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Transition-Metal-Substituted Diphosphenes. 8.[1] Synthesis, Structure, and Reactivity of Mononuclear Complexes of Zirconium and Hafnium Containing the Bis(trimethylsilyl)phosphide Ligand

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The reaction of $(\eta^5\text{-}C_5H_5)_2MCl_2$ (M = Zr, Hf) with 2 equiv of $LiP(SiMe_3)_2$ afforded the complexes $(\eta^5\text{-}C_5H_5)_2M[P(SiMe_3)_2]_2$. Treatment of $(\eta^5\text{-}C_5H_5)_2HfCl_2$ with an equimolar amount of $LiP(SiMe_3)_2$ led to $(\eta^5\text{-}C_5H_5)_2Hf(Cl)[P(SiMe_3)_2]$. Complexes $(\eta^5\text{-}C_5H_5)_2M(CH_3)[P(SiMe_3)_2]$ (M = Zr, Hf) were obtained by metathesis of $(\eta^5\text{-}C_5H_5)_2M(CH_3)Cl$ with $LiP(SiMe_3)_2$. The molecular structure of $(\eta^5\text{-}C_5H_5)_2Hf[P(SiMe_3)_2]_2$ was established by a complete crystal diffraction study [space group *Pbca*, $Z = 8$, $a = 9.479$ (3) Å, $b = 29.044$ (6) Å, $c = 21.824$ (4) Å, at −110 °C, $R = 0.031$, $R_w = 0.031$] and exhibits two distinct types of phosphide ligands.

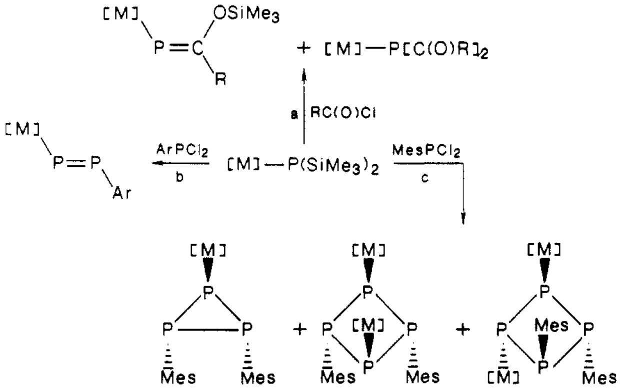
Introduction

Bis(trimethylsilyl)phosphide complexes such as $(\eta^5\text{-}C_5H_5)(CO)(L)FeP(SiMe_3)_2$ (L = CO,[2,3] PPh_3[4]), $(\eta^5\text{-}C_5Me_5)(CO)_2MP(SiMe_3)_2$ (M = Fe,[5] Ru,[6] Os[7]), or $(\eta^5\text{-}C_5Me_5)(CO)(NO)MnP(SiMe_3)_2$[8] are versatile and valuable reagents in phosphorus organometallic chemistry and are converted by carbon acid chlorides into alkylidenephosphide and/or diacylphosphide complexes (Scheme I, path a),[7,9–11] whereas treatment with 2,4,6-tri-*tert*-butylphenyldichlorophosphine ($ArPCl_2$) yielded the first diphosphenyl complexes[4,8,12] (Scheme I, path b). Replacement of the very bulky supermesityl substituent by the sterically less demanding mesityl group in the organodichlorophosphine furnished three- and four-membered cyclophosphines (Scheme I, path c).[13]

We were interested in the general applicability of the synthetic approach depicted in Scheme I, and we turned to the early transition metals zirconium and hafnium. Here we report on disilylphosphide complexes of these metals as well as on the reaction of such a zirconium complex with an organodichlorophosphine.

Dicyclopentadienylzirconium and -hafnium complexes with dialkylphosphide and diarylphosphide ligands have been described in the literature by Issleib and Häckert,[14] Ellermann and Poersch,[15] Wallbridge et al.,[16] Baker et al.,[17] Bercaw et al.,[18] and Gelmini and Stephan.[19] Recently Hey et al. presented the reaction of $(\eta^5\text{-}C_5H_5)_2Zr[P(SiMe_3)_2]_2$ with white phosphorus in a brief communication.[20]

Scheme I. Reactivity of Bis(trimethylsilyl)phosphide Complexes with Acid Halides of the Types RC(O)Cl and R′PCl$_2$[a]



[a] [M] = $(\eta^5\text{-}C_5H_5)(L)(CO)Fe$, $(\eta^5\text{-}C_5Me_5)(CO)_2Fe$, $(\eta^5\text{-}C_5Me_5)(CO)_2Ru$, $(\eta^5\text{-}C_5Me_5)(CO)_2Os$, $(\eta^5\text{-}C_5Me_5)(CO)(NO)Mn$; Ar = 2,4,6-*t*-$Bu_3C_6H_2$; Mes = 2,4,6-$Me_3C_6H_2$.

Experimental Section

General Information. Standard inert-atmosphere techniques were used for the manipulation of all reagents and reaction products. Infrared spectra were recorded on a Perkin-Elmer Model 597 spectrometer. The ^1H, ^{13}C, and ^{31}P NMR spectra were taken on a Varian XL 200 spectrometer. Spectral standards were $SiMe_4$ (^1H, ^{13}C) and 85% H_3PO_4 (^{31}P). All NMR spectra were registered in C_6D_6 at 22 °C. Electron-impact mass spectra were recorded on a Varian MAT 312 spectrometer at 70 eV and ca. 70 °C. Elemental analyses were obtained from the Microanalytical Laboratory of the University Essen and from Microanalytical Laboratory Dornis and Kolbe, Mülheim, Germany.

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Materials. The complexes $(\eta^5\text{-}C_5H_5)_2ZrCl_2$,[21] $(\eta^5\text{-}C_5H_5)_2HfCl_2$,[21] $(\eta^5\text{-}C_5H_5)_2Zr(CH_3)Cl$,[22] and $(\eta^5\text{-}C_5H_5)_2Hf(CH_3)Cl$[22] as well as the phosphorus compounds $LiP(SiMe_3)_2\cdot 2.2THF$[23] and 2,4,6-*t*-$Bu_3C_6H_2PCl_2$ ($ArPCl_2$)[24] were prepared as described in the literature. All solvents were rigorously dried with an appropriate drying agent and distilled before use.

Preparation of Compounds. $(\eta^5\text{-}C_5H_5)_2Zr[P(SiMe_3)_2]_2$ (3a). To a solution of 5.14 g (17.58 mmol) of $(\eta^5\text{-}C_5H_5)_2ZrCl_2$ (**1a**) in 100 mL of cyclopentane was added a solution of 17.58 mmol of $LiP(SiMe_3)_2\cdot 2.2THF$ (**2**) in 50 mL of cyclopentane dropwise at −78 °C. The color of the solution rapidly became dark violet. The reaction mixture was stirred for 1 h at −78 °C and then slowly warmed up to 20 °C. Subsequently the solvent and all volatiles were removed in vacuo to give a dark violet residue, which was taken up with 100 mL of *n*-pentane. It was filtered, and the filter cake was extracted repeatedly with pentane until the extracts became colorless. Concentrating the combined extracts led to the precipitation of 1.24 g (25%) of dark blue dicyclopentadienylbis[bis(trimethylsilyl)phosphido]zirconium (**3a**): mp 74 °C; IR (Nujol) 1251 m ($\delta(Si(CH_3)_3)$), 1040 w, 841 sh, 832 s ($\rho(Si(CH_3)_3)$ and $\pi(CH)_{ring}$), 800 m, 760 w m, 688 w, 627 m, 448 w, 432 w cm^{-1}; ^1H NMR δ 0.52 (d, $^3J(PH)$ = 4 Hz, 36 H, $SiMe_3$), 5.82 (t, $^3J(PH)$ = 1 Hz, 10 H, C_5H_5); $^{13}C\{^1H\}$ NMR δ 6.37 (d, $^2J(PC)$ = 9.2 Hz, $Si(CH_3)_3$), 108.88 (s, C_5H_5); $^{31}P\{^1H\}$ NMR δ −72.18 (s). Anal. Calcd for $C_{22}H_{46}P_2Si_4Zr$: C, 45.87; H, 8.05; mol wt, 576.1. Found: C, 45.26; H, 8.12; mol wt, 574 (MS/EI).

Benzene extraction of the yellow filter cake did not afford $(\eta^5\text{-}C_5H_5)_2Zr(Cl)[P(SiMe_3)_2]$ as it was the case with $(\eta^5\text{-}C_5H_5)_2Hf(Cl)[P(SiMe_3)_2]$ (**4**) (see below). When **1a** was treated with 2 equiv of **2** analogously, the yield of **3a** was improved to 64%.

$(\eta^5\text{-}C_5H_5)_2Hf[P(SiMe_3)_2]_2$ (3b). To a suspension of 1.02 g (2.69 mmol) of $(\eta^5\text{-}C_5H_5)_2HfCl_2$ (**1b**) in 50 mL of cyclopentane was added a solution of 5.38 mmol of $LiP(SiMe_3)_2\cdot 2.2THF$ in 50 mL of cyclopentane dropwise at −30 °C. It was allowed to warm up slowly to ambient temperature. At ca. 0 °C the colorless suspension turned yellow and then slowly orange-red. After 1 h of stirring at 20 °C solvents were removed in vacuo, and the orange-red residue was extracted with 30 mL of pentane. The filtered extract was concentrated to ca. 10 mL and stored overnight at −28 °C to yield 1.78 g (76%) of red crystalline dicyclopentadienylbis[bis(trimethylsilyl)phosphido]hafnium (**3b**) (mp 103–105 °C): IR (Nujol) 1245 m s ($\delta(Si(CH_3)_3)$), 838 sh, 830 s ($\rho(Si(CH_3)_3)$ and $\pi(CH)_{ring}$), 800 m, 628 w, 520 w cm^{-1}; ^1H NMR δ 0.48 ($AA'X_{18}$, X'_{18}-spin system, 36 H, $SiMe_3$) 5.96 ("t", $J(PH)$ = 1.2 Hz, 10 H, C_5H_5); $^{13}C\{^1H\}$NMR δ 6.71 ("t", $J(PC)$ = 5 Hz, $Si(CH_3)_3$), 108.35 ("t", $J(PC)$ = 0.6 Hz, C_5H_5); $^{31}P\{^1H\}$ NMR δ −98.83 (s). Anal. Calcd for $C_{22}H_{46}HfP_2Si_4$: C, 39.89; H, 7.00; mol wt, 662.4. Found: C, 38.83; H, 6.92; mol wt, 665 (MS/EI).

$(\eta^5\text{-}C_5H_5)_2Hf(Cl)[P(SiMe_3)_2]$ (4). To a suspension of 5.00 g (13.2 mmol) of **1b** in 150 mL of cyclopentane was added 13.2 mmol of solid **2** at −40 °C. After 1 h of stirring at −30 °C stirring was continued at 20 °C. Then the orange-red suspension was brought to dryness, and the residue was taken up in 100 mL of pentane and filtered. After the mixture was washed with pentane (2 × 10 mL), the filter cake was extracted with 100 mL of benzene. The extract was concentrated in vacuo to furnish 2.70 g (43%) of orange crystalline chlorodicyclopentadienyl[bis(trimethylsilyl)phosphido]hafnium (**4**); mp 119 °C; IR (Nujol) 1251 m s ($\delta(Si(CH_3)_3)$), 1010 w, 830 s, br ($\rho(Si(CH_3)_3)$ + $\pi(CH)_{ring}$) cm^{-1}; ^1H NMR δ 0.48 (d, $^3J(PH)$ = 4 Hz, 18 H, $SiMe_3$), 5.95 (d, $^3J(PH)$ = 1 Hz, 10 H, C_5H_5); $^{13}C\{^1H\}$ NMR δ 6.35 (d, $^2J(PC)$ = 10.1 Hz, $Si(CH_3)_3$), 112.29 (d, $^2J(PC)$ = 2.1 Hz, C_5H_5); $^{31}P\{^1H\}$ NMR: δ −153.97 (s). Anal. Calcd for $C_{16}H_{28}ClHfPSi_2$: C, 36.85; H, 5.41; Cl, 6.80; mol wt, 521.5. Found: C, 36.56; H, 5.47; Cl, 6.97; mol wt, 523 (MS/EI).

$(\eta^5\text{-}C_5H_5)_2(CH_3)Zr[P(SiMe_3)_2]$ (6a). To the suspension of 2.61 g (9.6 mmol) of $(\eta^5\text{-}C_5H_5)_2Zr(CH_3)Cl$ (**5a**) in 100 mL of cyclopentane was added 9.6 mmol of solid **2** at −60 °C. The ochre suspension slowly became orange-red. Stirring was continued for 30 min at −30 °C and then for another 30 min at room temperature. All volatiles were removed in vacuo, and the red residue was extracted with 50 mL of *n*-pentane. After filtration and concentration to 10 mL the extract was stored overnight at −28 °C, affording 3.24 g (82%) of red-brown solid dicyclopentadienylmethyl[bis(trimethylsilyl)phosphido]zirconium (**6a**); mp 86–88 °C dec; IR (Nujol) 1400 w, 1248 s ($\delta(Si(CH_3)_3)$), 1068 w, 1018 m, 958 w, 892 w, 844 sh, 808 vs, b ($\rho(Si(CH_3)_3)$ + $\pi(CH)_{ring}$), 691 w, 626 m, 454 m, 432 w cm^{-1}; ^1H NMR δ 0.02 (d, $^3J(PH)$ = 4 Hz, 3 H, $ZrCH_3$), 0.38 (d, $^3J(PH)$ = 4 Hz, 18 H, $SiMe_3$), 5.88 (d, $^3J(PH)$ = 1 Hz, 10 H, C_5H_5); $^{13}C\{^1H\}$ NMR (C_6D_6, 22 °C) δ 6.50 (d, $^2J(PC)$ = 9.7 Hz, $Si(CH_3)_3$), 34.60 (d, $^2J(PC)$ = 1.7 Hz, $ZrCH_3$), 110.32 (d, $^2J(PC)$ = 1.2 Hz, C_5H_5); $^{31}P\{^1H\}$ NMR (C_6D_6, 22 °C) δ −121.68 (s). Anal. Calcd for $C_{17}H_{31}PSi_2Zr$: C, 49.34; H, 7.55; Zr, 22.04; mol wt, 413.8. Found: C, 49.50; H, 7.17; Zr, 22.09; Mol wt, 412 (MS/EI).

$(\eta^5\text{-}C_5H_5)_2(CH_3)Hf[P(SiMe_3)_2]$ (6b). To a suspension of 4.06 g (11.30 mmol) of $(\eta^5\text{-}C_5H_5)_2Hf(CH_3)Cl$ (**4b**) in 20 mL of cyclopentane was added 11.3 mmol of solid **2** at −60 °C. Analogous workup yielded 3.01 g (53%) of brown solid dicyclopentadienylmethyl[bis(trimethylsilyl)phosphido]hafnium (**6b**): mp 92 °C; IR (Nujol) 1246 (s, δ $((Si(CH_3)_3))$), 1012 w, 972 w, 800 s, br ($\rho((Si(CH_3)_3))$ + $\pi(CH)_{ring}$), 740 sh, 675 w, 520 w cm^{-1}; ^1H NMR δ −0.18 (d, $^3J(PH)$ = 4 Hz, 3 H, $HfCH_3$), 0.38 (d, $^3J(PH)$ = 4 Hz, 18 H, $SiMe_3$), 5.78 (d, $^3J(PH)$ = 1 Hz, C_5H_5); $^{13}C\{^1H\}$ NMR δ 6.64 (d, $^2J(PC)$ = 10.2 Hz, $Si(CH_3)_3$), 40.84 (d, $^2J(PC)$ = 2.5 Hz, $HfCH_3$), 109.93 (s, C_5H_5); $^{31}P\{^1H\}$ NMR δ −141.92 (s). Anal. Calcd for $C_{17}H_{31}HfPSi_2$: C, 40.75; H, 6.24; mol wt, 501.1. Found: C, 40.55; H, 6.43; mol wt, 502 (MS/EI).

Reaction of 6a with $ArPCl_2$. A solution of 0.59 g (1.42 mmol) of $(\eta^5\text{-}C_5H_5)_2Zr(CH_3)[P(SiMe_3)_2]$ in 10 mL of THF was treated with 0.40 g (1.15 mmol) of solid $ArPCl_2$ at 0 °C. Stirring was continued for 15 min, and then a ^{31}P NMR spectrum of the dark brown reaction mixture was recorded. The low-field region of the spectrum was dominated by two doublets at δ 632.31 and 490.80 ($^1J(PP)$ = 584.0 Hz) and the singlet for Ar—P=P—Ar at δ 493. In the high-field area two doublets at δ 107.09 and −142.26 ($^1J(PP)$ = 200.8 Hz) were observed.

Solvent was removed in vacuo, and the residue was taken up in 20 mL of pentane. It was filtered, and the filtrate was placed over night at −28 °C. A cream colored solid (0.15 g) separated which was identified as $(C_5H_5)_2Zr(CH_3)Cl$ by comparison of the ^1H NMR data (C_6D_6, δ 5.75 (s, 10 H, Cp) and 0.42 (s, 3 H, CH_3)) with an authentic sample (lit.[25] C_6H_6, δ 5.78 (s) and 0.42 (s)).

Reaction of $LiP(SiMe_3)_2\cdot 2.2THF$ (2) with $ArPCl_2$. To the solution of 1.99 mmol of **2** in 10 mL of THF in a NMR tube was added 0.69 g (1.99 mmol) of solid $ArPCl_2$. The solution was allowed to warm up to room temperature which was accompanied by a color change from burgundy red to orange. After 10 min a $^{31}P\{^1H\}$ NMR spectrum was recorded. Two doublets at δ 632.38 and 490.94 ($^1J(PP)$ = 583.8 Hz) were attributed to diphosphene Me_3Si—P=P—Ar (lit.[26] $^{31}P\{^1H\}$ (in $CDCl_3$) δ 628.2 and 486.8 ($^1J(PP)$ = 575 Hz)). A singlet at δ 493.04 was due to diphosphene ArP=PAr. The isolation of the unsymmetrically substituted diphosphene failed.

X-ray Structure Determination of $(\eta^5\text{-}C_5H_5)_2Hf[P(SiMe_3)_2]_2$ (3b). Crystals of **3b** were grown from pentane at −28 °C. An irregular-shaped crystal with the approximate dimensions of 0.25 × 0.37 × 0.6 mm was sealed in a glass capillary and cooled to −110 °C on a Nicolet R3 four-circle diffractometer (Mo Kα radiation, graphite monochromator). The cell dimensions were determined by refinement of the setting angles of 25 reflections ($20° \leq 2\theta \geq 25°$). The orthorhombic lattice was established by oscillation photos [a = 9.479 (3) Å, b = 29.044 (6) Å, c = 21.824 (4) Å, $\alpha = \beta = \gamma = 90°$, V = 6008 (2) Å^3]. Systematic extinctions were consistent with the space group *Pbca* (No. 61),[27b] Z = 8, D_{calcd} = 1.467 g/cm^3, μ = 39.2 cm^{-1}, and ω-scan data collection of 5451 independent reflections ($2\theta_{max}$ = 50°), 4542 of which were treated as observed ($F_o \geq 3.5\sigma(F)$). An empirical absorption correction based on ψ scans of six suitable reflections, distributed on the

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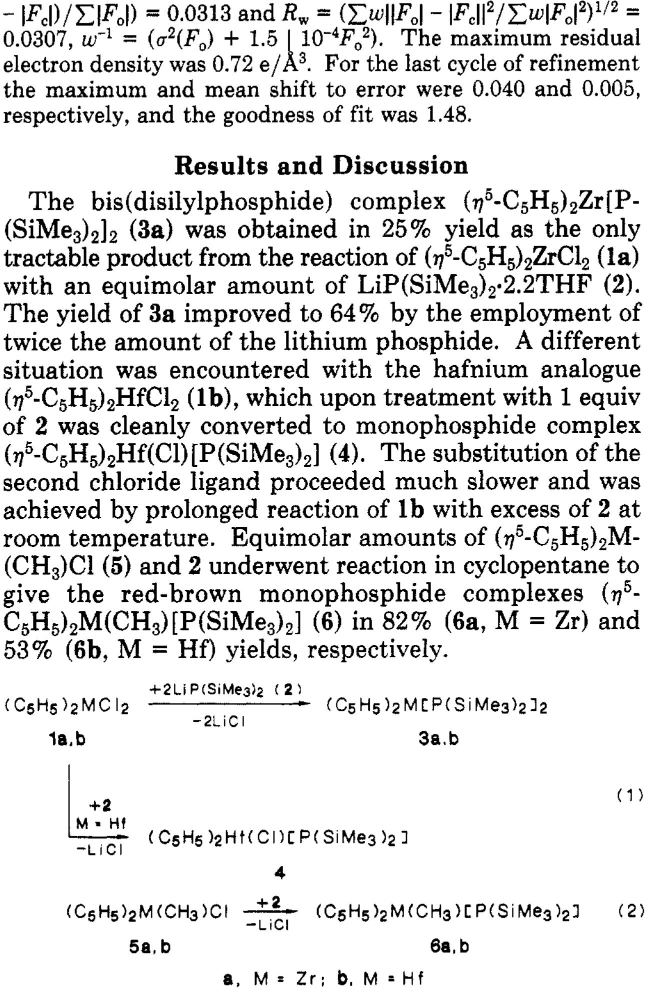
2θ range, and the approximation of an ellipsoid close to the crystal shape dropped an internal R value from 15.4% to 2.0% (minimum/maximum transmission = 0.475/0.917). The structure was solved by Patterson methods and successive difference Fourier maps and refined by least-squares methods. Crystallographic programs were those of SHELXTL[27a] on a Nova 3/12 computer (Data General) with the atomic scattering factors taken as incorporated in SHELXTL and for Hf taken from ref 27b. All non-hydrogen atoms were given anisotropical thermal displacement parameters except the disordered cyclopentadienyl ring (C6 to C10 and C6A to C10A). The hydrogen atoms were treated as rigid groups (C–H = 0.96 Å, H–C–H = 109.5° for methyl, and C–C–H = 126° for cyclopentadienyl), and the isotropic U value was given the 1.2-fold of the orthogonalized $\mathbf{U}_{ij}$ tensor of the corresponding C atom. Cp rings also were treated as rigid rings (C–C = 1.42 Å and C–C–C = 108°), the disordered rings had a site occupation factor of 0.5, the centers were slipped by 0.285 Å and rotated by 15.9° with respect to each other. R values, based on the final model refined with 266 parameters, were $R = (\sum(|F_o| - |F_c|)/\sum|F_o|) = 0.0313$ and $R_w = (\sum w||F_o| - |F_c||^2/\sum w|F_o|^2)^{1/2} = 0.0307$, $w^{-1} = (\sigma^2(F_o) + 1.5 \mid 10^{-4}F_o^2)$. The maximum residual electron density was 0.72 e/Å^3. For the last cycle of refinement the maximum and mean shift to error were 0.040 and 0.005, respectively, and the goodness of fit was 1.48.

Results and Discussion

The bis(disilylphosphide) complex $(\eta^5\text{-}C_5H_5)_2Zr[P(SiMe_3)_2]_2$ (**3a**) was obtained in 25% yield as the only tractable product from the reaction of $(\eta^5\text{-}C_5H_5)_2ZrCl_2$ (**1a**) with an equimolar amount of $LiP(SiMe_3)_2\cdot 2.2THF$ (**2**). The yield of **3a** improved to 64% by the employment of twice the amount of the lithium phosphide. A different situation was encountered with the hafnium analogue $(\eta^5\text{-}C_5H_5)_2HfCl_2$ (**1b**), which upon treatment with 1 equiv of **2** was cleanly converted to monophosphide complex $(\eta^5\text{-}C_5H_5)_2Hf(Cl)[P(SiMe_3)_2]$ (**4**). The substitution of the second chloride ligand proceeded much slower and was achieved by prolonged reaction of **1b** with excess of **2** at room temperature. Equimolar amounts of $(\eta^5\text{-}C_5H_5)_2M(CH_3)Cl$ (**5**) and **2** underwent reaction in cyclopentane to give the red-brown monophosphide complexes $(\eta^5\text{-}C_5H_5)_2M(CH_3)[P(SiMe_3)_2]$ (**6**) in 82% (**6a**, M = Zr) and 53% (**6b**, M = Hf) yields, respectively.



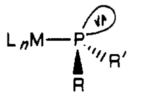
The disilylphosphide complexes **3**, **4**, and **6** are extremely air- and moisture-sensitive, diamagnetic solids, which are highly soluble in the usual aprotic organic solvents, and in the solid state can be stored under nitrogen atmosphere at −28 °C indefinitely. The electron-impact mass spectra of **3**, **4**, and **6** exhibit the peaks of the respective molecular ions as parent peaks, indicating the mononuclear character of the complexes in the gas phase. It is remarkable that in the fragmentation of **4** no extrusion of Me_3SiCl was detectable, which would lead to the phosphinidene complex $(\eta^5\text{-}C_5H_5)_2Hf{=}P{-}SiMe_3$.

Table I. ^{31}P NMR Data for Several $P(SiMe_3)_2$ Complexes

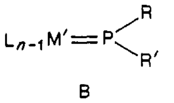
		δ	ref
[M]	$Cp(CO)_2FeP(SiMe_3)_2$	−266.3	2, 3
	$Cp(CO)(PPh_3)FeP(SiMe_3)_2$	−287.1	4
	$Cp^*(CO)_2FeP(SiMe_3)_2$	−216.8	5
	$Cp^*(CO)_2RuP(SiMe_3)_2$	−219.9	6
	$Cp^*(CO)_2OsP(SiMe_3)_2$	−254.5	7
	$Cp^*(CO)(NO)MnP(SiMe_3)_2$	−202.9	8
	3a	−69.60	this work
	3b	−98.83	this work
	4	−153.97	this work
	6a	−121.68	this work
	6b	−141.92	this work
	$P(SiMe_3)_3$	−251	2

[a] Cp* = C_5Me_5.

For terminal phosphide ligands generally two modes of coordination are possible. Complex fragments with a total of 17 valence electrons are attached to the phosphide in the σ-donor one-electron coordination mode A[5,28] with a pyramidally configurated P atom. On the other hand such fragments with 15 or less valence electrons may bind the ligand in the π-donor, three-electron coordination mode B,[29] featuring a planar P atom. In complexes of the type B the ^{31}P NMR resonances are usually significantly shifted to low field as compared to those of the ^{31}P atoms in ligands of coordination mode A. The P nuclei of the one-electron $P(SiMe_3)_2$ ligand in the known phosphide complexes resonate at high field between δ −202.9 and −287.1 (Table I). The molecular structure determination of **3b** revealed the presence of both types of phosphide ligands (A and B) (see below). In agreement with a rapid equilibration between both coordination modes, single resonances at −69.60 and −98.83 ppm were encountered in the $^{31}P\{^1H\}$ NMR spectra of **3a** and **3b**. Cooling of the NMR sample to −70 °C did not change the spectrum significantly. In the spectra of the monophosphide complexes **6a** and **6b** the ^{31}P resonances were found at considerably higher field (**6a**, δ −121.68; **6b**, δ −141.92).



A



B

Possibly in complexes **4**, **6a**, and **6b** $P(SiMe_3)_2$ ligands of coordination mode A are present. For an unambigions assignment, however, an X-ray determination of the one of these compounds is needed. $(\eta^5\text{-}C_5H_5)_2Zr(CH_3)[P(SiMe_3)_2]$ (**6a**) was treated with 2,4,6-t-$Bu_3C_6H_2PCl_2$ in THF solution at 0 °C. The course of the reaction was monitored by $^{31}P\{^1H\}$ NMR spectroscopy. In the low-field region of the spectrum two doublets at δ 632.31 and 490.80 with the coupling $^1J(PP)$ = 584.0 Hz are consistent with the presence of an unsymmetrically substituted diphosphene (**7**). At δ 493 a very intense singlet is due to diphosphene ArP=PAr (lit.[30] δ 494). In the high-field region of the spectrum two doublets at δ 107.09 and −142.26 ($^1J(PP)$ = 200.8 Hz) were observed.

Wallbridge presented the complexes $(C_5H_5)_2M(PPh_2)_2$ (M = Zr, Hf) as phosphide transfer reagents to halogenated

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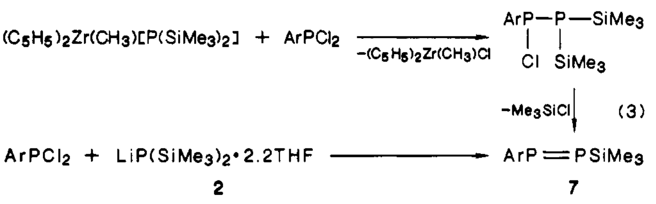
Table II. Atomic Coordinates (×10⁴) and Isotropic Thermal Parameters (Å² × 10³) of 3b

	x	y	z	U^a
Hf	3403 (1)	1322 (1)	337 (1)	21 (1)*
P(1)	1496 (1)	1315 (1)	1163 (1)	28 (1)*
P(2)	1907 (1)	1006 (1)	−601 (1)	20 (1)*
Si(1)	494 (2)	1857 (1)	1747 (1)	31 (1)*
Si(2)	406 (2)	653 (1)	1396 (1)	38 (1)*
Si(3)	15 (1)	1411 (1)	−887 (1)	28 (1)*
Si(4)	3056 (1)	923 (1)	−1489 (1)	25 (1)*
C(1)	3241 (4)	2048 (1)	−272 (1)	36 (2)*
C(2)	2723	2153	322	33 (2)*
C(3)	3859	2111	742	30 (1)*
C(4)	5080	1980	408	41 (2)*
C(5)	4698	1941	−219	45 (2)*
C(6)	4476 (7)	554 (2)	70 (2)	24 (2)
C(7)	3731	474	624	22 (2)
C(8)	4376	740	1092	23 (2)
C(9)	5520	985	827	26 (2)
C(10)	5581	871	196	38 (2)
C(6a)	4235 (7)	512 (2)	164 (3)	32 (2)
C(7a)	4083	577	806	49 (3)
C(8a)	5111	902	997	37 (2)
C(9a)	5899	1038	474	50 (3)
C(10a)	5357	797	−41	38 (2)
C(11)	1528 (6)	2399 (2)	1812 (3)	48 (2)*
C(12)	−1290 (5)	2026 (2)	1456 (3)	45 (2)*
C(13)	342 (7)	1645 (2)	2557 (2)	57 (2)*
C(14)	1345 (7)	303 (2)	1970 (3)	53 (2)*
C(15)	−1380 (7)	763 (3)	1744 (4)	101 (4)*
C(16)	19 (13)	329 (2)	700 (3)	129 (5)*
C(17)	−837 (5)	1692 (2)	−213 (2)	35 (2)*
C(18)	−1341 (5)	1003 (2)	−1193 (3)	51 (2)*
C(19)	294 (6)	1871 (2)	−1482 (2)	44 (2)*
C(20)	4010 (8)	1450 (2)	−1765 (3)	58 (2)*
C(21)	1798 (6)	744 (2)	−2104 (2)	44 (2)*
C(22)	4383 (6)	448 (2)	−1466 (2)	49 (2)*

[a] The asterisk indicates the equivalent isotropic U defined as one-third of the trace of the orthogonalised U_{ij} tensor.

compounds such as Ph_2PCl or Me_3SiCl.[16] In view of these results it was assumed that the unsymmetrical diphosphene in our reaction resulted from the transfer of the $P(SiMe_3)_2^-$ ion from **6a** to $ArPCl_2$ (eq 3).



$(C_5H_5)_2Zr(CH_3)Cl$ was isolated as cream colored crystals and identified by ^1H NMR (C_6D_6, δ 5.75 (Cp), 0.42 (CH_3)) with an authentic sample.[25] Unstable diphosphene ArP=P—$SiMe_3$ was postulated by Bickelhaupt as a product from the reaction of $P(SiMe_3)_3$ with Cl_2PAr in deuteriochloroform[26] (^{31}P δ 628.2 (s), 486.8 (d) ($^1J(PP)$ = 575 Hz)). For comparison we conducted the reaction of **2** with Cl_2PAr in THF. The ^{31}P NMR resonances of the generated diphosphene were identical with those obtained from the reaction mixture of **6a** with $ArPCl_2$. A similar situation was encountered with the Hf complexes. Evidently the high reactivity of the M–P bond in disilylphosphide complexes of zirconium an hafnium such as **4** and **6** precluded the syntheses of diphosphenyl complexes of such metals according to Scheme I.

X-ray Structure Analysis of 3b. An X-ray structure analysis of one of the disilylphosphide complexes was desirable to distinguish more precisely between the different modes of coordination (A or B) the phosphide ligands may adopt. The results of the structural determination of **3b** are shown in Figure 1. Positional parameters for the complex are given in Table II, and derived distances and angles are presented in Table III.

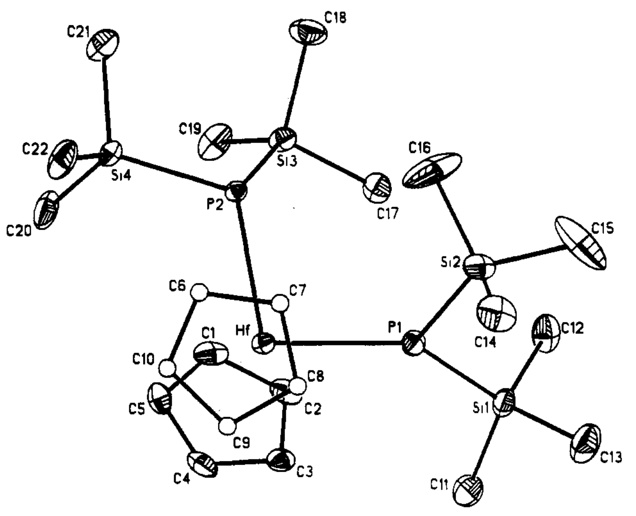


Figure 1. Molecular structure of **3b** in the crystal.

Table III. Selected Bond Lengths (Å) and Bond Angles (deg) of 3b

Hf–P(1)	2.553 (1)	Hf–P(2)	2.654 (1)
Hf–Cp(1)	2.182 (3)	Hf–Cp(2)	2.203 (3)
Hf–Cp(2a)	2.199 (3)	P(1)–Si(1)	2.237 (2)
P(1)–Si(2)	2.241 (2)	P(2)–Si(3)	2.234 (2)
P(2)–Si(4)	2.235 (2)		

P(1)–Hf–P(2)	99.4 (1)	P(1)–Hf–Cp(1)	105.5 (1)
P(2)–Hf–Cp(1)	110.2 (1)	P(1)–Hf–Cp(2)	104.0 (1)
P(2)–Hf–Cp(2)	101.9 (1)	P(1)–Hf–Cp(2a)	111.2 (1)
P(2)–Hf–Cp(2a)	102.0 (1)	Cp(1)–Hf–Cp(2a)	125.6 (1)
Cp(1)–Hf–Cp(2)	131.5 (1)	Cp(2)–Hf–Cp(2a)	7.4 (1)
Hf–P(1)–Si(1)	134.2 (1)	Hf–P(1)–Si(2)	119.6 (1)
Si(1)–P(1)–Si(2)	106.2 (1)	Hf–P(2)–Si(3)	117.6 (1)
Hf–P(2)–Si(4)	116.5 (1)	Si(3)–P(2)–Si(4)	101.9 (1)

Table IV. Anisotropic Thermal Parameters (Å² × 10³)[a]

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Hf	20 (1)	20 (1)	22 (1)	−2 (1)	−3 (1)	3 (1)
P(1)	36 (1)	22 (1)	26 (1)	1 (1)	5 (1)	−7 (1)
P(2)	21 (1)	19 (1)	19 (1)	−2 (1)	−1 (1)	2 (1)
Si(1)	29 (1)	40 (1)	23 (1)	−0 (1)	3 (1)	4 (1)
Si(2)	52 (1)	33 (1)	30 (1)	12 (1)	−7 (1)	−21 (1)
Si (3)	26 (1)	30 (1)	28 (1)	−6 (1)	−6 (1)	8 (1)
Si(4)	31 (1)	24 (1)	20 (1)	−2 (1)	2 (1)	4 (1)
C(1)	55 (4)	23 (2)	31 (3)	9 (2)	−13 (2)	−17 (2)
C(2)	36 (3)	16 (2)	46 (3)	5 (2)	−5 (2)	−9 (2)
C(3)	38 (3)	24 (2)	29 (2)	−0 (2)	−2 (2)	−12 (2)
C(4)	27 (3)	47 (3)	49 (3)	−1 (2)	−3 (2)	−16 (2)
C(5)	43 (3)	54 (4)	38 (3)	4 (3)	13 (3)	−21 (3)
C(11)	47 (4)	42 (3)	54 (3)	−21 (3)	10 (3)	1 (3)
C(12)	41 (3)	57 (4)	37 (3)	15 (3)	5 (3)	13 (3)
C(13)	62 (4)	82 (5)	29 (3)	3 (3)	5 (3)	12 (4)
C(14)	65 (4)	37 (3)	58 (4)	22 (3)	−8 (3)	−8 (3)
C(15)	40 (4)	67 (5)	195 (10)	45 (6)	4 (5)	−19 (4)
C(16)	276 (14)	75 (5)	36 (4)	−3 (3)	−5 (6)	−122 (7)
C(17)	25 (3)	42 (3)	38 (3)	2 (2)	−3 (2)	12 (2)
C(18)	30 (3)	59 (4)	64 (4)	−22 (3)	−15 (3)	2 (3)
C(19)	58 (4)	41 (3)	33 (3)	−1 (2)	−5 (3)	26 (3)
C(20)	88 (5)	48 (4)	36 (3)	−7 (3)	33 (3)	−20 (3)
C(21)	48 (4)	53 (3)	32 (3)	−10 (2)	−5 (3)	14 (3)
C(22)	52 (4)	64 (4)	32 (3)	−5 (3)	3 (3)	33 (3)

[a] The anisotropic temperature factor exponent takes the form $-2\pi^2 (h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12})$.

The hafnium atom is coordinated to two planar C_5H_5 rings, (one of which is being disordered) and the two phosphorus ligands in a highly distorted tetrahedral geometry, typical for Cp_2MX_2-type complexes. The distortion is evident by an angle of 131.5° between the hafnium and the ring center of Cp1 and Cp2 (125.8° between Cp1a

Table V. H-Atom Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$)

	x	y	z	U
H(1)	2701	2049	−644	43
H(2)	1772	2238	422	39
H(3)	3811	2163	1176	37
H(4)	6001	1927	576	49
H(5)	5315	1856	−549	46
H(6)	4269	419	−321	29
H(7)	2932	274	674	27
H(8)	4089	752	1514	19
H(9)	6142	1192	1039	29
H(10)	6253	986	−96	37
H(6a)	3676	311	−87	33
H(7a)	3404	427	1064	53
H(8a)	5250	1010	1408	48
H(9a)	6663	1254	469	55
H(10a)	5691	822	−455	19
H(11a)	1604	2579	1445	58
H(11b)	2453	2341	1973	58
H(11c)	981	2564	2110	58
H(12a)	−1927	1770	1431	54
H(12b)	−1252	2180	1067	54
H(12c)	−1616	2237	1763	54
H(13a)	−387	1417	2585	70
H(13b)	152	1888	2843	70
H(13c)	1236	1507	2651	70
H(14a)	2329	250	1893	62
H(14b)	881	14	2039	62
H(14c)	1243	494	2326	62
H(15a)	−2008	1017	1671	122
H(15b)	−1008	784	2152	122
H(15c)	−1886	479	1699	122
H(16a)	862	146	711	153
H(16b)	−21	495	320	153
H(16c)	−790	132	734	153
H(17a)	−294	1950	−74	41
H(17b)	−914	1469	110	41
H(17c)	−1762	1794	−330	41
H(18a)	−1023	838	−1547	62
H(18b)	−2168	1177	−1295	62
H(18c)	−1562	789	−872	62
H(19a)	804	1756	−1830	52
H(19b)	806	2122	−1302	52
H(19c)	−619	1976	−1611	52
H(20a)	4781	1476	−1481	70
H(20b)	3490	1734	−1771	70
H(20c)	4371	1387	−2167	70
H(21a)	1113	977	−2202	54
H(21b)	1325	458	−2024	54
H(21c)	2431	706	−2444	54
H(22a)	5156	550	−1217	60
H(22b)	4714	387	−1874	60
H(22c)	3992	171	−1295	60

and Cp2a) versus an angle of only 99.4° between the metal and the two phosphorus atoms. The most interesting structural feature of **3b** is the geometry of the two phosphide ligands which adopt distinctly different modes of coordination. The geometry about P2 is pyramidal while that of P1 is trigonal planar with the orthogonal lone pair involved in π-bonding with hafnium. The π-interaction results in a considerably shorter Hf–P1 bond (2.553 (1) Å) as compared to the Hf–P2 distance (2.654 (1) Å). However this π-interaction is less pronounced than that observed in $Cp_2Hf(PEt_2)_2$, where a difference in Hf–P bond lengths of nearly 0.2 Å (Hf–P1 = 2.488 (1) Å, Hf–P2 = 2.682 (1) Å) were encountered.[17] For comparison the phosphide-bridged hafnium complexes $[(C_5Me_5)Hf(Me)(\mu\text{-}H)\{\mu\text{-}P(CMe_3)_2\}]_2$ with a Hf–P single bond length of 2.806 Å (av) and $[Li(DME)][Hf(PCy_2)_5]$ (2.533, 2.475, and 2.504 Å) with terminal π-donor phosphides are also mentioned.[18] A maximum overlap of the phosphorus lone pair with the empty a_1 orbital of the $(\eta^5\text{-}C_5H_5)_2Hf^{IV}$ moiety is expected in an orthogonal orientation of the two planes defined by atoms Hf, P1, and P2 and atoms P1, Si1, and Si2, respectively.[31] In the case of **3b** a dihedral angle of 120.5° is realized, indicating a reduced Hf–P1 π-overlap as compared to that of $Cp_2Hf(PEt_2)_2$. A reason for this finding may be assumed in the steric bulk of the Me_3Si group which prevents the adoption of the idealized geometry. The phosphorus–silicon distances (2.234 (2)–2.241 (2) Å) are shorter than the corresponding data (2.25–2.30 Å) found in a series of silyl phosphines e.g., 2.278 (1) Å in $Ph(Me_3Si)PC(OSiMe_3)({=}NC_6H_4Cl)$,[32] and are comparable with the P–Si bond length in $(\eta^5\text{-}C_5Me_5)(CO)_2Ru\text{–}C(O)P(CMe_3)(SiMe_3)$ (2.226 (2) Å).[33]

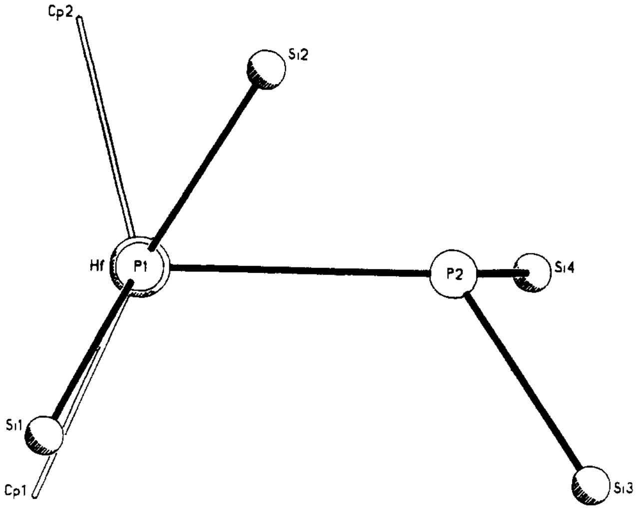


Figure 2. Orientation of the PSi_2 ligands with respect to the $HfCp_2$ fragment in **3b**. (Cp1 and Cp2 are the centers of the ring ligands.)

Acknowledgment. This work was generously supported by the Fonds der Chemischen Industrie, Frankfurt/M., West Germany.

Registry No. **1a**, 1291-32-3; **1b**, 12116-66-4; **3a**, 110487-82-6; **3b**, 110487-83-7; **4**, 110487-84-8; **5a**, 1291-45-8; **5b**, 110487-85-9; **6a**, 110487-86-0; **6b**, 110487-87-1; $ArPCl_2$, 79074-00-3; ArP=PAr, 79073-99-7; $Me_3Si\text{-}P{=}P\text{—}Ar$, 110510-83-3; $LiP(SiMe_3)_2$, 59624-91-8.

Supplementary Material Available: Tables of atomic coordinates and isotropic thermal parameters, bond distances, bond angles, and anisotropic thermal parameters (5 pages); a listing of structure factor amplitudes (27 pages). Ordering information is given on any current masthead page.

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