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Trimethylsilyl Derivatives of Bis(cyclopentadienyl)zirconium and -hafnium. Crystal Structure of $(\eta^5\text{-}C_5H_5)_2Zr(SiMe_3)(S_2CNEt_2)$

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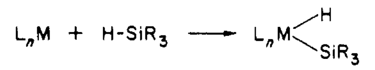
The early-transition-metal silyl complexes $(\eta^5\text{-}C_5H_5)_2M(SiMe_3)Cl$ (**2**, M = Zr; **3**, M = Hf) are prepared from the dichlorides $(\eta^5\text{-}C_5H_5)_2MCl_2$ and $Al(SiMe_3)_3\cdot OEt_2$. The zirconium derivative reacts with O_2 to give the siloxide $(\eta^5\text{-}C_5H_5)_2Zr(OSiMe_3)Cl$ and with H_2O to produce $HSiMe_3$ and $[(\eta^5\text{-}C_5H_5)_2ZrCl]_2O$. The chloride ligands in **2** and **3** readily exchange with other groups to afford $(\eta^5\text{-}C_5H_5)_2M(SiMe_3)X$ complexes (M = Zr and Hf; X = S_2CNEt_2, BH_4, and $OCMe_3$). $(\eta^5\text{-}C_5H_5)_2Zr(SiMe_3)(S_2CNEt_2)$ crystallizes in the triclinic space group $P\bar{1}$ with $a = 8.2358$ (9) Å, $b = 11.6843$ (12) Å, $c = 12.1532$ (15) Å, $\alpha = 76.461$ (9)°, $\beta = 70.700$ (9)°, $\gamma = 71.929$ (9)°, and $Z = 2$. The structure was refined to an R value of 2.59% for all 2698 data. The Si and two S atoms are bonded to Zr in a plane that nearly bisects the two cyclopentadienyl rings. The Zr–Si distance is 2.815 (1) Å.

Introduction

Studies in transition-metal silyl chemistry have focused mainly on the later members of the transition series.[1] This reflects the availability of convenient preparative routes to silyl transition-metal compounds that rely on oxidative additions to low-valent, electron-rich complexes (e.g., eq 1 and 2).[1] In addition, a number of catalytic reactions

$$L_nM^- + X\text{-}SiR_3 \rightarrow L_nM\text{-}SiR_3 + X^- \qquad (1)$$

$$X = \text{halide}$$



$$L_nM + H\text{-}SiR_3 \longrightarrow L_nM(H)(SiR_3) \qquad (2)$$

have been discovered that involve late-metal silyl species as intermediates, such as hydrosilylation,[1a,b] redistribution on silicon[2] and insertions into Si–Si bonds.[3] Low-valent transition-metal silane complexes are now attracting attention as useful intermediates in organic and organometallic synthesis.[4]

Early-transition-metal silyl chemistry, in contrast, has received little attention. In general, syntheses based on eq 1 and 2 are less applicable, given the more electropositive character of the early metals. Although a few titanium derivatives have been reported,[5,6] well-characterized zirconium and hafnium examples are limited to $(\eta^5\text{-}C_5H_5)_2M(SiPh_3)Cl$ (M = Zr and Hf).[7] The chemical properties of d^0 metal silyl complexes remain largely undefined. With the anticipation that these systems will exhibit chemical reactivity patterns heretofore unobserved in transition-metal silicon compounds, we have begun an investigation of early transition-metal silyl chemistry and herein report some initial observations concerning zirconium and hafnium.

Results and Discussion

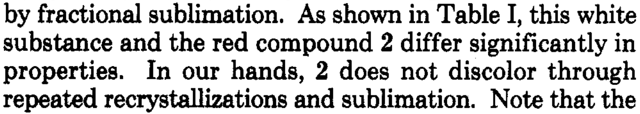
In 1980, Rösch et al. reported[6] the silylation of $(\eta^5\text{-}C_5H_5)_2TiCl_2$ with $Al(SiMe_3)_3\cdot OEt_2$[8] to form the green silyl complex $(\eta^5\text{-}C_5H_5)_2Ti(SiMe_3)Cl$ (**1**). We have used modifications of their procedure to prepare such compounds of zirconium and hafnium. The crystalline, sublimable compounds $(\eta^5\text{-}C_5H_5)_2M(SiMe_3)Cl$ (**2**, M = Zr; **3**, M = Hf) are isolated in high yield (ca. 80%) from the reactions shown in eq 3 and 4. The aluminum product(s) were neither isolated nor characterized. Some physical and spectral properties for **1**, **2**, and **3** are listed in Table I.

$$(\eta^5\text{-}C_5H_5)_2ZrCl_2 + Al(SiMe_3)_3\cdot OEt_2 \xrightarrow[\text{room temp}]{OEt_2} \underset{\mathbf{2}}{(\eta^5\text{-}C_5H_5)_2Zr(SiMe_3)Cl} \qquad (3)$$

$$(\eta^5\text{-}C_5H_5)_2HfCl_2 + Al(SiMe_3)_3\cdot OEt_2 \xrightarrow[\text{reflux}]{C_6H_6} \underset{\mathbf{3}}{(\eta^5\text{-}C_5H_5)_2Hf(SiMe_3)Cl} \qquad (4)$$

The zirconium silyl **2** has been described in an earlier report[9] as a white, powdery material. Its preparation was effected by extended reaction (9 days) between $(\eta^5\text{-}C_5H_5)_2ZrCl_2$ and $Hg(SiMe_3)_2$ in refluxing benzene, followed by fractional sublimation. As shown in Table I, this white substance and the red compound **2** differ significantly in properties. In our hands, **2** does not discolor through repeated recrystallizations and sublimation. Note that the only other zirconium silyl $(\eta^5\text{-}C_5H_5)_2Zr(SiPh_3)Cl$ is orange.[7c]

A problem previously encountered by others in an attempt to prepare a titanium silyl complex was the incorporation of adventitious oxygen to produce, instead, a siloxide. As a result, the compound originally described as $Ti(SiPh_3)_4$[5a] has been reformulated as $Ti(OSiPh_3)_4$.[7c] To eliminate the possibility of **2** being a siloxide, the compound $(\eta^5\text{-}C_5H_5)_2Zr(OSiMe_3)Cl$ (**4**) was independently prepared from $(\eta^5\text{-}C_5H_5)_2ZrCl_2$ and $KOSiMe_3$ (eq 5).



(5)

Complex **4** sublimes as a white powder and is similar in properties to the trimethylsilyl compound isolated by

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[1] (a) Cundy, C. S.; Kingston, B. M.; Lappert, M. F. *Adv. Organomet. Chem.* **1973**, *11*, 253. (b) Speier, J. L. *Adv. Organomet. Chem.* **1978**, *17*, 407. (c) Aylett, B. J. *J. Organomet. Chem. Libr.* **1980**, *9*, 327. (d) Aylett, B. J. *Adv. Inorg. Chem. Radiochem.* **1982**, *25*, 1. (e) Ang, H. G.; Lau, P. T. *Organomet. Chem. Rev. Sect. A* **1972**, *8*, 235.

[2] Curtis, M. D.; Epstein, P. S. *Adv. Organomet. Chem.* **1981**, *19*, 213.

[3] Carlson, C. W.; West, R. *Organometallics* **1983**, *2*, 1801 and references therein.

[4] Gladysz, J. A. *Acc. Chem. Res.* **1984**, *17*, 326.

[5] (a) Hengge, E.; Zimmerman, H. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 142. (b) Hencken, G.; Weiss, E. *Chem. Ber.* **1973**, *106*, 1747. (c) Razuvaev, G. A.; Latyaeva, V. N.; Vyshinskaya, L. I.; Malysheva, A. V.; Vasil'eva, G. A. *Dokl. Akad. Nauk SSSR* **1977**, *237*, 605. (d) Holtman, M. S.; Schram, E. P. *J. Organomet. Chem.* **1980**, *187*, 147.

[6] Rösch, L.; Altnau, G.; Erb, W.; Pickardt, J.; Bruncks, N. *J. Organomet. Chem.* **1980**, *197*, 51.

[7] (a) Cardin, D. J.; Keppie, S. A.; Kingston, B. M.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1967**, 1035. (b) Kingston, B. M.; Lappert, M. F. *Inorg. Nucl. Chem. Lett.* **1968**, *4*, 371. (c) Kingston, B. M.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1972**, *69*. (d) Muir, K. W. *J. Chem. Soc. A* **1971**, 2663.

[8] Rösch, L.; Altnau, G. *J. Organomet. Chem.* **1980**, *195*, 47.

[9] Blakeney, A. J.; Gladysz, J. A. *J. Organomet. Chem.* **1980**, *202*, 263.

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Table I. Physical and Spectral Properties of Some Trimethylsilyl Derivatives of Ti, Zr, and Hf

compd	ref	color	mp, °C	^{1}H NMR data[b] C_5H_5	^{1}H NMR data[b] $SiMe_3$	$^{13}C\{^1H\}$NMR data[c] C_5H_5	$^{13}C\{^1H\}$NMR data[c] $SiMe_3$
$(\eta^5\text{-}C_5H_5)_2Ti(SiMe_3)Cl$ (1)	6	green	119–121[a]	5.90	0.34	112.5	7.77
$(\eta^5\text{-}C_5H_5)_2Zr(SiMe_3)Cl$ (2)	this work	red	117–124[a]	5.75	0.35	110.1	6.41
$(\eta^5\text{-}C_5H_5)_2Hf(SiMe_3)Cl$ (3)	this work	orange	128–132[a]	5.69	0.43	109.2	7.31
$(\eta^5\text{-}C_5H_5)_2Zr(SiMe_3)Cl$	9	white	98–100	5.96[d]	0.10[d]	114.0[e]	1.90[e]
$(\eta^5\text{-}C_5H_5)_2Zr(OSiMe_3)Cl$ (4)	this work	white	103–104	6.00	0.12	114.0	1.8

[a] With decomposition. [b] Chemical shifts are in ppm, referenced to $SiMe_4$ (δ 0.00) at 360 MHz and 21 °C in C_6H_6, except where noted. [c] Shifts are in ppm, referenced to $SiMe_4$ (δ 0.00) at 50.3 MHz and 21 °C in C_6D_6, except where noted. [d] Spectrum measured at 60 MHz in C_6D_6. [e] Spectrum measured at 50 MHz in C_6D_6.

Table II. Physical Properties and ^{1}H NMR Data for Silyl Complexes 5–10

compound	color	mp, °C	^{1}H NMR data[a]	
$(\eta^5\text{-}C_5H_5)_2Zr(SiMe_3)(S_2CNEt_2)$ (5)	yellow	153–154	$Si(CH_3)_3$	0.54 (s)
			NCH_2CH_3	0.74 (t, J_{HH} = 7 Hz)
			NCH_2CH_3	0.82 (t, J_{HH} = 7 Hz)
			NCH_2CH_3	3.21 (q, J_{HH} = 7 Hz)
			NCH_2CH_3	3.27 (q, J_{HH} = 7 Hz)
			C_5H_5	5.62 (s)
$(\eta^5\text{-}C_5H_5)_2Hf(SiMe_3)(S_2CNEt_2)$ (6)	yellow	156–157	$Si(CH_3)_3$	0.60 (s)
			NCH_2CH_3	0.73 (t, J_{HH} = 7 Hz)
			NCH_2CH_3	0.81 (t, J_{HH} = 7 Hz)
			NCH_2CH_3	3.13 (q, J_{HH} = 7 Hz)
			NCH_2CH_3	3.18 (q, J_{HH} = 7 Hz)
			C_5H_5	5.60 (s)
$(\eta^5\text{-}C_5H_5)_2Zr(SiMe_3)(BH_4)$ (7)	orange	110–117 dec	BH_4	−0.77 (br q, $J_{^{11}BH}$ = 90 Hz)
			$Si(CH_3)_3$	0.31 (s)
			C_5H_5	5.50 (s)
$(\eta^5\text{-}C_5H_5)_2Hf(SiMe_3)(BH_4)$ (8)	yellow	136–138 dec	BH_4	not located
			$Si(CH_3)_3$	0.40 (s)
			C_5H_5	5.43 (s)
$(\eta^5\text{-}C_5H_5)_2Zr(SiMe_3)(OCMe_3)$ (9)	yellow	*b*	$Si(CH_3)_3$	0.43 (s)
			$OC(CH_3)_3$	0.89 (s)
			C_5H_5	5.65 (s)
$(\eta^5\text{-}C_5H_5)_2Hf(SiMe_3)(OCMe_3)$ (10)	beige	157–168 dec	$Si(CH_3)_3$	0.51 (s)
			$OC(CH_3)_3$	0.91 (s)
			C_5H_5	5.64 (s)

[a] Chemical shifts are in ppm, referenced to $SiMe_4$ (δ 0.00) at 360 MHz and 21 °C in C_6D_6. [b] The compound melts gradually above 105 °C with decomposition.

Blakeney and Gladysz (Table I). The siloxide 4 also resulted from the rapid, exothermic reaction of 2 with dry oxygen (eq 5). Red toluene solutions of 2 consumed 0.8 equiv of O_2 as the color of the solution faded to a pale orange. Within minutes, an unidentified white substance began to slowly precipitate from solution. As monitored by ^{1}H and $^{13}C\{^1H\}$ NMR (C_6D_6 solution), the only product observed in this reaction was the siloxide 4, in ca. 30% yield. On the basis of these observations, it appears likely that the compound reported earlier[9] is in fact the siloxide 4. Further proof that 2 is a true zrconium silyl is provided by its reaction chemistry and an X-ray crystal structure of a derivative (vide infra).

The thermal stabilities of compounds 2 and 3 follow the expected order 3 > 2. Thermolyses were monitored by ^{1}H NMR in sealed NMR tubes (C_6D_6 solution, 0.3 M). When heated to 97 °C, 2 decomposed within 2 h to $HSiMe_3$ (ca. 1 equiv by ^{1}H NMR and GLC) and a mixture of as yet unidentified organometallic compounds. The major zirconium-containing product (~50%) exhibits a ^{1}H NMR spectrum[10] similar to the one reported for $[(\eta^5\text{-}C_5H_5)(C_5H_4)ZrI]_n$.[11] On the basis of its ^{13}C NMR spectrum, the latter compound was posulated to contain a bridging fulvalene ($C_{10}H_8$) ligand. These results suggest a decomposition pathway involving silyl abstraction of proton from a cyclopentadienyl group. Analogous proton abstractions by alkyl ligands have been observed in the thermolyses of $(\eta^5\text{-}C_5H_5)_3MR$ (R = alkyl; M = U[12] and Th[13]) and in the reduction of $(\eta^5\text{-}C_5H_5)_2Zr(alkyl)Cl$[14] complexes. The thermolysis of 3 at 97 °C was slower (ca. 24 h) but gave similar results, producing 1 equiv of $HSiMe_3$ (identified by ^{1}H NMR and GLC) and uncharacterized hafnium compounds.

The zirconium silyl 2 is hydrolyzed cleanly over a few hours at room temperature according to eq 6 (≥95% yield

$$2(\eta^5\text{-}C_5H_5)_2Zr(SiMe_3)Cl + H_2O \rightarrow [(\eta^5\text{-}C_5H_5)_2ZrCl]_2O + 2HSiMe_3 \quad (6)$$

of both products by ^{1}H NMR). This reaction reflects considerable ionic character in the Zr–Si bond and implies a polarization of $Zr^+\text{–}Si^-$. The preferred site of nucleophilic attack in 2 should then be Zr rather than Si. This property is synthetically usefully since it permits the preparation of other mixed-ligand silyl complexes via chloride displacement reactions. Thus, when the chlorides 2 and 3 are treated with the nucleophilic reagents NaS_2CNEt_2, $LiBH_4$, and $LiOCMe_3$, reaction occurs at zirconium or hafnium to afford new silyl complexes (vide infra). Spectral properties

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(10) ^{1}H NMR (C_6D_6, 22 °C): δ 5.54 (s, 5 H), 4.91 ("pseudotriplet", J_{obsd} = 2.7 Hz, 2 H), 3.94 ("pseudotriplet", J_{obsd} = 2.7 Hz, 2 H).

(11) Gell, K. I.; Harris, T. V.; Schwartz, J. *Inorg. Chem.* **1981**, *20*, 481. ^{1}H NMR reported for $[(\eta^5\text{-}C_5H_5)(C_5H_4)ZrI]_n$ in this reference (C_6D_6): δ 5.61 (s, 5 H), 4.58 ("pseudotriplet", J_{obsd} = 2.8 Hz, 2 H), 4.16 ("pseudotriplet", J_{obsd} = 2.8 Hz, 2 H).

(12) Marks, T. J.; Seyam, A. M.; Kolb, J. R. *J. Am. Chem. Soc.* **1973**, *95*, 5529.

(13) Marks, T. J.; Wachter, W. A. *J. Am. Chem. Soc.* **1976**, *98*, 703.

(14) Schore, N. E.; Young, S. J.; Olmstead, M. M. *Organometallics* **1983**, *2*, 1769.

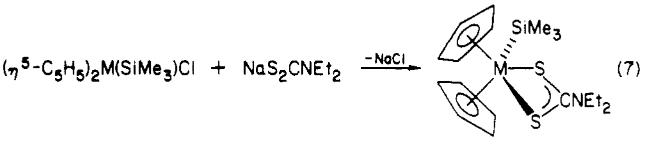
Table III. $^{13}C\{^1H\}$ NMR and IR Data for Silyl Complexes 5-10

compd	$^{13}C\{^1H\}$ NMR Data[a]		IR data[b]	
$(\eta^5\text{-}C_5H_5)_2Zr(SiMe_3)(S_2CNEt_2)$ (5)	$Si(CH_3)_3$	5.51	$\nu(C\overset{\cdot\cdot}{-}N)$	1496
	NCH_2CH_3	12.4	$\nu(C\overset{\cdot\cdot}{-}S)$	1014
	NCH_2CH_3	12.5		
	NCH_2CH_3	43.3		
	NCH_2CH_3	44.8		
	C_5H_5	104.9		
	S_2CN	206.4		
$(\eta^5\text{-}C_5H_5)_2Hf(SiMe_3)(S_2CNEt_2)$ (6)	$Si(CH_3)_3$	5.78	$\nu(C\overset{\cdot\cdot}{-}N)$	1497
	NCH_2CH_3	12.4	$\nu(C\overset{\cdot\cdot}{-}S)$	1014
	NCH_2CH_3	12.5		
	NCH_2CH_3	42.9		
	NCH_2CH_3	44.7		
	C_5H_5	104.1		
	S_2CN	206.3		
$(\eta^5\text{-}C_5H_5)_2Zr(SiMe_3)(BH_4)$ (7)	$Si(CH_3)_3$	7.33	$\nu(ZrBH_4)$	2448, 2403, 2252, 2022, 1951, 1905, 1382, 1130
	C_5H_5	105.9		
$(\eta^5\text{-}C_5H_5)_2Hf(SiMe_3)(BH_4)$ (8)	$Si(CH_3)_3$	7.84	$\nu(HfBH_4)$	2464, 2405, 2269, 2010, 1965, 1918, 1416, 1140
	C_5H_5	104.6		
$(\eta^5\text{-}C_5H_5)_2Hf(SiMe_3)(OCMe_3)$ (10)	$Si(CH_3)_3$	7.06		
	$OC(CH_3)_3$	32.6		
	C_5H_5	107.0		

[a] Shifts are in ppm, referenced to $SiMe_4$ (δ 0.00) at 50.3 MHz and 21 °C in C_6D_6. [b] Spectra were recorded as Nujol mulls between CsI plates; values are in cm^{-1}.

for these new compounds are listed in Tables II and III. Note that a common reactivity mode for late or low-valent transition-metal complexes is nucleophilic attack at the coordinated silicon atom.[1,4,15]

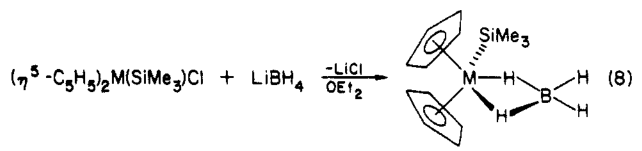
The pale yellow diethyl dithiocarbamate derivatives 5 and 6 are formed in high yield by reaction of 2 or 3 with NaS_2CNEt_2 in diethyl ether (eq 7). These compounds are



5, M = Zr
6, M = Hf

more thermally stable than their chloride precursors, melting without decomposition above 150 °C. Consistent with the chelate structure shown, the infrared spectra contain a single $\nu(C\overset{\cdot\cdot}{-}S)$ absorption[16] near 1000 cm^{-1} and the ethyl groups are inequivalent by ^1H and ^{13}C NMR (21 °C). This structure has been confirmed by a single-crystal X-ray structure determination for 5 (vide infra). The related compounds $(\eta^5\text{-}C_5H_5)_2ZrCl(S_2CNR_2)$ (R = Me and Et) also contain chelating dialkyl dithiocarbamate groups.[17]

The borohydrides 7 and 8 are obtained upon reactions of 2 and 3, respectively, with 1 equiv of $LiBH_4$ in diethyl ether (eq 8). These pentane-soluble complexes exhibit



7, M = Zr
8, M = Hf

infrared spectra characteristic of bidentate BH_4 ligands.[18] For 7, the terminal B–H stretching frequencies are found at 2448 and 2403 cm^{-1}, bridging B–H stretches occur at 1951 and 1905 cm^{-1}, the diagnostic bridge stretching absorption occurs as a strong, broad band centered at 1382 cm^{-1}, and a BH_2 deformation band appears at 1130 cm^{-1}. In the ^1H NMR spectrum, the BH_4 protons of 7 were observed as a broadened quartet at −0.77 ppm. The BH_4 protons of 8 were not observed, presumably due to fluctionality and/or ^{11}B broadening.[18,19]

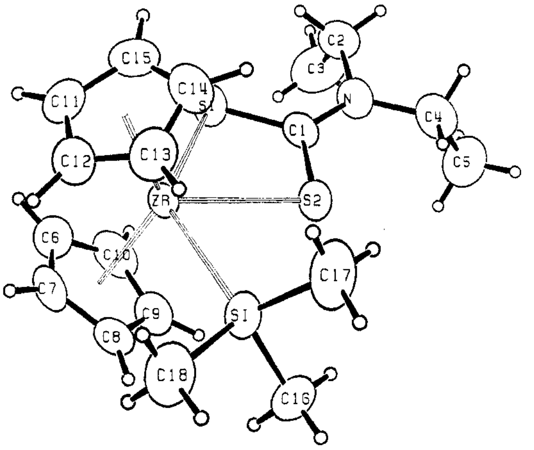


Figure 1. An ORTEP[31] drawing of 5 with the atoms labeled. Thermal elliposids are represented at 50% probability.

Reactions of 2 and 3 with $LiOCMe_3$ in diethyl ether produce the alkoxides $(\eta^5\text{-}C_5H_5)_2Zr(SiMe_3)(OCMe_3)$ (9) and $(\eta^5\text{-}C_5H_5)_2Hf(SiMe_3)(OCMe_3)$ (10), respectively. Compound 9 is thermally unstable, decomposing slowly (over weeks) under nitrogen at room temperature, whereas 10 is stable under the same conditions for months.

Description of the Structure of 5. In order to unequivocally establish the presence of a metal–silicon bond in the silyl complexes described above, it was desirous to obtain a crystal structure of one of them. Due to our inability to obtain suitable crystals of 2, the structure of a derivative, 5, was determined by X-ray diffraction. Crystal and data collection parameters are summarized in Table IV. A view of the molecule is provided (Figure 1),

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(15) (a) Berry, A. D.; MacDiarmid, A. G. *Inorg. Nucl. Chem. Lett.* **1969**, *5*, 601. (b) Chalk, A. J. *J. Chem. Soc., Chem. Commun.* **1970**, 847. (c) Schafer, H.; MacDiarmid, A. G. *Inorg. Chem.* **1976**, *15*, 848. (d) Colomer, E.; Corriu, R. J. P. *J. Chem. Soc. Chem. Commun.* **1976**, 175. (e) Marsi, M.; Gladysz, J. A. *Organometallics* **1982**, *1*, 1467. (f) Johnson, D. L.; Gladysz, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 6433. (g) Aylett, B. J.; Campbell, J. M. *J. Chem. Soc., Chem. Commun.* **1967**, 159.

(16) Bonati, F.; Ugo, R. *J. Organomet. Chem.* **1967**, *10*, 257.

(17) Silver, M. E.; Eisenstein, O.; Fay, R. C. *Inorg. Chem.* **1983**, *22*, 759.

(18) Marks, T. J.; Kolb, J. R. *Chem. Rev.* **1977**, *77*, 263.

(19) Wolczanski, P. T.; Bercaw, J. *Organometallics* **1982**, *1*, 793.

Table IV. Crystal and Data Collection Parameters for 5

(A) Crystal Parameters at 25 °C[a,b]

a = 8.2358 (9) Å
b = 11.6843 (12) Å
c = 12.1532 (15) Å
α = 76.461 (9), deg
β = 70.700 (9) deg
γ = 71.929 (9) deg
V = 1038.0 (2) Å^3

size of crystal: 0.18 × 0.25 × 0.28 mm
space group: $P\bar{1}$
fw = 442.9 amu
Z = 2
d_{calcd} = 1.42 g cm^{-3}
μ(calcd) = 7.70 cm^{-1}

(B) Data Measurement Parameters

radiation: Mo Kα (γ = 0.71073 Å)
monochromator: highly oriented graphite (2θ = 12.2°)
detector: crystal scintillation counter, with PHA
reflctns measd: $+h,\pm k,\pm l$
2θ range: 3° → 45°
scan type: θ–2θ
scan speed: 0.6 → 6.7 (θ, deg/min)
scan width: $\Delta\theta = 0.5 + 0.347 \tan\theta$
background: measured over 0.25$\Delta\theta$ added to each end of the scan
aperture → crystal = 173 mm
vertical aperture = 3.0 mm
horizontal aperture = 2.0 + 1.0 tan θ mm (variable)
no. of unique reflctns collected: 2698
intensity standards: (080), (50$\bar{1}$), (03$\bar{7}$); measured every hour of X-ray exposure time; over the data collection period no decrease in intensity was observed
orientation: 3 reflections were checked after every 250 measurements; crystal orientation was redetermined if any of the reflections were offset from their predicted positions by more than 0.1°; reorientation was performed once during data collection

[a] Unit cell parameters and their esd's were derived by a least-square fit to the setting angles of the unresolved Mo Kα components of 24 reflections with 2θ near 28°. [b] In this and all subsequent tables the esd's of all parameters are given in parentheses, right-justified to the least significant digit(s) given.

Table V. Positional Parameters and Their Estimated Standard Deviations for 5[a]

atom	x	y	z	B, Å^2
Zr	0.15734 (2)	0.25820 (2)	0.21084 (2)	2.622 (5)
S1	0.26521 (8)	0.18535 (6)	−0.00388 (5)	4.08 (2)
S2	−0.10135 (7)	0.24759 (6)	0.12987 (5)	3.42 (1)
Si	−0.17656 (8)	0.33072 (7)	0.37312 (6)	3.92 (2)
N	0.0070 (3)	0.1566 (2)	−0.0738 (2)	4.02 (5)
C1	0.0505 (3)	0.1933 (2)	0.0057 (2)	3.18 (5)
C2	0.1456 (4)	0.1030 (2)	−0.1740 (2)	4.59 (7)
C3	0.2007 (5)	0.1944 (3)	−0.2781 (3)	7.0 (1)
C4	−0.1819 (4)	0.1554 (3)	−0.0590 (2)	4.71 (7)
C5	−0.2642 (4)	0.2522 (3)	−0.1399 (3)	6.4 (1)
C6	0.3766 (3)	0.3856 (2)	0.1398 (3)	4.62 (7)
C7	0.2711 (3)	0.4130 (2)	0.2518 (2)	4.24 (6)
C8	0.1006 (3)	0.4721 (2)	0.2450 (2)	4.06 (6)
C9	0.0997 (3)	0.4825 (2)	0.1282 (2)	4.41 (7)
C10	0.2699 (4)	0.4305 (2)	0.0642 (2)	4.86 (7)
C11	0.4081 (3)	0.1059 (3)	0.2810 (2)	4.66 (7)
C12	0.2777 (3)	0.1488 (2)	0.3806 (2)	4.35 (7)
C13	0.1286 (4)	0.1091 (3)	0.3977 (2)	4.57 (7)
C14	0.1668 (4)	0.0411 (3)	0.3064 (3)	5.12 (7)
C15	0.3388 (4)	0.0385 (3)	0.2369 (2)	5.15 (8)
C16	−0.3322 (3)	0.4724 (3)	0.3156 (3)	5.59 (8)
C17	−0.3181 (4)	0.2171 (3)	0.4287 (3)	6.21 (9)
C18	−0.1582 (4)	0.3673 (3)	0.5123 (2)	6.80 (9)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(^4/_3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table VI. Bond Distances (Å) and Angles (deg) for 5[a]

distances		angles	
Zr–S1	2.713 (1)	Cp1–Zr–S1	101.78
Zr–S2	2.670 (1)	Cp–Zr–S2	115.37
Zr–Si	2.815 (1)	Cp1–Zr–Si	96.80
Zr–C6	2.501 (2)	Cp1–Zr–Cp2	129.93
Zr–C6	2.501 (2)	Cp2–Zr–S1	101.60
Zr–C7	2.486 (2)	Cp2–Zr–S2	114.63
Zr–C8	2.504 (2)	Cp2–Zr–Si	97.68
Zr–C9	2.533 (2)	S1–Zr–S2	64.41 (1)
Zr–C10	2.545 (2)	S1–Zr–Si	134.06 (2)
Zr–Cp1	2.219	S2–Zr–Si	69.66 (1)
Zr–C11	2.517 (2)	Zr–S1–C1	90.21 (6)
Zr–C12	2.491 (2)	Zr–S2–C1	91.44 (6)
Zr–C13	2.509 (2)	S1–C1–S2	113.78 (9)
Zr–C14	2.519 (2)	S1–C1–N	122.66 (14)
Zr–C15	2.545 (2)	S2–C1–N	123.51 (14)
Zr–Cp2	2.220	C1–N–C2	120.68 (16)
C1–S1	1.708 (2)	C1–N–C4	121.88 (15)
C1–S2	1.718 (2)	C2–N–C4	117.13 (14)
C1–N	1.328 (2)	N–C2–C3	114.09 (18)
N–C2	1.475 (2)	N–C4–C5	112.14 (18)
N–C4	1.511 (2)	Zr–Si–C16	114.59 (7)
C2–C3	1.495 (3)	Zr–Si–C17	116.57 (8)
C4–C5	1.466 (3)	Zr–Si–C18	112.55 (7)
Si–C16	1.899 (2)	C16–Si–C17	102.57 (10)
Si–C17	1.896 (2)	C16–Si–C18	104.88 (11)
Si–C18	1.902 (2)	C17–Si–C18	104.35 (12)
C6–C7	1.400 (3)	C10–C6–C7	107.45 (17)
C7–C8	1.379 (3)	C6–C7–C8	108.37 (18)
C8–C9	1.399 (3)	C7–C8–C9	107.66 (18)
C9–C10	1.382 (3)	C8–C9–C10	108.00 (17)
C10–C6	1.384 (3)	C9–C10–C6	108.50 (18)
C11–C12	1.400 (3)	C15–C11–C12	107.48 (19)
C12–C13	1.380 (3)	C11–C12–C13	109.00 (18)
C13–C14	1.410 (3)	C12–C13–C14	106.81 (19)
C14–C15	1.384 (3)	C13–C14–C15	108.29 (19)
C15–C11	1.382 (3)	C14–C15–C11	108.41 (19)

[a] Cp1 and Cp2 are the centroids of the cyclopentadienyl rings.

and relevant geometrical parameters are given in Tables V and VI.

The structure consists of well-separated molecules of the compound. There are no abnormally short intermolecular distances. The two sulfur atoms and the silicon atom lie in a plane which very closely bisects the angle between the two η^5-C_5H_5 planes. The dithiocarbamate plane (S1, S2, C1, N, C2, C4) is tilted slightly with respect to the coordination plane (Zr, S1, S2, Si), but only by 6.8° (see supplementary material). Overall, the coordination geometry is similar to that found in $(\eta^5\text{-}C_5H_5)_2ZrCl(S_2CNEt_2)$,[17] with a few minor exceptions. In the dithiocarbamate ligand, the terminal methyl groups lie on the same side of the dithiocarbamate plane, whereas the methyl groups are located on opposite sides of the corresponding plane in $(\eta^5\text{-}C_5H_5)_2ZrCl(S_2CNEt_2)$. The cyclopentadienyl rings in **5** are slightly canted from the eclipsed conformation, with an average torsion angle of about 10° between corresponding carbon atoms in the two rings.

The Si–C bonds in the $SiMe_3$ ligand are staggered with respect to the Zr–Cp1, Zr–Cp2, and Zr–S2 vectors. Distances and angles within the $SiMe_3$ ligand itself are unexceptional.[20] The Zr–Si bond length of 2.815 (1) Å in complex **5** does not differ significantly from the value of 2.813 (2) Å found in $(\eta^5\text{-}C_5H_5)_2Zr(SiPh_3)Cl$,[7d] despite the different coordination number. As noted earlier, this distance is surprisingly long considering the covalent radii of zirconium and silicon.[7d]

Experimental Section

All manipulations were conducted under an inert-atmosphere of nitrogen. All solvents were distilled from sodium benzophenone ketal prior to use. Elemental analyses were performed by Galbraith or Schwartzkopf microanalytical laboratories. Infrared spectra were recorded on a Perkin-Elmer 1330 infrared spectrometer. ^{1}H NMR spectra were recorded at 360 MHz with a

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(20) Couldwell, M. C.; Simpson, J. *J. Chem. Soc., Dalton Trans.* **1976**, 714.

spectrometer fabricated locally by Dr. John Wright. $^{13}C\{^1H\}$ NMR spectra were recorded at 50.3 MHz with a Nicolet WB-200 spectrometer.

$(\eta^5\text{-}C_5H_5)_2Zr(SiMe_3)Cl$ (2). A 250-mL flask was charged with $(\eta^5\text{-}C_5H_5)_2ZrCl_2$ (3.65 g, 12.5 mmol), $Al(SiMe_3)_3{\cdot}OEt_2$[8] (4.00 g, 12.5 mmol), and diethyl ether (130 mL). Stirring at room temperature produced a clear red solution after 2.5 days. The solvent was removed by evacuation, and the red residue was extracted with pentane (3 × 100 mL). The combined extracts were concentrated and cooled (−15 °C) to yield red crystals of the product in an overall yield of 80% (3.31 g). Anal. Calcd for $C_{13}ClH_{19}SiZr$: C, 47.3; Cl, 10.7; H, 5.80; Si, 8.51. Found: C, 47.1; Cl, 10.9; H, 5.88; Si, 8.31. IR (Nujol, CsI, cm^{-1}): 3108 w, 1433 m, 1360 w, 1230 m, 1222 w sh, 1008 s, 800 vs br, 721 m, 668 m, 657 m, 607 m, 348 m, 289 m.

$(\eta^5\text{-}C_5H_5)_2Hf(SiMe_3)Cl$ (3). Benzene (90 mL) was added to a flask containing $(\eta^5\text{-}C_5H_5)_2HfCl_2$ (3.00 g, 7.90 mmol) and $Al(SiMe_3)_3{\cdot}OEt_2$ (2.53 g, 7.89 mmol). The resulting mixture was refluxed for 2 h, resulting in a dark orange-brown solution. Removal of solvent, extraction with pentane (2 × 75 mL), concentration of the combined pentane extracts, and cooling (−15 °C) afforded orange crystals of 3 (2.37 g, 72%). Anal. Calcd for $C_{13}ClH_{19}SiHf$: C, 37.4; Cl, 8.49; H, 4.59; Si, 6.73. Found: C, 37.1; Cl, 8.64; H, 4.88; Si, 7.03. IR (Nujol, CsI, cm^{-1}): 3104 w, 1440 m, 1365 w, 1232 m, 1013 s, 811 vs br, 725 m, 659 m, 611 m, 305 m.

$(\eta^5\text{-}C_5H_5)_2Zr(OSiMe_3)Cl$ (4). The compounds $(\eta^5\text{-}C_5H_5)_2ZrCl_2$ (3.00 g, 10.0 mmol) and $KOSiMe_3$ (Petrarch, 1.32 g, 10.0 mmol) were stirred together in 1,2-dimethoxyethane (40 mL) for 2 days and then refluxed for 2 h. The reaction mixture was evaporated to dryness, and the compound 4 was extracted from the residue with toluene (40 mL). Concentration and cooling (−15 °C) of the toluene solution gave colorless crystals (0.87 g, 25%) that sublimed (80 °C, 10^{-4} mmHg) as a white powder. Anal. Calcd for $C_{13}ClH_{19}OSiZr$: C, 45.1; Cl, 10.2; H, 5.53; Si, 8.12. Found: C, 45.0; Cl, 10.8; H, 5.56; Si, 7.82. IR (Nujol, CsI, cm^{-1}): 3103 w, 1440 m, 1364 w, 1310 w, 1246 s, 1063 w, 1011 s, 937 vs br, 834 m, 802 vs br, 744 m, 680 m, 610 m, 406 m, 336 s.

$(\eta^5\text{-}C_5H_5)_2Zr(SiMe_3)(S_2CNEt_2)$ (5). The chloride 2 (0.50 g, 1.51 mmol) and NaS_2CNEt_2 (0.26 g, 1.52 mmol) were combined in a flask, and diethyl ether (40 mL) was added. After being stirred for 10 h, the reaction mixture was evaporated to dryness. The product was extracted into pentane (50 mL) and crystallized by concentration and cooling (−15 °C). Yellow needles were isolated in 81% yield (0.54 g). Anal. Calcd for $C_{18}H_{29}NS_2SiZr$: C, 48.7; H, 6.59; N, 3.16; S, 14.4; Si, 6.55. Found: C, 48.7; H, 6.59; N, 3.06, S, 14.6; Si, 6.84. IR (Nujol, CsI, cm^{-1}): 1496 s, 1432 m, 1359 m, 1278 m br, 1248 w, 1230 m, 1210 m, 1145 m, 1090 w, 1014 s, 803 vs br, 728 m, 657 m, 607 m, 341 m.

$(\eta^5\text{-}C_5H_5)_2Hf(SiMe_3)(S_2CNEt_2)$ (6). This compound was prepared by the same method used to prepare 5. The yield of 6 was 79% (0.31 g). Anal. Calcd for $C_{18}H_{29}HfNS_2Si$: C, 40.8; H, 5.51; N, 2.64; S, 12.1; Si, 5.30. Found: C, 41.2; H, 5.70; N, 2.74; S, 12.0; Si, 5.54. IR (Nujol, CsI, cm^{-1}): 1497 s, 1434 m, 1360 w, 1280 m br, 1248 w, 1231 m, 1212 m, 1047 m, 1090 w, 1014 s, 809 vs br, 727 m, 655 m, 609 m, 290 m.

$(\eta^5\text{-}C_5H_5)_2Zr(SiMe_3)(BH_4)$ (7). The chloride 2 (0.50 g, 1.51 mmol) and $LiBH_4$ (0.033 g, 1.52 mmol) were combined in a flask and the solids cooled to −78 °C. After the addition of diethyl ether (40 mL, cooled to −78 °C) the mixture was allowed to slowly warm to room temperature with stirring. After 10 h, the ether was removed by vacuum tansfer and the residue extracted with pentane (40 mL). Filtration, concentration, and cooling (−15 °C) of the pentane solution effected crystallization of the compound in an overall yield of 73% (0.34 g). Anal. Calcd for $BC_{13}H_{23}SiZr$: B, 3.49; C, 50.5; H, 7.49; Si, 9.08. Found: B, 3.44; C, 50.7; H, 7.73; Si, 9.21. IR (Nujol, CsI, cm^{-1}): 3104 w, 2448 m, 2403 m, 2252 w, 2022 w, 1951 m, 1905 m, 1382 s, 1232 m, 1130 s, 1009 s, 800 vs br, 727 m, 667 m, 658 m, 608 m, 419 w br, 360 w, 289 w.

$(\eta^5\text{-}C_5H_5)_2Hf(SiMe_3)(BH_4)$ (8). The procedure used was identical with the one used to obtain 7. Yellow crystals of 8 were isolated in 85% yield (0.24 g). Anal. Calcd for $BC_{13}H_{23}HfSi$: B, 2.72; C, 39.4; H, 5.84; Si, 7.08. Found: B, 2.50; C, 39.9; H, 5.74; Si, 7.40. IR (Nujol, CsI, cm^{-1}): 3112 w, 2464 m, 2405 m, 2269 w, 2010 m, 1965 m, 1918 m, 1416 s, 1252 w, 1235 m, 1140 s, 1067 w, 1013 s, 812 vs br, 730 m, 663 m, 612 m, 414 w, 302 w br.

$(\eta^5\text{-}C_5H_5)_2Zr(SiMe_3)(OCMe_3)$ (9). Diethyl ether (40 mL), 2 (0.50 g, 1.51 mmol), and $LiOCMe_3$ (0.12 g, 1.50 mmol) were stirred together at room temperature for 1 day. The ether was removed under vacuum and the residue extracted with pentane (60 mL). Concentration and cooling of the pentane solution gave 9 as yellow crystals (0.47 g, 85%). Anal. Calcd for $C_{17}H_{28}OSiZr$: C, 55.5; H, 7.67. Found: C, 54.8; H, 7.76. IR (Nujol, CsI, cm^{-1}): 3084 w, 1352 m, 1222 m, 1186 s, 1013 s, 830 s, 790 vs br, 721 m, 658 m, 604 m, 526 w, 472 w, 326 m.

$(\eta^5\text{-}C_5H_5)_2Hf(SiMe_3)(OCMe_3)$ (10). Compound 3 (0.25 g, 0.60 mmol) and $LiOCMe_3$ (0.05 g, 0.62 mmol) were stirred in diethyl ether (20 mL) for 13 h. The solvent was removed by vacuum transfer and the product sublimed (100 °C, 10^{-4} mm Hg) from the resulting residue in 70% yield (0.19 g). Anal. Calcd for $C_{17}H_{28}HfOSi$: C, 44.9; H, 6.20. Found: C, 44.7; H, 6.17. IR (Nujol, CsI, cm^{-1}): 3091 w, 1359 m, 1231 m, 1197 s, 1034 vs br, 838 s, 800 vs br, 726 m, 663 m, 612 m, 526 w, 478 w, 280 m.

Collection of X-ray Diffraction Data. Clear, yellow, bladelike crystals of the compound were obtained by slow crystallization from diethyl ether. Fragments cleaved from some of these crystals were mounted in quartz capillaries in an inert-atmosphere glovebox, and the capillaries were flame sealed. Preliminary precession photographs indicated triclinic Laue symmetry. The crystal used for data collection was then transferred to an Enraf-Nonius CAD-4 diffractometer[21] and centered in the beam. Automatic peak search and indexing procedures yielded a triclinic reduced primitive cell. Inspection of the Niggli values[22] revealed no conventional cells of higher symmetry. The final cell parameters and specific data collection parameters are given in Table IV. The 2698 unique raw intensity data were converted to structure factor amplitudes and their esds by correction for scan speed, background, and Lorentz and polarization effects.[23-25] No correction for crystal decomposition was necessary. Inspection of the azimuthal scan data[26] showed a variation $I_{min}/I_{max} = 0.95$ for the average curve. An empirical correction for absorption, based on the azimuthal scan data, was applied to the intensities.

The structure was solved by Patterson methods and refined via standard least-squares and Fourier techniques. The assumption tht the space group was centric was confirmed by the successful solution and refinement of the structure. In a difference Fourier map calculated following refinement of all non-hydrogen atoms with anisotropic thermal parameters, peaks corresponding to the expected positions of most of the hydrogen atoms were found. Hydrogens were included in the structure factor calculations in their expected positions based on idealized bonding geometry but were not refined in least squares. A secondary extinction parameter[27] was refined in the final cycles of least-squares (refined value, $g = 4.9\ (6) \times 10^{-7}$, maximum correction to any structure factor was 6%). The final residuals[28] for 209 variables refined against the 2451 data for which $F^2 > 3\sigma(F^2)$ were

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[21] The crystal structure was determined by Dr. F. J. Hollander, staff crystallographer at the U.C. Berkeley X-Ray Crystallographic Facility (CHEXRAY), which consists of two Enraf-Nonius CAD-4 diffractometers, one controlled by a DEC PDP 8/a with an RK05 disk and the other by a DEC PDP 8/e with an RL01 disk. Both use Enraf-Nonius software as described in the "CAD-4 Operation Manual"; Enraf-Nonius: Delft, 1977, updated 1980.

[22] Roof, R. B., Jr. "A Theoretical Extension of the Reduced-Cell Concept in Crystallography", Publication LA-4083; Los Alamos Scientific Laboratory: Los Alamos, NM, 1969.

[23] All calculations were performed on a PDP 11/60 equipped with 128 kilowords of memory, twin RK07 28 MByte disk drives, Versatec printer/plotter, and TU10 tape drive using local-modified Nonius-SDP software operating under RSX-11M.

[24] Structure Determination Package User's Guide, 1982, B.A. Frenz and Associates, College Station, TX 77840.

[25] The data reduction formulas (see ref 24) are $F_o^2 = (\omega/Lp)\ (C - 2B)$, $\sigma_o(F_o^2) = (\omega/Lp)(C + 4B)^{1/2}$, $F_o = (F_o^2)^{1/2}$, and $\sigma_o(F) = \sigma_o(F_o^2)/2F_o$.

[26] Reflections used for azimuthal scans were located near $\chi = 90°$, and the intensities were measured at 10° increments of rotation of the crystal about the diffraction vector.

[27] Zachariesen, W. H. *Acta Crystallogr.* **1963**, *16*, 1139.

[28] $R = \sum||F_o| - |F_c||/\sum|F_o|$, $wR = \{\sum w(|F_o| - |F_c|)^2/wF_o^2\}^{1/2}$, and GOF $= \{\sum w(|F_o| - |F_c|)^2/(n_o - n_v)\}^{1/2}$ (see ref 24).

[29] Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography", The Kynoch Press: Birmingham, England, 1984; Vol. IV, Table 2.2B.

$R = 2.08\%$, $wR = 3.20\%$, and GOF = 2.184. The R value for all 2698 data was 2.59%.

The quantity minimized by the least-squares program was $\sum w(|F_o| - |F_c|)^2$ where w is the weight of a given observation. The p factor,[28] used to reduce the weight of intense reflections, was set to 0.02 in the last cycles of refinement. The analytical forms of the scattering factors were corrected for both the real and imaginary components of anomalous dispersion.[30] Inspection of the residuals ordered in ranges of $(\sin \theta)/\lambda$, $|F_o|$, and parity and value of the individual indexes showed no unusual features or trends. The largest peak in the final difference Fourier map had an electron density of 0.48 e/Å^3 and was located near one of the ethyl groups of the dithiocarbamate ligand. The positional and thermal parameters of the non-hydrogen atoms are given in Table V.

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Registry No. **2**, 76772-61-7; **3**, 97011-30-8; **4**, 97011-31-9; **5**, 97011-32-0; **6**, 97011-33-1; **7**, 97011-34-2; **8**, 97011-35-3; **9**, 96503-79-6; **10**, 97011-36-4; $(\eta^5\text{-}C_5H_5)_2ZrCl_2$, 1291-32-3; $Al(SiMe_3)_3$, 65343-66-0; $(\eta^5\text{-}C_5H_5)_2HfCl_2$, 12116-66-4; $KOSiMe_3$, 10519-96-7; NaS_2CNEt_2, 148-18-5; $[(\eta^5\text{-}C_5H_5)_2ZrCl]_2O$, 12097-04-0.

Supplementary Material Available: Tables of anisotropic thermal parameters for **5**, the values of F_o and F_c, the positions of the hydrogen atoms, and least-squares planes and torsion angles (20 pages). Ordering information is given on any current masthead page.

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(30) Cromer, D. T., ref 29, Table 2.3.1.

(31) Johnson, C. K. Report ORNL-3794; Oak Ridge National Laboratory: Oak Ridge, TN, 1965.

Communications

Mechanisms of Reactions of Binuclear Iron Bis(μ-phosphido) Carbonyl Complexes with Protic Acid, Hydride, and Alkyl Halides

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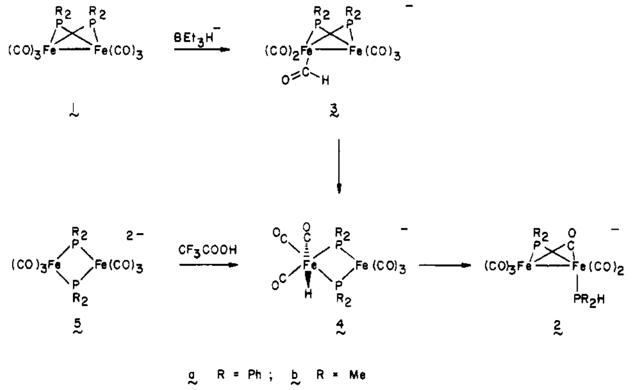
Summary: The mechanisms of the reactions of $Fe_2(CO)_6(\mu\text{-}PR_2)_2$ (**1a**, R = Ph; **1b**, R = Me) with 1 equiv of BEt_3H^- (and BEt_3D^-) and of $[Fe_2(CO)_6(\mu\text{-}PR_2)_2]^{2-}$ (**5**) with 1 equiv of CF_3COOH, both of which proceed with $\overline{\mathrm{Fe{-}(\mu{-}PR_2)}}$ bond cleavage to yield $[(CO)_3Fe(\mu\text{-}PR_2)(\mu\text{-}CO)Fe(CO)_2(PR_2H)]^-$ (**2**), were investigated by variable-temperature ^{31}P, ^2H, and ^1H NMR in THF solution. Treatment of **1** with BEt_3H^- first affords spectroscopically characterized binuclear iron–formyl anions $[Fe_2(CO)_5(C(O)H)(\mu\text{-}PR_2)_2]^-$ (**3**). These rearrange at −25 to −20 °C to the hydrido complexes $[Fe_2(CO)_6(H)(\mu\text{-}PR_2)_2]^-$ (**4**), which at −5 to 0 °C reductively eliminate H and μ-PR$_2$ to furnish **2**. Protonation of **5** with CF_3COOH in THF at −25 °C yields the same binuclear iron hydrides **4**, which convert to **2** on warming. Alkylation reactions of **5a** with 1 equiv of R′I (R′ = Me and Et) in THF occur at −70 to 25 °C without an observable (by ^{31}P NMR) intermediate to give the binuclear iron acyls $[Fe_2(CO)_5(C(O)R')(\mu\text{-}PR_2)_2]^-$ (**6a**). In contrast, **5b** and R′I (R′ = Me (and CD$_3$), Et, and allyl) yield intermediate species **7b** at −75 to −70 °C. From ^{31}P and ^2H NMR, **7b** are assigned binuclear iron–alkyl structures $[Fe_2(CO)_6(R')(\mu\text{-}PR_2)_2]^-$ analogous to those of the iron hydrides **4**. On warming, **7b** convert to the acyl complexes **6b** (rather than reductively eliminate R′ and μ-PR$_2$) in the order R′ = Et > Me > allyl, consistent with the greater propensity of metal alkyls than of metal hydrides to participate in intramolecular CO insertion.

Phosphido-bridged transition-metal complexes represent an important class of binuclear and polynuclear compounds.[1] The binuclear complexes have received attention in the synthesis of metal clusters and in studies of cooperative reactivity effects. In general, phosphido ligands provide stable bridges between metals which retard fragmentation of the molecular framework.[2] However, ex-

Scheme I



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(1) Representative recent publications: (a) Rosenberg, S.; Whittle, R. R.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1984**, *106*, 5934. (b) Glaser, R.; Kountz, D. J.; Waid, R. D.; Gallucci, J. C.; Meek, D. W. *Ibid.* **1984**, *106*, 6324. (c) Iggo, J. A.; Mays, M. J.; Raithby, P. R.; Henrick, K. *J. Chem. Soc., Dalton Trans.* **1984**, 633. (d) Regragui, R.; Dixneuf, P. H.; Taylor, N. J.; Carty, A. J. *Organometallics* **1984**, *3*, 1020. (e) Casey, C. P.; Bullock, R. M. *Ibid.* **1984**, *3*, 1100. (f) Kyba, E. P.; Mather, J. D.; Hassett, K. L.; McKennis, J. S.; Davis, R. E. *J. Am. Chem. Soc.* **1984**, *106*, 5371. (g) Bender, R.; Braunstein, P.; Metz, B.; Lemoine, P. *Organometallics* **1984**, *3*, 381. (h) Jones, R. A.; Lasch, J. G.; Norman, N. C.; Stuart, A. L.; Wright, T. C.; Whittlesey, B. R. *Ibid.* **1984**, *3*, 114. (i) Seyferth, D.; Wood, T. G.; Fackler, J. P., Jr.; Mazany, A. M. *Ibid.* **1984**, *3*, 1121. (j) Finke, R. G.; Gaughan, G; Pierpont, C.; Noordik, J. H. *Ibid.* **1983**, *2*, 1481. (k) Baker, R. T.; Krusic, P. J.; Tulip, T. H.; Calabreze, J. C.; Wreford, S. S. *J. Am. Chem. Soc.* **1983**, *105*, 6763. (l) Klingert, B.; Werner, H. *J. Organomet. Chem.* **1983**, *252*, C47. (m) Vahrenkamp, H.; Wucherer, E. J.; Wolters, D., *Chem. Ber.* **1983**, *116*, 1219. (n) Schneider, J.; Huttner, G. *Ibid.* **1983**, *116*, 917. (o) Ritchey, J. M.; Zozulin, A. J.; Wrobleski, D. A.; Ryan, R. R.; Wasserman, H. J.; Moody, D. C.; Paine, R. T. *J. Am. Chem. Soc.* **1985**, *107*, 501.

(2) (a) Roberts, D. A.; Steinmetz, G. R.; Breen, M. J.; Shulman, P. M.; Morrison, E. D.; Duttera, M. R.; DeBrosse, C. W.; Whittle, R. R.; Geoffroy, G. L. *Organometallics* **1983**, *2*, 846. (b) Breen, M. J.; Geoffroy, G. L.; Rheingold, A. L.; Fultz, W. C. *J. Am. Chem. Soc.* **1983**, *105*, 1069. (c) Mott, G. N.; Carty, A. J. *Inorg. Chem.* **1983**, *22*, 2726. (d) Carty, A. J. *Pure Appl. Chem.* **1982**, *54*, 113. (e) Finke, R. G.; Gaughan, P.; Pierpont, C.; Cass; M. E. *J. Am. Chem. Soc.* **1981**, *103*, 1394.

0276-7333/85/2304-1457$01.50/0