CO)(dppm)(Cp)][PF_6]$ to give a stable zwitterion,[16] and the reported

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(9) Crystal structure data for I: a well-formed crystal approximately 0.3 mm × 0.5 mm × 0.5 mm was coated with epoxy and mounted on the end of a glass fiber. Data were collected on an Enraf-Nonius CAD4 diffractometer using Mo Kα radiation: space group $P2_1/n$, $Z = 4$, $a = 10.9466$ (9) Å, $b = 17.754$ (3) Å, $c = 20.532$ (2) Å, $\beta = 94.225$ (9)°, $V = 3979.4$ Å^{-3}, $\rho_{calcd} = 1.442$ g·cm^{-3}, $\nu = 6.16$ cm^{-1}. A total of 5731 reflections were collected, and of these 3875 with $(F_0)^2 \geq 3\sigma(F_o)^2$ were used. The iron atom and three phosphorus atoms were located by direct methods, and the remaining atoms were found by difference Fourier methods. Cyclopentadienyl carbons were successfully refined as two rigid groups with C–C distances of 1.44 Å and angles of 108°. A multiplier of 0.50 and an independently varied isotropic thermal parameter were applied to each cyclopentadienyl carbon. Hydrogen atom H1 was located in a difference Fourier map but was not refined. Phenyl and half-weighted cyclopentadienyl protons were added as a fixed contribution with d(C–H) = 1.00 Å and $B = 6.0$ Å^2. Phenyl carbons were refined with isotropic thermal parameters, and other atoms were refined with anisotropic thermal parameters. The atoms CS, Cl1S, and Cl2S, refined at half occupancy, apparently constitute 0.5 equiv of methylene chloride of solvation (corroborated by NMR) lying near the crystallographic center of inversion. The 13 largest peaks (0.05–0.11 e·Å^{-3}) in the final difference Fourier were associated with the phenyl rings and the PF_6^- anion. The largest shift/esd parameters in the final least-squares cycle (–2.37 to +1.94) were associated with the CH_2Cl_2 atoms. Full-matrix least-squares refinement led to $R = 6.2\%$ and $R_w = 7.5\%$.

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(15) Properties of $[Fe(MeCN)(\eta^2\text{-tppm})(Cp)][PF_6]$: red-orange, air-stable crystals; 79% yield; IR (Nujol) ν(CN) 2249, 2271 cm^{-1}; ^{1}H NMR (CD_3CN, 90 MHz) δ 7.6–6.9 (30 H, m, Ph), 5.88 (1 H, dt, $^2J_{P-H} = 8$ Hz, $^2J_{P-H} = 10$ Hz, 6 H), 4.47 (5 H, dist t, $^3J_{P-H} = 1.5$ Hz, Cp), 1.33 (3 H, dist t, $^5J_{P-H} = 1.3$, CH_3); ^{31}P NMR (CH_3CN, 80.96 MHz) δ_P 58.3 (3 P, d, $^2J_{PP} = 15$ Hz, Fe–*P*), –20.6 (1 P, t, free P), –143.0 (1 P, sept, $J = 706$ Hz, PF_6^-). Anal. Found (Calcd): C, 60.17 (60.35); H, 4.54 (4.50); P, 14.27 (14.15).

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deprotonations of tppm[2b,17] and its sulfides.[18] Perhaps the deprotonation of tppm in I would produce a planar P_3C ligand[19] which could not be accommodated by a single iron atom. Studies of tppm complexes with other metals are in progress to address this point.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, Occidental Research Corp., and Ashland Oil for financial support.

Registry No. I, 95156-04-0; I·CH_2Cl_2, 95156-05-1; III, 95192-55-5; tppm, 28926-65-0; [Fe(*p*-xylene)(Cp)][PF_6], 34978-37-5.

Supplementary Material Available: Listings of positional, thermal, and group parameters (Tables II–V) and experimental and calculated structure factors (Table VI) (31 pages). Ordering information is given on any current masthead page.

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Organometallic Compounds of the Lanthanides. 24.[1] Synthesis and X-ray Crystallographic Characterization of the First Organolanthanide Derivative with a Lanthanide–Silicon Bond

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Summary: Bis(cyclopentadienyl)samarium chloride and bis(cyclopentadienyl)lutetium chloride react with (trimethylsilyl)lithium in 1,2-dimethoxyethane (dme) to give complexes of the type $[Li(dme)_3][(C_5H_5)_2Ln(Si(CH_3)_3)_2]$ (Ln = Sm, Lu). The molecular structure of $[Li(dme)_3][(C_5H_5)_2Sm(Si(CH_3)_3)_2]$ has been elucidated through complete X-ray analysis. The crystals are monoclinic, space group $P2/n$ (nonstandard setting of $P2/c$, No. 13), with a = 14.460 (4) Å, b = 9.018 (3) Å, c = 14.558 (7) Å, β = 103.96 (3)°, V = 1842.3 Å^3, ρ_{calcd} = 1.269 g/cm^3, and Z = 2. The structure was solved by Patterson and Fourier techniques from 2621 unique reflections ($I \geq 3\sigma(I)$) corrected for Lorentz and polarization effects but not for absorption (μ = 15.89 cm^{-1}). The final R value is 0.062 (R_w = 0.079). Principal dimensions are as follows: Sm–Cp = 2.316 (7) Å, Sm–Si = 2.880 (2) Å, Cp-Sm-Cp′ = 131.6 (2)°, Si-Sm-Si′ = 90.07 (7)°.

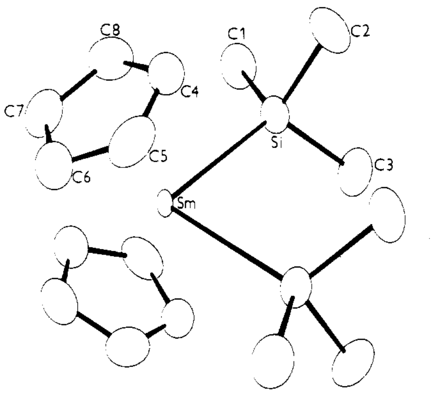
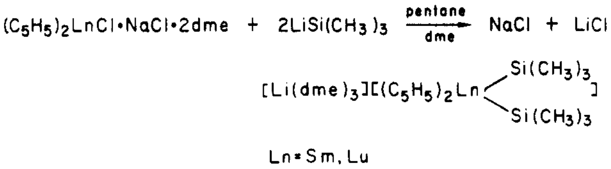


Figure 1. ORTEP plot of the $[(C_5H_5)_2Sm(Si(CH_3)_3)_2]^-$ anion.

Lanthanides are generally thought to be hard Lewis acids.[2] Thus the most thermodynamically stable compounds are formed between carbon, halogen, or oxygen donors and lanthanide acceptors.[3] Only few examples of organometallic compounds of the lanthanides with bonds to soft donors such as P,[4-8] As,[9] and S[10] are known. We reported the synthesis of the first bis(cyclopentadienyl)lanthanide triphenylgermyl and triphenylstannyl complexes.[11] Organometallic compounds of the lanthanides with bonds to silicon have not been described as yet. The lanthanide–silicon bond might possess a high degree of "covalency" because of the good donor properties of the trimethylsilyl ligand, although the bonding in organoactinides and organolanthanides is considered to be ionic.[12]

Reaction of $(C_5H_5)_2SmCl·NaCl·2dme$ (dme = 1,2-dimethoxyethane) or $(C_5H_5)_2LuCl·NaCl·2dme$ with an equimolar amount of $LiSi(CH_3)_3$ in dme at −78 °C does not yield the hoped for bis(cyclopentadienyl)lanthanide trimethylsilyl complexes $(C_5H_5)_2Ln–Si(CH_3)_3$ (Ln = Sm, Lu) but instead the cation–anion pairs $[Li(dme)_3][(C_5H_5)_2Ln(Si(CH_3)_3)_2]$ (Ln = Sm, Lu) (eq 1).[13]



$$(C_5H_5)_2LnCl·NaCl·2dme + 2LiSi(CH_3)_3 \xrightarrow[dme]{pentane} NaCl + LiCl + [Li(dme)_3][(C_5H_5)_2Ln(Si(CH_3)_3)_2] \quad (1)$$

Ln = Sm, Lu

The yellow complexes are extremely sensitive toward moisture and air. They decompose slowly at room tem-

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(13) $Na(C_5H_5)$ (0.84 g, 9.4 mmol) was added to a suspension of $SmCl_3$ (1.2 g, 4.7 mmol) in 70 mL of dme. After 3 h of stirring, the reaction mixture was cooled to −78 °C. Formation of $(C_5H_5)_2SmCl·NaCl·2dme$ in 80% yield was assumed and an equimolar amount of $LiSi(CH_3)_3$ (3.76 mmol, 18.8 mL of a 0.2 M pentane solution) was added slowly. After the mixture was warmed to room temperature, stirred for an additional 14 h, decanted from the LiCl formed, and concentrated to 20 mL, pentane (20 mL) was added. After the mixture was cooled to −23 °C for 1 week, yellow crystals of $[Li(dme)_3][(C_5H_5)_2Sm(Si(CH_3)_3)_2]$ were collected in 20% yield, based on $SmCl_3$.

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