inside was filled with nitrogen by using a needle technique. A nitrogen-saturated benzene solution (3 mL) of complex 1 (4×10^{-4} M) was poured into the cell with a syringe, and the cell was kept in a constant-temperature UV compartment. From a stock solution of a given concentration of PPh_3 kept in a constant-temperature water bath was transferred a 1-mL portion into the cell quickly by using a syringe. At appropriate intervals change of the absorption at 350 nm was recorded. Plots of ln $\{[1]_0 - [Pt(0)]\}$ vs time gave straight lines up to ca. 50% conversion. The absorption change at 400 nm gave the same rate data. The reactions of **2** were carried out similarly. The initial rates for the reaction of 1 with PPh_3 in dichloromethane were determined from the data up to ca. 15% conversion.

Yields of the coupling product $CH_2{=}CMeCH_2CH(COMe)_2$ were determined by GLC analysis (SE-30, 3 mm × 2 m, 150 C; internal standard, *n*-tridecane). Initial rates of the reaction between 1 (5×10^{-3} M) and an equivalent dppe in dichloromethane were determined by observing increase of the coupling product by GLC.

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Registry No. 1, 33012-06-5; **2**, 32660-97-2; **3**, 71504-60-4; **6**, 120906-43-6; **7**, 120906-45-8; **8**, 120906-46-9; **9**, 120906-48-1; **10**, 120906-49-2; **11**, 120906-50-5; **12**, 110270-78-5; $CH_2{=}C(CH_3)CH_2CH(COCH_3)_2$, 84884-24-2; $Pt(\eta^3\text{-}CH_2CHCH_2)Cl(PPh_3)$, 35770-09-3; $(C_6H_3Cl_2\text{-}2,5)Li$, 68099-30-9.

Phosphido Derivatives of Bis(pentamethylcyclopentadienyl)zirconium and -hafnium Complexes and the Molecular Structure of (η-$C_5Me_5)_2Hf(H)(PHPh)$

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Primary and secondary phosphines react with $Cp^*{}_2HfH_2$ ($Cp^* = \eta\text{-}C_5Me_5$) with extrusion of H_2 to give the phosphido derivatives $Cp^*{}_2Hf(H)(PRR')$ (**1**, R = R′ = Ph; **2**, R = H, R′ = Ph; **3**, R = H, R′ = c-C_6H_{11}). Reactions of **1** generally proceed with elimination of $PHPh_2$. Thus, **1** reacts with 1 atm of H_2, CO, and C_2H_4 to give $PHPh_2$ and $Cp^*{}_2HfH_2$, $Cp^*{}_2Hf(CO)_2$, and the metallacyclopentane $Cp^*{}_2Hf(C_4H_8)$, respectively. However, carbon dioxide reacts with **1** *without* loss of $PHPh_2$ to give a product resulting from the insertion of CO_2 into the Hf-P bond, $Cp^*{}_2Hf(H)(Ph_2PCO_2)$ (**4**). A second equivalent of CO_2 will insert into the Hf-H bond of **4** to cleanly give $Cp^*{}_2Hf(HCO_2)(Ph_2PCO_2)$ (**5**). Reaction of 1 equiv of LiPHPh or $LiPH(C_6H_{11})$ with $Cp^*{}_2MX_2$ (M = Hf, Zr; X = Cl, I) affords the phosphido halide complexes $Cp^*{}_2Hf(X)(PHR)$ (**6**, X = I, R = Ph; **7**, X = I, R = C_6H_{11}; **8**, X = Cl, R = C_6H_{11}) and $Cp^*{}_2Zr(Cl)\{PH(C_6H_{11})\}$ (**9**) in high yields. Orange prisms of **2** were grown from petroleum ether solution and crystallized in the orthorhombic space group *Pnma* with $Z = 4$, $a = 13.180$ (2) Å, $b = 14.157$ (2) Å, and $c = 13.191$ (2) Å. An X-ray diffraction study was carried out, and the least-squares refinement converged to $R(F) = 5.8\%$ and $R_w(F) = 6.2\%$ for 1328 unique reflections with $F_o > 5\sigma(F_o)$. The structure of **2** is disordered about a crystallographic mirror plane that contains the Cp* ring centroids and the Hf atom. Salient metrical parameters of the structure include the following: Hf-P = 2.549 (8) Å; Hf-centroid = 2.222 (18) Å (average); centroid-Hf-centroid = 144.2 (7)°; P-Hf-centroids = 110.8 (6)° and 101.2 (6)°.

Introduction

The chemistry of the metallocene derivatives of the group 4 transition metals has been extensively investigated during the past 2 decades and has been comprehensively reviewed.$^{1-3}$ A particularly rich and well-developed area of this chemistry involves the reactions of bis(pentamethylcyclopentadienyl) complexes of the formula $Cp^*{}_2M(X)(X')$ ($Cp^* = \eta\text{-}C_5Me_5$; M = Zr, Hf; X, X′ = monoanionic donor ligand). We were interested in exploring the chemistry of a new class of compounds of this type, the monophosphido derivatives of permethylzirconocene and permethylhafnocene, from two perspectives. First, although analogous complexes containing amides (i.e., $Cp^*{}_2M(NRR')(X)$) have been previously prepared and their chemistry explored in some detail,$^{4-6}$ the related phosphides have not been reported and we were curious whether the structures and reactivities of such complexes having "soft" PR_2 ligands would differ substantially from those possessing "hard" NR_2 (or alkoxide) donor ligands. Second, it seemed likely that steric constraints imposed by the two bulky pentamethylcyclopentadienyl ligands would strongly favor monomeric phosphido complexes that in turn might serve as useful precursors to monomeric phosphinidene (PR^{2-}) complexes.^{7}

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Table I. Spectroscopic Data for New Compounds

compound	type[a]	data[b]
$Cp^*_2Hf(H)(PPh_2)$ (**1**)	^1H[c]	1.96 (s, 30 H), 6.99 (mult, 2 H), 7.08 (mult, 4 H), 7.32 (mult, 4 H), 14.66 (d, 1 H, J_{PH} = 7 Hz)
	^{31}P[c]	45.5 (d, J_{PH} = 7 Hz)
	IR[d]	3056 (vw), 2721 (vw), 1630 (s, br), 1577 (m), 1465 (s), 1435 (s), 1062 (w), 908 (w, br), 749 (w), 735 (s), 696 (s), 527 (w), 509 (m), 464 (w)
$Cp^*_2Hf(H)(PHPh)$ (**2**)	^1H	1.95 (s, 30 H), 4.58 (d, 1 H, J_{PH} = 227 Hz), 7.01 (mult, 1 H), 7.09 (mult, 2 H), 7.59 (mult, 2 H), 13.85 (s, 1 H)
	^{31}P	30.5 (d, J_{PH} = 227 Hz)
	IR	3063 (vw), 3047 (vw), 2319 (m), 1643 (s, br), 1580 (m), 1476 (s), 1453 (s), 1431 (s), 1064 (w), 925 (w), 892 (m), 801 (w), 782 (w), 737 (m), 729 (s), 696 (s), 532 (w, br)
$Cp^*_2Hf(H)(PHCy)$ (**3**)	^1H	2.02 (s, 30 H), 1–2.6 (mult, 11 H), 3.90 (dd, 1 H, J_{PH} = 232 Hz, $^3J_{HH}$ = 9 Hz), 12.86 (s, 1 H)
	^{31}P	96.3 (d, J_{PH} = 232 Hz)
	IR	2718 (vw), 2322 (m), 1630 (s, br), 1488 (s), 1446 (s), 1259 (m), 1116 (m), 999 (m), 907 (w), 880 (vw), 838 (w), 804 (vw), 779 (w), 588 (w), 533 (w)
$Cp^*_2Hf(H)(Ph_2PCO_2)$ (**4**)	^1H	1.93 (s, 30 H), 7.06 (mult, 2 H), 7.11 (mult, 4 H), 7.77 (mult, 4 H), 12.32 (s, 1 H)
	^{13}C	11.66 (q, J_{CH} = 126 Hz), 116.2 (s), 128–135 (aryl mult), 193.8 (d, J_{CP} = 23 Hz)
	^{31}P	−3.5 (s)
	IR	3052 (vw), 1640 (s, br), 1586 (w), 1480 (s), 1457 (s), 1438 (s), 1389 (s), 1343 (s), 1309 (w), 1104 (w), 1066 (w), 1000 (w), 859 (s), 745 (s), 697 (s), 517 (m), 497 (w), 467 (w), 450 (w)
$Cp^*_2Hf(HCO_2)(Ph_2PCO_2)$ (**5**)	^1H	1.78 (s, 30 H), 7.10 (mult, 6 H), 7.71 (mult, 4 H), 8.69 (s, 1 H)
	^{13}C	11.18 (q, J_{CH} = 127 Hz), 120.1 (s), 128–134 (aryl mult), 163.7 (d, J_{CH} = 209 Hz), 191.4 (d, J_{CP} = 24 Hz)
	^{31}P	−1.9 (s)
	IR	3050 (vw), 1645 (s), 1604 (vw), 1488 (m), 1481 (m), 1441 (m), 1434 (m), 1397 (m), 1354 (s), 1267 (vs), 1101 (w), 998 (w), 865 (s), 776 (m), 757 (m), 747 (m), 702 (s), 517 (m), 491 (m)
$Cp^*_2Hf(I)(PHPh)$ (**6**)	^1H	1.94 (s, 30 H), 4.00 (d, 1 H, J_{PH} = 226 Hz), 6.99 (mult, 1 H), 7.13 (mult, 2 H), 7.90 (mult, 2 H)
	^{31}P	34.4 (d, J_{PH} = 226 Hz)
	IR	3059 (vw), 3037 (vw), 2309 (w), 2280 (w), 1578 (m), 1477 (s), 1456 (s), 1431 (s), 896 (w), 736 (m), 696 (m), 588 (m)
$Cp^*_2Hf(I)(PHCy)$ (**7**)	^1H	2.00 (s, 30 H), 1.0–2.5 (mult, 11 H), 3.30 (dd, 1 H, J_{PH} = 220 Hz, $^3J_{HH}$ = 6 Hz)
	^{31}P	72.1 (d, J_{PH} = 220 Hz)
	IR	2330 (m), 1487 (m), 1457 (s), 1446 (s), 1261 (w), 999 (m), 923 (w), 873 (w), 845 (w), 719 (w), 607 (w), 588 (m)
$Cp^*_2Hf(Cl)(PHCy)$ (**8**)	^1H	1.93 (s, 30 H), 1.8–2.4 (mult, 11 H), 3.23 (dd, 1 H, J_{PH} = 215 Hz, $^3J_{HH}$ = 7 Hz)
	^{31}P	36.9 (d, J_{PH} = 215 Hz)
	IR	2718 (vw), 2341 (m), 1483 (s), 1444 (s), 1333 (w), 1290 (vw), 1260 (w), 1193 (vw), 1116 (w), 999 (s), 909 (m), 873 (vw), 842 (m), 801 (vw), 573 (w), 588 (w)
$Cp^*_2Zr(Cl)(PHCy)$ (**9**)	^1H	1.87 (s, 30 H), 0.9–2.4 (mult, 11 H), 3.49 (dd, 1 H, J_{PH} = 203 Hz, $^3J_{HH}$ = 7 Hz)
	^{31}P	71.1 (d, J_{PH} = 203 Hz)
	IR	2317 (m), 1486 (m), 1446 (s), 1262 (w), 1189 (vw), 1170 (vw), 1110 (vw), 1066 (vw), 998 (m), 923 (w), 876 (w), 845 (w), 805 (vw), 721 (w, br), 587 (w)

[a] See the Experimental Section for conditions and solvents. [b] Phenyl proton resonances are reported as multiplets, although at 500-MHz some approach first-order patterns. [c] Chemical shifts in ppm. [d] In cm^{-1}, Nujol mull.

With these notions in mind, we set out to prepare a series of complexes of the type $Cp^*_2M(PRR')(X)$ (R, R′ = H, alkyl, or aryl; X = H or halide) and to examine their chemistry. Herein we report some results of our synthetic, reactivity, and structural studies of these group 4 phosphides. A preliminary account of this work has been presented,[8] and while these studies were underway, other groups have reported preliminary data in related systems.[9,10]

Experimental Section

Reactions were carried out under an argon atmosphere by using standard high-vacuum and Schlenk techniques using dry, air-free solvents. NMR spectra were recorded in C_6D_6 by using a Chicago-built 500-MHz instrument (^1H), a Varian XL-400 spectrometer (^{13}C, 100.6 MHz), and a Nicolet NTC-200 spectrometer (^{31}P, 81 MHz). Elemental analyses were performed by Dornis und Kolbe (West Germany) and Galbraith Laboratories, Inc., Knoxville, TN. Hydrogen gas was purified by passing it over MnO on vermiculite followed by activated 4-Å molecular sieves. Carbon monoxide (Matheson) was used directly from a lecture bottle. Carbon dioxide from a lecture bottle (bone dry, Matheson) was subjected to several freeze–pump–thaw cycles to remove residual noncondensable gases. The phosphines PH_2Ph, $PHPh_2$, PH_2Cy, and $PHCy_2$ (Cy = c-C_6H_{11}) were purchased from Strem Chemicals. The lithiated phosphides [LiPHPh·dioxane] and [LiPHCy·dioxane] were prepared according to a general literature procedure.[11] $Cp^*_2ZrCl_2$, $Cp^*_2HfCl_2$, $Cp^*_2HfI_2$, and $Cp^*_2HfH_2$ were prepared by the literature methods.[12,13]

General spectroscopic data (^1H, ^{13}C, and ^{31}P NMR; IR) for the new complexes reported here are summarized in Table I.

Preparation of $Cp^*_2Hf(H)(PPh_2)$ (1). To a solution of 0.40 g (0.89 mmol) of $Cp^*_2HfH_2$ in 10 mL of petroleum ether was added 155 μL (0.89 mmol) of $PHPh_2$ by using a microliter syringe. A deep purple color immediately developed along with gas (H_2) evolution. The solution was stirred at ambient temperature for 30 min, and then the solvent was removed under vacuum, yielding a foam. A fresh 5-mL portion of petroleum ether was added to the residue, vigorously stirred, and then cooled to −78 °C to precipitate the product. Filtration of the cold mixture afforded 0.48 g (86%) of **1** as a beautiful dark purple powder. Anal. Calcd for $C_{32}H_{41}HfP$: C, 60.51; H, 6.51; P, 4.88. Found: C, 60.16; H,

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7.07; P, 4.78. UV–vis (hexane): λ_{max} = 580 nm ($\epsilon = 1.4 \times 10^3$ L·cm^{-1}·mol^{-1}).

Preparation of $Cp^*_2Hf(H)(PHPh)$ (2). PH_2Ph (105 μL, 0.95 mmol) was added via syringe to a solution of 0.42 g (0.94 mmol) of $Cp^*_2HfH_2$ in 7 mL of petroleum ether. Vigorous hydrogen evolution occurred, and the solution became dark orange in color. After the mixture was stirred for 15 min at ambient temperature, the volume of the solvent was reduced to 3 mL and the solution was cooled to −78 °C. Filtration of the cold mixture yielded 0.36 g (69%) of orange **2**. Anal. Calcd for $C_{26}H_{37}HfP$: C, 55.86; H, 6.67; P, 5.54. Found: C, 56.02; H, 6.65; P, 5.54. UV–vis (hexane): λ_{max} = 415 nm ($\epsilon = 1.4 \times 10^3$ L·cm^{-1}·mol^{-1}).

Preparation of $Cp^*_2Hf(H)(PHCy)$ (3). PH_2Cy (130 μL, 0.98 mmol) was added to a solution of 0.44 g (0.98 mmol) of $Cp^*_2HfH_2$ in 10 mL of petroleum ether. The solution was stirred for 15 min at ambient temperature during which time gas evolution (H_2) was apparent. The solvent was removed from the orange solution, giving a foamy material that solidified upon standing under a dynamic vacuum. Isolation of the solid yielded yellow-orange **3** (0.46 g, 83%). Anal. Calcd for $C_{26}H_{43}HfP$: C, 55.26; H, 7.67; P, 5.48. Found: C, 55.40; H, 7.66; P, 5.38. UV–vis (hexane): λ_{max} = 422 nm ($\epsilon = 1.5 \times 10^3$ L·cm^{-1}·mol^{-1}).

Preparation of $Cp^*_2Hf(H)(Ph_2PCO_2)$ (4). A 0.10-g (0.16-mmol) sample of **1** in 10 mL of toluene was frozen at liquid-nitrogen temperature. To this was added 0.15 mmol of carbon dioxide by using a calibrated volume. The solution was warmed to −78 °C and stirred at this temperature for 30 min; it was then warmed to ambient temperature and stirring was continued for 2 h. The solvent was removed under vacuum to give an oily residue that was triturated with 5 mL of cold petroleum ether to afford 0.10 g of **4** as a white powder (94% yield). Anal. Calcd for $C_{33}H_{41}HfO_2P$: C, 58.36; H, 6.09. Found: C, 57.91; H, 6.23.

Preparation of $Cp^*_2Hf(HCO_2)(Ph_2PCO_2)$ (5). A 0.15-g (0.24-mmol) sample of **1** in 10 mL of toluene was frozen at liquid-nitrogen temperature. To this was added 0.52 mmol of carbon dioxide (via a calibrated volume); the solution was warmed and stirred at −78 °C for 30 min and then at ambient temperature for an additional 2 h. Removal of the solvent gave an oily residue that was triturated with cold petroleum ether (10 mL) to yield colorless, microcrystalline **5** (0.14 g, 82%). Anal. Calcd for $C_{34}H_{41}HfO_4P$: C, 56.47; H, 5.71. Found: C, 55.95; H, 5.84.

Preparation of $Cp^*_2Hf(I)(PHPh)$ (6). A solution of PH_2Ph (180 μL, 1.64 mmol) in 15 mL of THF was treated with 1.0 mL of *n*-BuLi (1.6 M in hexanes). The resulting yellow solution was cooled to −78 °C and added to a cold, stirred solution of $Cp^*_2HfI_2$ (1.04 g, 1.48 mmol) in 10 mL of THF. An intermediate color change from yellow to dark orange occurred. The solution was stirred for 3 h at ambient temperature, and then the solvent was removed under vacuum. The residue was taken up in 10 mL of heptane and filtered to remove a small amount of pale precipitate. The volume of the filtrate was reduced to about 3 mL, and the solution was cooled to −78 °C, resulting in precipitation of 0.65 g (64%) of brick-red **6**. Anal. Calcd for $C_{26}H_{36}HfIP$: C, 45.59; H, 5.30. Found: C, 46.02; H, 5.49. Alternatively, **6** can be prepared by treating a THF solution of $Cp^*_2HfI_2$ with a stoichiometric amount of solid LiPHPh·dioxane and working up in the same manner as described above. **$Cp^*_2Hf(I)(PHCy)$ (7)** was analogously prepared in 64% yield by using PH_2Cy instead of PH_2Ph.

Preparation of $Cp^*_2Hf(Cl)(PHCy)$ (8). To a stirred, cold (−78 °C) solution of $Cp^*_2HfCl_2$ (0.40 g, 0.77 mmol) in 10 mL of THF was added 0.20 g (0.93 mmol) of LiPHCy·dioxane. After the cold bath was removed, the solution slowly turned deep red-orange in color. Stirring was continued for 90 min, and then the solvent was removed under vacuum. The residue was taken up in petroleum ether (8 mL), and the solution was filtered. The filtrate was reduced in volume to about 2 mL and cooled to −78 °C and the product isolated by filtration to yield 0.28 g (61%) of yellow **8**. Anal. Calcd for $C_{26}H_{42}ClHfP$: C, 52.09; H, 7.06. Found: C, 52.44; H, 7.27. **$Cp^*_2Zr(Cl)(PHCy)$ (9)** was analogously prepared as an orange solid in 78% yield from 0.19 g of $Cp^*_2ZrCl_2$ and 0.10 g of LiPHCy·dioxane. Anal. Calcd for $C_{26}H_{42}ClPZr$: C, 60.96; H, 8.26. Found: C, 61.11; H, 8.45.

Reaction of 1 with H_2. This reaction was conveniently monitored in a sealed-tube NMR experiment. A 10-mg sample of **1** was placed in a 5-mm NMR tube sealed to a ground-glass joint and attached to a vacuum line by way of a Teflon needle valve adapter. C_6D_6 (~0.4 mL) was vacuum transferred into the tube at −78 °C, then 700 torr of H_2 was admitted into the line, the needle valve above the tube was closed, and the tube was sealed with a torch. As the benzene thawed, an immediate reaction ensued resulting in the elimination of $PHPh_2$ (^1H and ^{31}P NMR) and the formation of $Cp^*_2HfH_2$ (^1H NMR) as an equilibrium mixture with **1**. Under these conditions, $[Cp^*_2HfH_2]$:[**1**] = 2:1. In contrast, neither **2** nor **3** reacts noticeably with H_2 under similar conditions (25 °C, 4 days).

Reaction of 1 with CO. A sealed-tube NMR sample of **1** was prepared as above except that carbon monoxide was used instead of H_2. After about 3 h at ambient temperature, **1** had been cleanly converted to a single new hafnium product (identified as $Cp^*_2Hf(CO)_2$ by comparison with an authentic sample prepared by an independent method[13]) and free $PHPh_2$ (^{31}P NMR). Although analogous experiments with **2** and **3** indicate that these compounds also react with CO over the course of several days, the reactions are not clean ones and give complex mixtures of Cp*-containing products without forming the free phosphines (PH_2Ph and PH_2Cy).

Reaction of 1 with C_2H_4. A sealed-tube NMR sample of **1** was prepared as above except that ethylene was used instead of H_2. Over the course of 2 days, the dark purple color of **1** gradually bleached as the complex was cleanly converted to a single new hafnium product (identified as the metallacyclopentane complex $Cp^*_2Hf(C_4H_8)$ by comparison with an authentic sample prepared by an independent route[13]) and free $PHPh_2$ (^{31}P NMR).

Crystallographic Characterization of 2. Beautiful orange prisms of **2** with well-formed faces were grown from a cold (−20 °C), saturated petroleum ether solution. A crystal (0.26 × 0.31 × 0.38 mm) was mounted on a glass fiber with epoxy cement. A combination of photographic evidence, systematic absences in the diffraction data, and the lack of symmetry-related dependency for the 13.180 and 13.191 Å axes (that eliminated tetragonal symmetry) revealed that either of the orthorhombic space groups *Pnma* or *Pn*2$_1$*a* were possible. *E*-value statistics (e.g., $E^2 - 1$ = 0.977) strongly favored the centrosymmetric alternative. In this setting there is mirror plane disorder (described below) which was unrelieved in *Pn*2$_1$*a*. Since few molecular parameters are unaffected by this disorder, no fully conclusive space group assignment was possible. The structure is reported as *Pnma* as this setting provided a more consistent set of bond parameters for chemically similar environments.

The data were corrected for absorption by an empirical procedure and for ~13% linear decay in diffraction intensity. The structure was solved by heavy-atom methods and subsequent difference Fourier syntheses. The Cp* rings are rotationally disordered in two approximately equal orientations. The crystallographic mirror plane, which contains the Cp* ring centroids and the Hf atom, produces two equally occupied sites for the P atom. The phenyl ring is approximately bisected by the mirror plane and is, therefore, also disordered. None of the three ring systems could be fully modelled to produce overlaid orientations each containing satisfactory sets of bond distances due to insufficient resolution in the diffraction data. Hence, this structure is provided as a proof of composition and coordination geometry and to eliminate alternative structures for which our data are clearly incompatible. Artifacts created by the disorder reduce the reliability of individual bond parameters (the only reliable bond metrics are given in the caption to Figure 1). Anisotropic refinement was possible only for the Hf and P atoms. The remaining atoms were isotropically refined. No attempt was made to incorporate H atom contributions. All computations used the SHELXTL (5.1) program library (G. Sheldrick, Nicolet XRD, Madison, WI). General crystallographic parameters are summarized in Table II. Listings of atomic coordinates and isotropic thermal parameters (Table III), bond lengths (Table IV), bond angles (Table V), anisotropic thermal parameters (Table VI), and observed and calculated structure factors are available as supplementary material.

Results and Discussion

Treatment of petroleum ether solutions of $Cp^*_2HfH_2$ with the primary and secondary phosphines H_2PPh, H_2PCy, and $HPPh_2$ results in the rapid evolution of 1 equiv

Table II. Crystallographic Data for $(\eta^5\text{-}C_5Me_5)_2Hf(H)(PHPh)$

(a) Crystal Parameters			
formula	$C_{26}H_{37}HfP$	V, Å^3	2461.3 (6)
cryst system	orthorhombic	Z	4
space group	*Pnma*	μ(Mo Kα), cm^{-1}	45.3
a, Å	13.180 (2)	temp, K	293
b, Å	14.157 (2)	T_{max}/T_{min}	1.23
c, Å	13.191 (2)	D(calcd), g·cm^{-3}	1.509
(b) Data Collection			
diffractometer	Nicolet R3m	octants colltd	$+h,+k,+l$
radiatn	Mo Kα	rflns colltd	2469
monochromator	graphite	obsd rflns, $5\sigma(F_0)$	1328
scan limits, deg	$4 \leq 2\theta \leq 50$	std rflns	3 stds/197 rflns
scan method	Wyckoff	decay	~13%
(c) Refinement			
$R(F)$, %	5.79	Δ/σ(final)	0.021
$R_w(F)$, %	6.17	$\Delta(\rho)$, e·Å^{-3}	0.88
GOF	1.591	N_0/N_v	12.5

of dihydrogen and the formation of the corresponding monophosphido hafnium derivatives $Cp^*_2Hf(H)(PRR')$ (**1**, R = R′ = Ph; **2**, R = H, R′ = Ph; **3**, R = H, R′ = C_6H_{11}), as shown in eq 1. Even in the presence of excess phos-

$$Cp^*_2HfH_2 + HPRR' \rightarrow \underset{\mathbf{1-3}}{Cp^*_2Hf(H)(PRR')} + H_2 \quad (1)$$

phine, only 1 equiv is consumed under these conditions (20 °C), and the bis(phosphido) complexes are not formed. In contrast, the bulkier dicyclohexylphosphine ($HPCy_2$) does not react with $Cp^*_2HfH_2$ over a period of days at 105 °C. Complexes **1**–**3** are rare examples of molecules containing both a hydride and a phosphide ligand[14] and have been characterized by standard spectroscopic (see Table I) and analytical methods. The phenylphosphido complex **2** has also been the subject of an X-ray structural study (see below). The reaction depicted in eq 1 is quite similar to the related reactions of protic amines (HNRR′) with decamethylhafnocene dihydride that give H_2 and $Cp^*_2Hf(H)(NRR')$.[4–6]

The physical and chemical properties of **1** differ markedly from those of **2** and **3**. The most striking physical difference is in the colors of the compounds: the diphenylphosphido derivative **1** is intensely purple both in the solid state and in solution (λ_{max} = 580 nm) while the primary phosphido derivatives **2** and **3** are both orange compounds (λ_{max} = 415 and 422 nm, respectively). The ^1H NMR resonances for the hydride ligands of **1**, **2**, and **3** are also noteworthy. As has been pointed out by Bercaw and co-workers, key electronic and structural information is contained in the ^1H NMR chemical shift value for the Hf–*H* resonance in compounds of the type $Cp^*_2Hf(H)(X)$.[6,13] Specifically, the positions of these resonances appear to reflect the degree of π donation to Hf from (potential) π-donor ligands X. Thus, the Hf–*H* chemical shift of **1** at δ 14.7 is suggestive of very little $Ph_2P \rightarrow Hf$ π interaction while the corresponding chemical shift values for **2** (δ 13.9) and **3** (δ 12.9) indicate increasingly stronger π interactions. By analogy to arguments made for the related $Cp^*_2Hf(H)(NRR')$ system,[6] this seems to be a consequence of the increased steric congestion about the Cp^*_2Hf center associated with the secondary phosphide ligand (PPh_2) as compared with the smaller primary phosphide ligands (PHPh and PHCy). The diphenylphosphido ligand in **1** is unable to adopt the geometry required for effective P → Hf π donation because this would require the two Ph groups to be directed toward the Cp* rings. This steric argument is consistent with the observation that $PHCy_2$ does not react according to eq 1 to give a PCy_2 derivative. The hydride resonance in **1** is weakly coupled to phosphorus ($^2J_{PH}$ = 7 Hz), but those of **2** and **3** are not. Although this coupling is substantially reduced with respect to the $^1J_{PH}$ = 226 Hz in diphenylphosphine (thus, the P–H bond has clearly been broken), it is noteworthy that $^2J_{XH}$ coupling is usually not observed in $Cp^*_2M(H)(X)$ complexes (M = Zr, Hf), the exceptions being the hydrido fluorides $Cp^*_2M(H)(F)$.

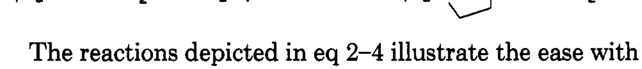
The reaction chemistry of **1** also varies from the chemistries of **2** and **3**, with the chemistry of **1** dominated by a facile *formal* reductive elimination of diphenylphosphine. For example, although both **2** and **3** are stable for days under an atmosphere of dihydrogen, an equilibrium is rapidly established between **1** and $Cp^*_2HfH_2$ as shown in eq 2; at 25 °C with P_{H_2} = 1 atm, $[Cp^*_2HfH_2]:[\mathbf{1}] \approx 2$.

$$Cp^*_2Hf(H)(PPh_2) + H_2(1\ atm) \rightleftharpoons Cp^*_2HfH_2 + PHPh_2 \quad (2)$$

When **1** is placed under an atmosphere of carbon monoxide, diphenylphosphine is eliminated (^{31}P NMR) and a very clean conversion of **1** to the Hf(II) dicarbonyl complex $Cp^*_2Hf(CO)_2$ ensues, according to eq 3. In contrast, **2** and

$$Cp^*_2Hf(H)(PPh_2) + CO(0.5\ atm) \rightarrow Cp^*_2Hf(CO)_2 + PHPh_2 \quad (3)$$

3 react only slowly with CO, giving mixtures of products, *but not* the free phosphines (PH_2Ph and PH_2Cy, respectively). The relative facility of the **1** → $Cp^*_2Hf(CO)_2$ transformation can be compared to the previously reported reductive carbonylation of $Cp^*_2HfH_2$, a reaction that proceeds at ambient temperature under 1500 psi of carbon monoxide.[13] When **1** is exposed to an ethylene atmosphere, formal reductive elimination of diphenylphosphine again occurs, followed by oxidative coupling of 2 equiv of ethylene to afford the known metallacyclopentane derivative $Cp^*_2Hf(C_4H_8)$,[13] shown in eq 4.



The reactions depicted in eq 2–4 illustrate the ease with which the Hf–P bond is cleaved in **1** and are in striking contrast to typical reactions of otherwise similar hard π-base ligands like amides (NRR′), alkoxides (OR), and even the sterically smaller phosphide ligands of **2** and **3**. In fact, the reactivity of **1** with CO and C_2H_4 more closely mimics the chemistry of $Cp^*_2HfH_2$ than it does the related amides or alkoxides,[13] supporting the idea of a very weak or negligible hafnium–phosphide π interaction in **1** (as discussed above).

Carbon dioxide (1 equiv) reacts smoothly with **1** *without* loss of $PHPh_2$ to afford the product of insertion of CO_2 into the Hf–P bond, $Cp^*_2Hf(H)(Ph_2PCO_2)$ (**4**) (eq 5). Evidence that insertion occurs preferentially at the diphenylphosphide ligand and not at the hydride site is provided by the ^{13}C NMR spectrum of **4** that exhibits a doublet for the unique carbon atom of **4** at δ 194 ($^1J_{CP}$ = 23 Hz). The phosphinocarboxylato ligand of **4** is probably

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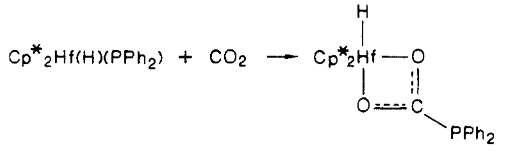
(14) Monomeric examples of $L_nM(H)(PR_2)$: (a) Domaille, P. J.; Foxman, B. M.; McNeese, T. J.; Wreford, S. S. *J. Am. Chem. Soc.* **1980**, *102*, 4114. (b) Baker, R. T.; Calabrese, J. C.; Harlow, R. L.; Williams, I. D. *Abstracts of Papers*, 3rd Chemical Congress of North America, Toronto, Canada; June 1988; INOR 80. There are numerous examples of H and PR_2 bridging multiple metal centers and clusters. For example, see: (c) Roddick, D. M.; Santarsiero, B. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1985**, *107*, 4670. (d) Arif, A. M.; Jones, R. A.; Schwab, S. T. *J. Organomet. Chem.* **1986**, *307*, 219. (e) Arif, A. M.; Heaton, D. E.; Jones, R. A. *J. Chem. Soc., Chem. Commun.* **1985**, *1506*. (f) Arif, A. M.; Jones, R. A.; Seeberger, M. H.; Whittlesey, B. R.; Wright, T. C. *Inorg. Chem.* **1986**, *25*, 3943. (g) Patel, V. D.; Cherkas, A. A.; Nucciarone, D.; Taylor, N. J.; Carty, A. J. *Organometallics* **1985**, *4*, 1792.



$$Cp^*_2Hf(H)(PPh_2) + CO_2 \rightarrow Cp^*_2Hf(H)(O_2CPPh_2) \quad (5)$$

4

chelating on the basis of infrared data (no $\nu(OCO)$ above 1500 cm^{-1}) and the electron count of the complex. Several other examples (all chelating or bridging) of $R_2PCO_2^-$-type ligands have been recently reported.[15] **4** reacts further with CO_2, with insertion occurring at the Hf-H bond, to cleanly give a formato derivative of **4**, $Cp^*_2Hf(HCO_2)(Ph_2PCO_2)$ (**5**) (eq 6). In the absence of an X-ray structural study, we cannot unambiguously assign binding modes (chelating vs monodentate) to the carboxylate ligands of **5**.

$$\underset{\mathbf{4}}{Cp^*_2Hf(H)(Ph_2PCO_2)} + CO_2 \rightarrow \underset{\mathbf{5}}{Cp^*_2Hf(HCO_2)(Ph_2PCO_2)} \quad (6)$$

Lithium phosphides (LiPHR, R = Ph, Cy) undergo metathesis with the decamethylmetallocene dihalides $Cp^*_2ZrCl_2$, $Cp^*_2HfCl_2$, and $Cp^*_2HfI_2$ to afford LiCl or LiI and high yields of the corresponding orange group 4 phosphido complexes of the type $Cp^*_2M(X)(PHR)$, as shown in eq 7. Several such derivatives were prepared

$$Cp^*_2MX_2 + LiPHR \rightarrow Cp^*_2M(X)(PHR) + LiX \quad (7)$$

$$\begin{aligned} &\mathbf{6}, M = Hf, X = I, R = Ph \\ &\mathbf{7}, M = Hf, X = I, R = Cy \\ &\mathbf{8}, M = Hf, X = Cl, R = Cy \\ &\mathbf{9}, M = Zr, X = Cl, R = Cy \end{aligned}$$

in order to test possible synthetic routes (via dehydrohalogenation reactions) to group 4 terminal phosphinidene complexes. The reactions shown in eq 7 work well in THF solutions either by using lithium phosphide reagents freshly generated in situ from the corresponding primary phosphine and *n*-BuLi or by using isolated, crystalline [LiPHR·dioxane] adducts, but we prefer the latter method owing to the ease in the control of stoichiometry.

Our attempts to dehydrohalogenate complexes **6**–**9** were not totally successful. Product mixtures were generally obtained on treatment of **6**–**9** with a variety of anionic bases (i.e., KH, *n*-BuLi, $NaN(SiMe_3)_2$). The most promising results were obtained when THF solutions of **6** were allowed to react with the hindered base $NaN(SiMe_3)_2$. On warming such solutions from −78 °C to ambient temperature, $HN(SiMe_3)_2$ and NaI were liberated and a new, red product was formed. The ^1H NMR spectrum of this new compound showed only a Cp* resonance at δ 2.02 (30 H) and phenyl hydrogen multiplets at δ 7–8 (5 H), establishing the empirical formula as $[Cp^*_2Hf(PPh)]_x$. The ^{31}P NMR spectrum of this compound exhibited a new, sharp singlet (no P–H coupling) resonance at δ 376 relative to external 85% H_3PO_4, characteristic of sp^2-hybridized phosphorus.[7,16] Although the reaction appeared to proceed cleanly when monitored by ^1H and ^{31}P NMR, the orange powder isolated from preparative scale reactions always was contaminated with 10–20% of starting material and other impurities, thus far precluding its proper, complete characterization. Specifically, we cannot yet differentiate between the monomeric and dimeric structures shown below, although since the dimeric structure as depicted implies a Hf(II) formal oxidation state, it is probably less appealing on electronic grounds than is the monomeric phosphinidene structure. Nonetheless, this should give some direction to other workers interested in pursuing these phosphinidene species.

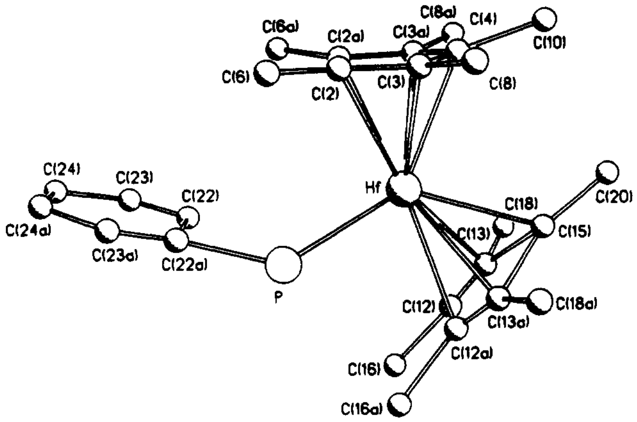


Figure 1. The molecular structure of $Cp^*_2Hf(H)(PHPh)$. For clarity, the view shown is that for an ordered model, but the molecule contains a crystallographic mirror plane with the Cp* ring centroids and the Hf atom residing in the plane. The P atom is disordered across the mirror plane. The Cp* rings are also rotationally disordered (see text): Hf–P, 2.549 (8) Å; Hf–centroid, 2.222 (18) Å (average); centroid–Hf–centroid, 144.2 (7)°; P–Hf–centroid(1), 110.8 (6)°; P–Hf–centroid(2), 101.2 (6)°.

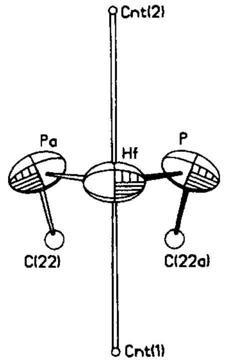
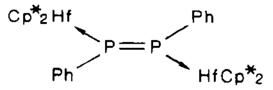


Figure 2. A view of $Cp^*_2Hf(H)(PHPh)$, with the crystallographic mirror plane vertical and perpendicular to the page, showing the P atom disorder across the plane. The phenyl ring is shown as the ipso carbon atom only.

$Cp^*_2Hf{=}PPh$



$$(Cp^*_2Hf)(Ph)P{=}P(Ph)(HfCp^*_2)$$

Molecular Structure of $Cp^*_2Hf(H)(PHPh)$ (2). The structure of **2** consists of discrete monomeric molecules in the unit cell, with no significant intermolecular nonbonded contacts. A perspective view of the complex together with the labeling scheme is shown in Figure 1. As described in the Experimental Section, there is a crystallographic mirror plane that contains the Hf atom and the two Cp* ring centroids. Figure 2 shows a view of **2** down this mirror plane, clearly illustrating the P atom disorder across the mirror. Because of the disorder, most of the intramolecular

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[15] (a) Buhro, W. E.; Chisholm, M. H.; Folting, K.; Huffman, J. C. *Inorg. Chem.* **1987**, *26*, 3087. (b) Baker, R. T. *Abstracts of Papers*, 192nd National Meeting of the American Chemical Society, Anaheim, CA; American Chemical Society: Washington, DC, 1986; INOR 96. (c) Hey, E.; Lappert, M. F.; Atwood, J. L.; Bott, S. G. *J. Chem. Soc., Chem. Commun.* **1987**, 421.

[16] For ^{31}P NMR data for diphosphenes and their complexes, see: Cowley, A. H.; Norman, N. C. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis: Organic Compounds and Metal Complexes*; Verkade, J. G., Quin, L. D., Eds.; Verlag: Weinheim, 1987; p 621 ff.

metrical parameters are unreliable; those that are precisely determined are given in the caption to Figure 1.

Although a detailed discussion of the structure is unwarranted, two of its features merit comment. First, the gross structural features and geometry of **2** are similar to those of the related amido complex $Cp^*_2Hf(H)(NHMe)$ in which a degree of N-to-Hf π bonding is important;[6] at the very least we know that the PHPh ligand of **2** is in an orientation consistent with the molecular geometry required for effective P-to-Hf π overlap.[17] Second, the Hf-P bond length of 2.549 (8) Å indicates multiple-bond character in this linkage. The classic structure of $(C_5H_5)_2Hf(PEt_2)_2$ by Baker et al. gives good values for Hf-P single and double bonds since the geometry of one of the PEt_2 ligands is essentially pyramidal about P (Hf—P, 2.682 (1) Å) and that of the other is trigonal planar about P (Hf=P, 2.488 (1) Å).[18] Thus, the Hf-P bond order in **2** is about 1.5 on the basis of the bond length.

Conclusions

A series of monomeric $Cp^*_2M(X)(PRR')$ (M = Zr, Hf) complexes has been prepared from primary and secondary phosphines and derived lithium phosphide reagents, and the molecular structure of one of these complexes, $Cp^*_2Hf(H)(PHPh)$ (**2**), was determined by single-crystal X-ray diffraction methods. The structure of **2**, when considered with its ^1H NMR data and reactivity characteristics, suggests that the phenylphosphido ligand is a moderately effective π-donor in this complex. Some reactions of these complexes with small molecules like CO, CO_2, H_2, and C_2H_4 have been explored. Particularly interesting results were obtained for the purple complex $Cp^*_2Hf(H)(PPh_2)$ (**1**), where the steric demands of the two bulky Cp* ligands usually result in facile reductive eliminations of diphenylphosphine; consistent with these reactivity trends, ^1H NMR data suggest that diphenylphosphide is a poor π-donor ligand in **1**. Carbon dioxide reacts with **1** to give the product of insertion, with a surprising preference for insertion of CO_2 into the Hf-P bond instead of the Hf-H bond. Initial attempts to utilize halide complexes of primary phosphides as precursors to terminal phosphinidene complexes were not entirely successful, but the dehydrohalogenation of $Cp^*_2Hf(I)(PHPh)$ with $NaN(SiMe_3)_2$ appears to have resulted in the formation of a complex with the empirical formula "$Cp^*_2Hf(PPh)$".

The phosphide complexes reported here complement the array of known complexes of decamethylzirconocene and decamethylhafnocene that contain related amide and alkoxide ligands.

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Registry No. **1**, 121055-41-2; **2**, 121055-42-3; **3**, 121055-43-4; **4**, 121055-44-5; **5**, 121055-45-6; **6**, 121055-46-7; **7**, 121055-47-8; **8**, 121055-48-9; **9**, 121055-49-0; $Cp^*_2HfH_2$, 81956-87-8; $Cp^*_2HfI_2$, 92786-75-9; $Cp^*_2HfCl_2$, 85959-83-7; $Cp^*_2ZrCl_2$, 54039-38-2; $Cp^*_2Hf(CO)_2$, 76830-38-1; $Cp^*_2Hf(C_4H_8)$, 92786-86-2; $PHPh_2$, 829-85-6; PH_2Ph, 638-21-1; PH_2Cy, 822-68-4; LiPHCy, 51918-33-3; C_2H_4, 74-85-1.

Supplementary Material Available: Table III (atomic coordinates and isotropic thermal parameters), Table IV (bond lengths), Table V (bond angles), and Table VI (anisotropic thermal parameters) (4 pages); a listing of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

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Synthesis and Structure of the $[Rh_2(dmpe)_4(\mu\text{-}dmpe)]^{2+}$ Salt of the Naked Cyclopentadienyl Anion: A Comparison of the Reactivity of $[(\eta\text{-Indenyl})Rh(\eta\text{-}C_2H_4)_2]$ and $[(\eta\text{-}C_5H_5)Rh(\eta\text{-}C_2H_4)_2]$

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Excess $Me_2PCH_2CH_2PMe_2$ (dmpe) displaces all π-bound ligands from $[(\eta\text{-}C_9H_7)Rh(\eta\text{-}C_2H_4)_2]$ (**1**) much faster than from $[(\eta\text{-}C_5H_5)Rh(\eta\text{-}C_2H_4)_2]$ (**3**) as shown by a competition experiment. Direct reaction of **3** with a large excess of dmpe yields the salt $[Rh_2(dmpe)_4(\mu\text{-}dmpe)]^{2+}[C_5H_5^-]_2$ (**4**), which has been characterized by X-ray crystallography. A square-pyramidal geometry at each rhodium center was found with the bridging dmpe bonded weakly in the apical site. The C_5H_5 anions deviate only slightly from D_{5h} symmetry. Crystal data for **4**: triclinic, $P\bar{1}$; a = 9.405 (1), b = 10.259 (2), c = 14.951 (3) Å; α = 111.38 (1), β = 99.55 (1), γ = 93.41 (1)°; U = 1313.4 (4) Å^3; Z = 1; R = 0.028, R_w = 0.032.

Introduction

The question of ring slippage in transition-metal cyclopentadienyl and indenyl complexes has attracted much recent attention[1] in light of the enhanced reactivity of indenyl complexes compared with their $\eta^5\text{-}C_5H_5$ analogues.[2-5] During the course of our investigations[6] of

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