Organometallics **1989**, *8*, 324–330

Dimesitylsilyl Derivatives of Zirconium

Dean M. Roddick, Richard H. Heyn, and T. Don Tilley*

Chemistry Department, D-006, University of California, San Diego, La Jolla, California 92093

Received March 3, 1988

The preparation and characterization of $\mathrm{(THF)_2LiSiHMes_2}$ (**1**, Mes = mesityl) are reported. Compound **1** reacts with $\mathrm{Cp_2Zr(Me)Cl}$ (Cp = η^5-$\mathrm{C_5H_5}$) to afford thermally unstable $\mathrm{Cp_2Zr(SiHMes_2)Me}$ (**2**), characterized by NMR spectroscopy. Similarly, the reaction of **1** with $\mathrm{Cp^*_2Zr(Me)Br}$ (Cp* = η^5-$\mathrm{C_5Me_5}$) provides the mixed alkyl silyl $\mathrm{Cp^*_2Zr(SiHMes_2)Me}$ (**3**), which is stable for prolonged periods at room temperature. Compound **3** reacts cleanly with 1 equiv of HCl to give the chloro derivative $\mathrm{Cp^*_2Zr(SiHMes_2)Cl}$ (**4**) and methane. Whereas carbon monoxide inserts cleanly into the Zr–C bond of **2**, preferential CO insertion into the Zr–Si bond of **3** is observed. These reactions give $\mathrm{Cp_2Zr(\eta^2\text{-}COMe)SiHMes_2}$ (**5**) and $\mathrm{Cp^*_2Zr(\eta^2\text{-}COSiHMes_2)Me}$ (**6**), respectively. Compound **6** is not stable in solution and slowly isomerizes to the enolate hydride $\mathrm{Cp^*_2Zr[OC({=}CH_2)SiHMes_2]H}$ (**7**). The mechanism of the latter conversion is discussed. Hydrogen is shown to cleave the Zr–Si bond of **3** faster than the Zr–C bond. Reaction of **3** with $\mathrm{AgOSO_2CF_3}$ results in oxidative cleavage of the Zr–Si bond giving $\mathrm{Mes_2HSiSiHMes_2}$, $\mathrm{Mes_2SiH(OSO_2CF_3)}$, $\mathrm{Mes_2SiH(Me)}$, and $\mathrm{Cp^*_2Zr(Me)OSO_2CF_3}$ (**9**), which was independently prepared from $\mathrm{Cp^*_2ZrMe_2}$ and $\mathrm{AgOSO_2CF_3}$. Reaction of $\mathrm{Cp^*_2ZrCl_2}$ with 2 equiv of **1** does not give a bis(silyl) complex but instead results in dehydrohalogenation to $\mathrm{Mes_2SiH_2}$ and the metallacycle $\mathrm{Cp^*_2\underline{ZrCH_2\overline{CCHCMeCHCMeC}}SiHMes}$ (**10**).

Introduction

The development of early-transition-metal silicon chemistry has been hampered by a lack of general synthetic methods. To date most d^0 metal silyl complexes have been prepared by displacement of halide ion from the metal by a silyl anion (eq 1).[1,2] However, application of

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

this procedure is somewhat restricted by the availability of suitable silyl anion sources.[3] In particular, there is a limited range of reagents for preparation of primary and secondary metal silyl complexes, since stable silyl anion reagents with Si–H bonds are quite rare. The alkali-metal derivatives $\mathrm{KSiH_3}$,[4] $\mathrm{LiSiHPh_2}$ (formed in solution in low yield),[5] $\mathrm{KSiH(SiH_3)_2}$,[6] $\mathrm{KSiH_2SiH_3}$,[7] and $\mathrm{LiSiHMes_2}$ (formed in solution, Mes = mesityl)[8] have been reported; however, their application to transition-metal silyl chemistry has not been appreciably investigated. The silylene-bridged compound $\mathrm{Cp_2Ti(\mu\text{-}SiH_2)_2TiCp_2}$ (Cp = η^5-$\mathrm{C_5H_5}$), characterized by X-ray diffraction, was obtained upon reaction of $\mathrm{Cp_2TiCl_2}$ with $\mathrm{KSiH_3}$.[9]

We have an interest in the chemistry of early metal silyl compounds containing Si–H bonds, $\mathrm{L_nM\text{-}SiHR_2}$, since such compounds may undergo activation of the Si–H bond at a transition-metal center to produce terminal ($\mathrm{L_nM{=}SiR_2}$) or bridging ($\mathrm{L_nM{-}SiR_2{-}M'L_n'}$) silylene complexes. Herein we describe the preparation and isolation of the lithium silyl $\mathrm{(THF)_2LiSiHMes_2}$, its use as a reagent for the synthesis of zirconium silyls, and reactions of complexes $\mathrm{Cp_2Zr(SiHMes_2)Me}$ (**2**) and $\mathrm{Cp^*_2Zr(SiHMes_2)Me}$ (**3**, Cp* = η^5-$\mathrm{C_5Me_5}$) with small molecules. Many reactions of these mixed alkyl silyl complexes with simple substrates are observed to be highly selective. They therefore provide some useful comparisons of metal–carbon and metal–silicon bond reactivity in these zirconium systems.

Results and Discussion

Preparation of $\mathrm{(THF)_2LiSiHMes_2}$ (1). Weidenbruch and Kramer have reported the generation of $\mathrm{LiSiHMes_2}$ in solution from the reaction of $\mathrm{Mes_2SiHCl}$ with lithium metal in tetrahydrofuran.[8] Following a slightly modified procedure, we have isolated the solvate $\mathrm{(THF)_2LiSiHMes_2}$ (**1**) in 71% yield as off-white crystals from diethyl ether. The synthesis of **1** is accomplished by slow, dropwise addition of a tetrahydrofuran solution of $\mathrm{Mes_2SiHCl}$ to a rapidly stirred suspension of lithium powder in tetrahydrofuran at 0 °C (eq 2).

$$\mathrm{Mes_2SiHCl + 2Li \xrightarrow{THF,\ 0\ ^{\circ}C} \underset{\mathbf{1}}{(THF)_2LiSiHMes_2} + LiCl} \qquad (2)$$

Compound **1** is thermally stable (mp 124–126 °C) and hydrolyzes rapidly in air to give $\mathrm{Mes_2SiH_2}$. The anionic nature of the silicon center in **1** is clearly reflected by the ^{1}H and ^{29}Si NMR data (see Table I). For $\mathrm{Mes_2SiHCl}$, $\mathrm{Mes_2SiH_2}$, and **1** the ^{1}H NMR chemical shifts for the SiH protons, at δ 6.32, 5.28, and 4.71, respectively, correlate with electron density at the silicon. The ^{29}Si NMR spectrum of **1** is particularly revealing: the $|^1J_{\mathrm{SiH}}|$ coupling constant of 101 Hz is substantially smaller than typical values[10] and appears diagnostic for silanes with electropositive substituents (vide infra). This coupling constant is, however, larger than the one reported for $\mathrm{KSiH_3}$ ($|^1J_{\mathrm{SiH}}|$ = 75 Hz).[11] An additional feature to note is the infrared

---

(1) (a) Kingston, B. M.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1972**, 69. (b) Hencken, G.; Weiss, E. *Chem. Ber.* **1973**, *106*, 1747. (c) Holtman, M. S.; Schram, E. P. *J. Organomet. Chem.* **1980**, *187*, 147. (d) Rösch, L.; Altnau, G.; Erb, W.; Pickardt, J.; Bruncks, N. *J. Organomet. Chem.* **1980**, *197*, 51. (e) Tilley, T. D. *Organometallics* **1985**, *4*, 1452. (f) Arnold, J.; Shina, D. N.; Tilley, T. D.; Arif, A. M. *Organometallics* **1986**, *5*, 2037. (g) Arnold, J.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J. *Organometallics* **1987**, *6*, 473. (h) Campion, B. K.; Falk, J.; Tilley, T. D. *J. Am. Chem. Soc.* **1987**, *109*, 2049.

(2) For alternate synthetic methods see: (a) Curtis, M. D.; Bell, L. G.; Butler, W. M. *Organometallics* **1985**, *4*, 701. (b) Aitken, C. T.; Harrod, J. F.; Samuel, E. *J. Am. Chem. Soc.* **1986**, *108*, 4059. (c) Berry, D. H.; Jiang, Q. *J. Am. Chem. Soc.* **1987**, *109*, 6270.

(3) (a) Davis, D. D.; Gray, C. E. *Organomet. Chem. Rev., Sect. A* **1970**, *6*, 283. (b) Corriu, R. J. P.; Guerin, C.; Kolani, B. *Bull. Soc. Chim. Fr.* **1985**, 973.

(4) Ring, M. A.; Ritter, D. M. *J. Am. Chem. Soc.* **1961**, *83*, 802.

(5) Gilman, H.; Steudel, W. *Chem. Ind. (London)* **1959**, 1094.

(6) Feher, F.; Freund, R. *Inorg. Nucl. Chem. Lett.* **1973**, *9*, 937.

(7) Feher, F.; Freund, R. *Inorg. Nucl. Chem. Lett.* **1974**, *10*, 561.

(8) Weidenbruch, M.; Kramer, K. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1985**, *40B*, 601.

(9) Hencken, G.; Weiss, E. *Chem. Ber.* **1973**, *106*, 1747.

(10) Williams, E. A.; Cargioli, J. D. In *Annual Reports on NMR Spectroscopy*; Webb, G. A., Ed.; Academic Press: New York, Vol. 9, pp 221–318.

0276-7333/89/2308-0324$01.50/0

ν(Si–H) stretching frequency for 1 which appears at 1910 cm^{-1}, over 100 cm^{-1} lower in energy than typical values for silanes.[12] This is also consistent with the presence of a substituent of very low effective electronegativity.[13]

Dimesitylsilyl Derivatives of Zirconium. The reactivity of 1 toward a range of metal chlorides has been examined. Treatment of $Cp_2Zr(Me)Cl$ with 1 equiv of 1 in toluene gave the silyl derivative $Cp_2Zr(SiHMes_2)Me$ (2) as an orange solid from pentane (eq 3). Compound 2 is only marginally stable at ambient temperature in the solid state and decomposes in benzene solution at room temperature over several hours.

$$Cp_2Zr(Me)Cl + 1 \xrightarrow{\text{toluene}} \underset{2}{Cp_2Zr(SiHMes_2)Me} + LiCl \qquad (3)$$

A mixed alkyl silyl complex more amenable to study has been prepared from reaction of 1 with $Cp^*{}_2Zr(Me)Br$ (eq 4). The product 3 was isolated from toluene/pentane as an orange, crystalline solid in 84% yield. ^{29}Si NMR (δ −21.94 (d, $^1J_{SiH}$ = 142 Hz)) and IR (ν(Si–H) = 2060 cm^{-1}) data are analogous to values obtained for 2. The $^1J_{SiH}$ coupling constants suggest an electronic environment about the Si atoms in 2 and 3 that is intermediate between that of lithium silyl 1 and Mes_2SiH_2 ($^1J_{SiH}$ = 195 Hz).

$$Cp^*{}_2Zr(Me)Br + 1 \xrightarrow{\text{toluene}} \underset{3}{Cp^*{}_2Zr(SiHMes_2)Me} + LiBr \qquad (4)$$

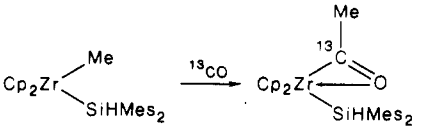
Variable-temperature ^1H NMR data for 3 reveal significant steric interactions between the mesityl groups and the C_5Me_5 rings, resulting in restricted rotation about both the Zr–Si and Si–C(Mes) bonds. At −80 °C in toluene-d_8 a static low-temperature limit is observed, with inequivalent ortho methyls for the mesityl groups appearing as two sets of singlets at δ 2.08, 2.12 and 2.47, 2.54. The para methyl groups (δ 2.18, 2.20) and meta protons (δ 6.67, 6.71, 6.84, 6.88) are also inequivalent; separate resonances for the C_5Me_5 rings were not resolved. At −58 °C the low-field pair of ortho methyl resonances coalesce, giving a value of $\Delta G^\ddagger = 10.4 \pm 0.2$ kcal mol^{-1} for the barrier to rotation about the Si–C(Mes) bond. Both sets of ortho methyl resonances collapse to a single coalescence at −23 °C, corresponding to $\Delta G^\ddagger = 11.8 \pm 0.2$ kcal mol^{-1} for the rotational barrier about the Zr–Si bond. Variable-temperature ^1H NMR spectra for 2 (in toluene-d_8) revealed no restricted rotation down to −85 °C, consistent with the lesser steric influence of C_5H_5 as compared to C_5Me_5 ligands.

Reactivity of Mixed Alkyl Silyl Complexes. Thermolysis of the mixed alkyl silyl 3 in benzene-d_6 at 80 °C was monitored by ^1H NMR. Disappearance of 3 occurred over the course of 24 h, concomitant with formation of free silane, Mes_2SiH_2. Although the zirconium-containing product(s) were not characterized, no methane was observed (by ^1H NMR and GC).

The reactions of 3 with various reagents serve as a probe into the relative nature of alkyl and silyl bonding in early-transition-metal systems. Addition of 1 equiv of HCl gas to a toluene solution of 3 at −78 °C results in rapid loss of methane and nearly quantitative generation of the chloro silyl 4 (eq 5). Compound 4 has been characterized by NMR, IR, and analytical data. Variable-temperature ^1H NMR indicates that silyl rotation in 4 is restricted, with the observed rotational barriers for Si–C(Mes) (T_c = −5 °C, $\Delta\nu$ = 97 Hz, $\Delta G^\ddagger = 12.8 \pm 0.2$ kcal mol^{-1}) and Zr–Si ($T_c \approx 10$ °C, $\Delta\nu$ = 129 Hz, $\Delta G^\ddagger = 13.4 \pm 0.5$ kcal mol^{-1}) bonds being slightly greater than those observed for 3.

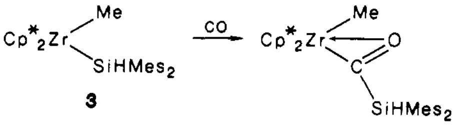
$$\underset{3}{Cp^*{}_2Zr(SiHMes_2)Me} + HCl \xrightarrow{-78\ ^\circ C} \underset{4}{Cp^*{}_2Zr(SiHMes_2)Cl} + CH_4 \qquad (5)$$

In other mixed alkyl silyl compounds of the type $Cp_2Zr(SiR_3)R'$ (R = Me, $SiMe_3$; R′ = alkyl), we have observed a marked preference for insertion of carbon monoxide into the Zr–C(alkyl) bond.[1h,14] Similarly, compound 2 reacts rapidly with ^{13}CO to give predominantly the acyl $Cp_2Zr(\eta^2\text{-}^{13}COMe)SiHMes_2$ (5), as determined by ^1H and ^{13}C NMR (0 °C, toluene-d_8). As monitored by ^1H NMR, the reaction (eq 6) proceeds with a large downfield shift of the ZrMe resonance relative to 2. Also, 5 exhibits a resonance at δ 314.2 in the ^{13}C NMR spectrum which is characteristic of an η^2-acyl ligand on zirconium.[15] It was not possible to isolate 5 due to its rapid thermal decomposition at room temperature.



2 5 (6)

In contrast, treatment of 3 with CO at 20 °C results solely in insertion of CO into the Zr–Si bond to give initially the silaacyl complex $Cp^*{}_2Zr(\eta^2\text{-}COSiHMes_2)Me$ (6, eq 7). The mode of CO insertion is clearly indicated by ^1H NMR, which displays a characteristic high-field ZrMe resonance at δ −0.23, only slightly shifted from that of 3. The ^{13}C NMR spectrum of 6 prepared from ^{13}CO exhibits an extremely low-field resonance at δ 400.0, diagnostic for the presence of an η^2-silaacyl moiety.[1h,16,17] Compound 6 is unstable in benzene solution and rearranges cleanly after several hours to the enolate hydride $Cp^*{}_2Zr[OC(=CH_2)SiHMes_2]H$ (7). The formulation of 7 is supported by ^1H and ^{13}C NMR and IR data, which compare closely to analogous reported enolate complexes,[18] and by its reaction with MeI to yield the expected enolate iodide derivative $Cp^*{}_2Zr[OC(=CH_2)SiHMes_2]I$ (8).



3 6 (7)

An uncertainty exists regarding the isomeric preference of oxygen coordination in 5 and 6. Structural[19] and

---

[11] Burger, H.; Eujen, R.; Marsmann, H. C. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* 1974, *29B*, 149.

[12] Smith, A. L. *Spectrochim. Acta* 1960, *16*, 87.

[13] (a) Aylett, B. J. *J. Organomet. Chem., Libr.* 1980, *9*, 327. (b) Hofler, F. *Top. Curr. Chem.* 1974, *50*, 129.

[14] Campion, B. K.; Tilley, T. D., manuscript in preparation.

[15] (a) Marsella, J. A.; Huffman, J. C.; Caulton, K. G.; Longato, B.; Norton, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 6360. (b) Erker, G.; Rosenfeldt, F. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 605. (c) Lappert, M. F.; Luong-Thi, N. T.; Milne, C. R. C. *J. Organomet. Chem.* **1979**, *174*, C35.

[16] (a) Tilley, T. D. *J. Am. Chem. Soc.* **1985**, *107*, 4084. (b) Elsner, F. H.; Woo, H.-G.; Tilley, T. D. *J. Am. Chem. Soc.* **1988**, *110*, 313. (c) Arnold, J.; Woo, H.-G.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J. *Organometallics* **1988**, *7*, 2045.

[17] (a) Arnold, J.; Tilley, T. D. *J. Am. Chem. Soc.* **1985**, *107*, 6409. (b) Arnold, J.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J.; Arif, A. M. *J. Am. Chem. Soc.*, in press.

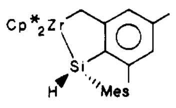
[18] Manriquez, J. M.; Fagan, P. J.; Marks, T. J.; Day, C. S.; Day, V. W. *J. Am. Chem. Soc.* **1978**, *100*, 7112.

[19] Fachinetti, G.; Fochi, G.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **1977**, 1946.

Table I. NMR Data for New Compounds

compound	nucleus[a]	assignt	chem shift (δ)	coupling (Hz)
$\mathrm{(THF)_2LiSiHMes_2}$ (**1**)	^{1}H NMR	THF	1.22, 3.37 m	
		$p\text{-}\mathrm{C_6H_2(C}H_3)_3$	2.28 s	
		$o\text{-}\mathrm{C_6H_2(C}H_3)_3$	2.72 s	
		$\mathrm{Si}H$	4.71 s	
		$\mathrm{C_6}H_2\mathrm{(CH_3)_3}$	6.91 s	
	^{29}Si NMR	Si	−71.78 d	$^1J_{\mathrm{Si-H}} = 101$
$\mathrm{Cp_2Zr(SiHMes_2)Me}$ (**2**)	^{1}H NMR	$\mathrm{ZrC}H_3$	−0.22 s	
		$p\text{-}\mathrm{C_6H_2(C}H_3)_3$	2.19 s	
		$o\text{-}\mathrm{C_6H_2(C}H_3)_3$	2.34 s	
		$\mathrm{Si}H$	4.73 s	
		$\mathrm{C_5}H_5$	5.79 s	
		$\mathrm{C_6}H_2\mathrm{(CH_3)_3}$	6.85 s	
	^{13}C NMR	$p\text{-}\mathrm{C_6H_2(}C\mathrm{H_3)_3}$	21.1 q	$^1J_{\mathrm{CH}} = 125$
		$o\text{-}\mathrm{C_6H_2(}C\mathrm{H_3)_3}$	25.3 q	$^1J_{\mathrm{CH}} = 125$
		$\mathrm{Zr}C\mathrm{H_3}$	42.8 q	$^1J_{\mathrm{CH}} = 117$
		$C_5\mathrm{H_5}$	110.0 d	$^1J_{\mathrm{CH}} = 176$
		$C_6\mathrm{H_2(CH_3)_2}$	128.9 d	$^1J_{\mathrm{CH}} = 161$
			144.0, 139.9, 136.9 s	
	^{29}Si NMR	Si	−12.36 d	$^1J_{\mathrm{SiH}} = 143$
$\mathrm{Cp^*_2Zr(SiHMes_2)Me}$ (**3**)	^{1}H NMR (−80 °C, toluene-d_8)	$\mathrm{ZrC}H_3$	−0.25 s	
		$\mathrm{C_5(C}H_3)_5$	1.65 s	
		$p\text{-}\mathrm{C_6H_2(C}H_3)_3$	2.18, 2.20 s (3 H, 3 H)	
		$o\text{-}\mathrm{C_6H_2(C}H_3)_3$	2.08, 2.12 s (3 H, 3 H)	
			2.47, 2.54 s (3 H, 3 H)	
		$\mathrm{Si}H$	4.71 s	
		$\mathrm{C_6}H_2\mathrm{(CH_3)_3}$	6.67, 6.71 s (1 H, 1 H)	
			6.84, 6.88 s (1 H, 1 H)	
	^{1}H NMR (50 °C, toluene-d_8)	$\mathrm{ZrC}H_3$	−0.29 s	
		$\mathrm{C_5(C}H_3)_5$	1.76 s	
		$p\text{-}\mathrm{C_6H_2(C}H_3)_3$	2.16 s	
		$o\text{-}\mathrm{C_6H_2(C}H_3)_3$	2.25 s	
		$\mathrm{Si}H$	4.74 s	
		$\mathrm{C_6}H_2\mathrm{(CH_3)_3}$	6.75 s	
	^{13}C{^{1}H} NMR (20 °C, toluene-d_8)	$\mathrm{C_5(}C\mathrm{H_3)_5}$	12.0	
		$p\text{-}\mathrm{C_6H_2(}C\mathrm{H_3)_3}$	21.1	
		$o\text{-}\mathrm{C_6H_2(}C\mathrm{H_3)_3}$	26.2	
		$\mathrm{Zr}C\mathrm{H_3}$	53.9	
		$C_5\mathrm{(CH_3)_5}$	120.0	
		$C_6\mathrm{H_2(CH_3)_3}$	144.6, 142.0, 135.9[b]	
	^{29}Si NMR (20 °C, toluene-d_8)	Si	−21.94 d	$^1J_{\mathrm{SiH}} = 142$
$\mathrm{Cp^*_2Zr(SiHMes_2)Cl}$ (**4**)	^{1}H NMR (−60 °C, toluene-d_8)	$\mathrm{C_5(C}H_3)_5$	1.68, 1.72 s	
		$p\text{-}\mathrm{C_6H_2(C}H_3)_3$	2.17, 2.20 s	
		$o\text{-}\mathrm{C_6H_2(C}H_3)_3$	2.13, 2.21 s (3 H, 3 H)	
			2.48, 2.82 s, (3 H, 3 H)	
		$\mathrm{Si}H$	5.10 s	
		$\mathrm{C_6}H_2\mathrm{(CH_3)_3}$	6.70, 6.74 s (1 H, 1 H)	
			6.87 s, br (2 H)	
	^{1}H NMR (50 °C, toluene-d_8)	$\mathrm{C_5(C}H_3)_5$	1.81 s	
		$p\text{-}\mathrm{C_6H_2(C}H_3)_3$	2.17 s	
		$o\text{-}\mathrm{C_6H_2(C}H_3)_3$	2.37 s	
		$\mathrm{Si}H$	5.14 s	
		$\mathrm{C_6}H_2\mathrm{(CH_3)_3}$	6.77 s	
	^{29}Si NMR (20 °C, toluene-d_8)	Si	−20.29 d	$^1J_{\mathrm{SiH}} = 148$
$\mathrm{Cp_2Zr(^{13}COMe)SiHMes_2}$ (**5**-^{13}C)	^{1}H NMR (0 °C, toluene-d_8)	$\mathrm{ZrCOC}H_3$	2.07 br s	
		$p\text{-}\mathrm{C_6H_2(C}H_3)_3$	2.20 s	
		$o\text{-}\mathrm{C_6H_2(C}H_3)_3$	2.77 s	
		$\mathrm{C_5}H_5$	5.19 s	
		$\mathrm{Si}H$	5.68 s	
		$\mathrm{C_6}H_2\mathrm{(CH_3)_3}$	6.89 s	
	^{13}C NMR (−30 °C, toluene-d_8)	$\mathrm{Zr}C\mathrm{OCH_3}$	314.2	
$\mathrm{Cp^*_2Zr(^{13}COSiHMes_2)Me}$ (**6**-^{13}C)	^{1}H NMR$^{(b)}$ (−10 °C, toluene-d_8)	$\mathrm{ZrC}H_3$	−0.23 s	
		$\mathrm{C_5(C}H_3)_5$	1.56 s	
		$p\text{-}\mathrm{C_6H_2(C}H_3)_3$	2.04 s	
		$o\text{-}\mathrm{C_6H_2(C}H_3)_3$	2.60 s	
		$\mathrm{C_6}H_2\mathrm{(CH_3)_3}$	6.66 s	
	^{13}C NMR (−10 °C, toluene-d_8)	$\mathrm{Zr}C\mathrm{OSiHMes_2}$	400.0	$^2J_{\mathrm{CH}} = 12$
$\mathrm{Cp^*_2Zr[O^{13}C({=}CH_2)SiHMes_2]H}$ (**7**-^{13}C)	^{1}H NMR (20 °C, toluene-d_8)	$\mathrm{C_5(C}H_3)_5$	2.01 s	
		$p\text{-}\mathrm{C_6H_2(C}H_3)_3$	2.14 s	
		$o\text{-}\mathrm{C_6H_2(C}H_3)_3$	2.62 s	
		$\mathrm{C{=}C}H_2$	4.66 d (1 H)	$^2J_{\mathrm{CH}} = 8$
		$\mathrm{C{=}C}H_2$	4.87 d (1 H)	$^2J_{\mathrm{CH}} = 7$
		$\mathrm{Si}H$	5.85 d	$^2J_{\mathrm{CH}} = 3$
		$\mathrm{Zr}H$	6.08 s	
		$\mathrm{C_6}H_2\mathrm{(CH_3)_3}$	6.78 s	

Table I (Continued)

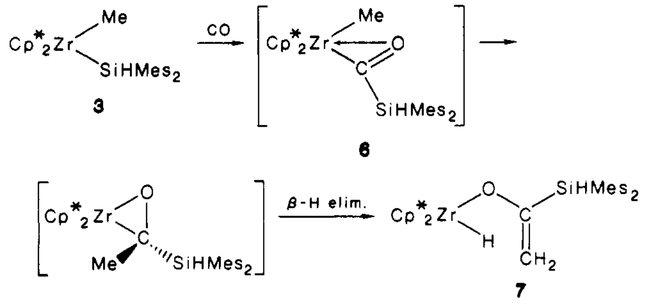
compound	nucleus[a]	assignt	chem shift (δ)	coupling (Hz)
$Cp^*_2Zr[OC(=CH_2)SiHMes_2]H$ (**7**)	^{13}C NMR	$C_5(\mathit{C}H_3)_5$	11.9 q	$^1J_{CH} = 126$
		$p\text{-}C_6H_2(\mathit{C}H_3)_3$	21.2 q	$^1J_{CH} = 127$
		$o\text{-}C_6H_2(\mathit{C}H_3)_3$	24.4 q	$^1J_{CH} = 127$
		$C{=}\mathit{C}H_2$	106.6 t	$^1J_{CH} = 156$
		$\mathit{C}_5(CH_3)_5$	118.3 s	
		$m\text{-}\mathit{C}_6H_2(CH_3)_3$	129.2 s	
		$i/p\text{-}\mathit{C}_6H_2(CH_3)_3$	130.7 s/139.0 s	
		$o\text{-}\mathit{C}_6H_2(CH_3)_3$	145.0 s	
		$\mathit{C}{=}CH_2$	168.9 s	
	^{29}Si NMR	Si	-41.51 dd	$^1J_{SiH} = 195$ $^3J_{SiH} = 12$
$Cp^*_2Zr[OC(=CH_2)SiHMes_2]I$ (**8**)	^1H NMR	$C_5(C\mathit{H}_3)_5$	1.99 s	
		$p\text{-}C_6H_2(C\mathit{H}_3)_3$	2.11 s	
		$o\text{-}C_6H_2(C\mathit{H}_3)_3$	2.60 s	
		$C{=}C\mathit{H}_2$	4.47 s	
		$C{=}C\mathit{H}_2$	5.03 s	
		$Si\mathit{H}$	5.80 s	
		$C_6\mathit{H}_2(CH_3)_3$	6.77 s	
$Cp^*_2Zr(Me)OSO_2CF_3$ (**9**)	^1H NMR	$ZrC\mathit{H}_3$	0.33 s	
		$C_5(C\mathit{H}_3)_5$	1.71 s	
	^{13}C NMR	$C_5(\mathit{C}H_3)_5$	11.2 q	$^1J_{CH} = 127$
		$Zr\mathit{C}H_3$	43.7 q	$^1J_{CH} = 120$
		$\mathit{C}_5(CH_3)_5$	122.1 s	
 **10**	^1H NMR	$ZrC\mathit{H}_2$	-0.85 dd (1 H)	$^2J_{HH} = 14$ $^3J_{HH} = 0.9$
		$C_5(C\mathit{H}_3)_5$	1.69 s 1.72 s	
		$C_6H_2(C\mathit{H}_3)_3$, $C_6H_2(C\mathit{H}_3)_2$	2.14 s (3H), 2.18 s (3H), 2.24 s (3H), 2.28 s (3H), 2.39 s (3H)	
		$ZrC\mathit{H}_2$	3.30 d (1H)	$^2J_{HH} = 14$
		$Si\mathit{H}$	5.16 s	
		$C_6\mathit{H}_2(CH_3)_3$	6.69, 6.83 (2H), 6.87	
	^{13}C NMR	$C_5(\mathit{C}H_3)_5$	11.41, 11.35 q	$^1J_{CH} = 127$
		$C_6H_2(\mathit{C}H_3)_3$, $C_6H_2(\mathit{C}H_3)_2$	21.25, 21.73, 22.98, 24.80, 25.64 (all q)	
		$Zr\mathit{C}H_2$	72.15 t	$^1J_{CH} = 117$
		$\mathit{C}_5(CH_3)_5$	119.44, 119.87	
		$m\text{-}\mathit{C}_6H_2(CH_3)_3$, $\mathit{C}_6H_2(CH_3)_2$	125.62, 129.11 m (other resonances obscured)	
		$i,o,p\text{-}\mathit{C}_6H_2(CH_3)_3$, $\mathit{C}_6H_2(CH_3)_3$	136.08, 136.15, 138.62, 140.66, 143.74, 144.49, 144.89, 157.50	
	^{29}Si NMR	Si	-15.72	$^1J_{SiH} = 156$

[a] Spectra recorded at 20 °C in benzene-d_6 unless otherwise noted. [b] ^1H NMR resonance for SiH was not observed due to masking by toluene and mesityl aryl proton resonances.

mechanistic[20] studies of $Cp_2Zr(\eta^2\text{-}COMe)Me$ conclude that the isomer in which the η^2-acyl oxygen occupies the central equatorial site is thermodynamically preferred. This situation is also observed in the solid state for the silaacyl $Cp_2Zr(\eta^2\text{-}COSiMe_3)Cl$.[16a] However, the more sterically hindered complex $Cp^*_2Zr(\eta^2\text{-}COCH_2CMe_3)Cl$ exists as an equilibrium mixture of lateral and centrally bonded isomers.[21] This change in isomeric preference may reflect decreased steric accommodation for the lateral region of a bent metallocene moiety. It is therefore difficult to assign exact structures to the acyl compounds **5** and **6** in absence of X-ray crystallographic data. Particularly for sterically encumbered **6**, the lateral silaacyl isomer, with the silaacyl oxygen pointing away from the ZrMe group, seems possible.

A proposed mechanism for the formation of **7** is shown in Scheme I. Migration of a methyl group to the silaacyl carbon of **6** to form an intermediate oxymetallacyclopropane complex has precedent in η^2-acyl chemistry, where similar migrations have been observed for $Cp^*_2Zr(\eta^2\text{-}COCH_2CHMe_2)H$,[22] $Cp_2Zr(\eta^2\text{-}COPh)Ph$,[23] and (presumably) $Cp^*Ta(\eta^2\text{-}COMe)Me_3$.[24] Formation of an enolate hydride analogous to **7** has also been demonstrated for $Cp^*_2Zr(\eta^2\text{-}COCH_2CHMe_2)H$.[22] Note that in the proposed oxymetallacyclopropane intermediate there are β-hydrogens on both silicon and carbon. However, β-hydrogen

Scheme I



---

[20] Erker, G.; Rosenfeldt, F. *J. Organomet. Chem.* **1980**, *188*, C1.

[21] Moore, E. J. Ph.D. Thesis, California Institute of Technology, 1984.

[22] Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 2716.

[23] Erker, G.; Rosenfeldt, F. *J. Organomet. Chem.* **1982**, *224*, 29.

[24] Wood, C. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 5421.

elimination from silicon would require formation of a silicon–carbon double bond and consequently is not favored in this system.

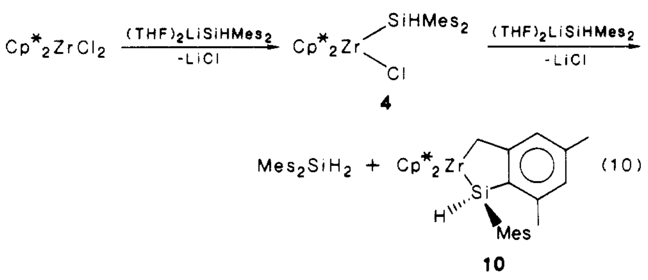
The reaction of **3** with hydrogen (1 atm, 34 °C) in benzene-d_6 was followed by ^{1}H NMR to determine the relative preferences for the Zr–Si and Zr–C bonds for hydrogenolysis. After 10 min **3** was quantitatively converted to $Cp^*_2Zr(Me)H$ and Mes_2SiH_2 (eq 8). In the presence of additional hydrogen $Cp^*_2Zr(Me)H$ reacted further to give $Cp^*_2ZrH_2$ and CH_4 as final products within ca. 1 h.

$$\underset{\mathbf{3}}{Cp^*_2Zr(SiHMes_2)Me} \xrightarrow{H_2,\ 1\ atm} Cp^*_2Zr(Me)H + Mes_2SiH_2 \quad (8)$$

An additional internal competition reaction that has been examined is an apparent oxidative cleavage by Ag^+. In the absence of available d electrons on the Zr(IV) center, attack of electrophilic Ag^+ at either the Zr–C or Zr–Si bond may lead to oxidation or cleavage in a selective manner. Indeed, the reaction of **3** with silver triflate is facile and quantitatively affords $Cp^*_2Zr(Me)OSO_2CF_3$ (**9**, eq 9). The formulation of **9** has been confirmed by independent preparation from $Cp^*_2ZrMe_2$ and $AgOSO_2CF_3$. In the latter reaction ethane was observed as product in what is, at least formally, an oxidative coupling. Jordan and coworkers have reported the reaction of Cp_2ZrMe_2 with $AgBPh_4$ in CH_3CN to give $[Cp_2ZrMe(CH_3CN)]^+BPh_4^-$ and ethane in a similar manner, and related oxidative cleavages of the benzyl derivative $Cp_2Zr(CH_2Ph)_2$ have been observed.[25] Three silicon-containing products, $Mes_2HSiSiHMes_2$, $Mes_2SiH(OSO_2CF_3)$, and $Mes_2SiH(Me)$, were observed for the reaction in eq 9. Identification of these products was made by comparisons of spectroscopic properties with authentic samples. The triflate $Mes_2SiH(OSO_2CF_3)$ was prepared independently from Mes_2SiHCl and $AgOSO_2CF_3$, and $Mes_2SiH(Me)$ was obtained straightforwardly from Mes_2SiHCl and MeLi. The disilane $Mes_2HSiSiHMes_2$ was prepared by a published procedure.[26] The ratio of silicon-containing products in eq 9 was found to vary considerably from one reaction to the next and is quite sensitive to reaction conditions such as solvent and concentration of reagents. In a typical reaction carried out in an NMR tube in benzene-d_6, the ratio of $Mes_2HSiSiHMes_2$ to $Mes_2SiH(OSO_2CF_3)$ to $Mes_2SiH(Me)$ was 1:5:≈0.1 (trace). In a scaled-up reaction in toluene, this ratio was ca. 1:1:0.3. These results indicate that oxidative cleavage of the Zr–Si bond of **3** generates the $Mes_2HSi^\bullet$ radical, which can dimerize to disilane, can be further oxidized by available $AgOSO_2CF_3$ to $Mes_2SiH(OSO_2CF_3)$, or can abstract a methyl group from a Zr–Me species to give $Mes_2SiH(Me)$. Consistent with this, when **3** was allowed to react with a large excess of $AgOSO_2CF_3$ (100 equiv), $Mes_2SiH(OSO_2CF_3)$ (but no $Mes_2HSiSiHMes_2$ or $Mes_2SiH(Me)$) is observed as product. When **3** is in large excess, only $Mes_2HSiSiHMes_2$ (but no $Mes_2SiH(OSO_2CF_3)$ or $Mes_2SiH(Me)$) is observed. However, it should be noted that the latter two reactions were not quantitative and other, unidentified silicon-containing products were present.

$$\underset{\mathbf{3}}{Cp^*_2Zr(SiHMes_2)Me} + AgOSO_2CF_3 \xrightarrow{toluene,\ -Ag^0} \underset{\mathbf{9}}{Cp^*_2Zr(Me)OSO_2CF_3} + Mes_2HSiSiHMes_2 + Mes_2SiH(OSO_2CF_3) + Mes_2SiH(Me) \quad (9)$$

Thus far attempts to prepare silyl complexes other than **3** and **4** from **1** have met with little success. Treatment of metal chlorides such as Cp^*MCl_3, MCl_4 (M = Zr, Hf), $TaCl_5$, Cp^*TaCl_4, and $FeCl_2$ with **1** yielded no tractable metal silyl derivatives. In every case, Mes_2SiH_2 was observed as the major silicon-containing product. Significantly, reaction of $Cp^*_2ZrCl_2$ with 1 equiv of **1** did not afford **4** as expected but again led to the formation of Mes_2SiH_2. These observations suggested the occurrence of a competing dehydrohalogenation reaction promoted by unreacted **1** subsequent to initial silylation of the metal center. Consistent with this notion, the reaction of $Cp^*_2ZrCl_2$ with an excess of **1** cleanly afforded the metallacycle **10** plus an equimolar amount of Mes_2SiH_2 (eq 10). Presumably, formation of compound **10** proceeds via initial silylation to give **4**, followed by deprotonation of an ortho benzylic methyl group by more **1** and nucleophilic displacement of Cl^- to afford the observed product (eq 10). Additional evidence for this process is found in the reaction of $Cp^*_2Zr(SiHMes_2)Cl$ (**4**) with **1** to give the metallacycle **10** (by ^{1}H NMR).



The structure of **10** was determined from ^{1}H and ^{13}C NMR data. In addition to five distinct mesityl methyl resonances in the ^{1}H and ^{13}C NMR spectra, asymmetry at the silicon center results in inequivalence of the C_5Me_5 rings. Most striking are the distinct doublets at δ −0.85 and 3.30 ($^2J_{HH}$ = 14 Hz) which are assigned to the $ZrCH_2C$ diastereotopic methylene protons. The methylene carbon exhibits a triplet in the ^{13}C NMR spectrum ($^1J_{CH}$ = 117 Hz) that is characteristic for a Zr-bound CH_2 group and is consistent with the proposed structure.

Concluding Remarks

In light of the preceding results, some tentative conclusions can be made regarding the relative nature of Zr–alkyl and Zr–silyl bonding. The preference for CO insertion into the Zr–Si bond of **3** may be attributed to an alleviation of steric strain generated by close Cp*–mesityl contacts. To date, all attempts to obtain suitable single crystals for structural studies have failed; however, the presence of steric strain may be inferred from the substantial barriers to rotation deduced by ^{1}H NMR. In any case, the reactions of CO with **2** and **3** indicate that the migratory aptitudes for silyl and alkyl groups in zirconocene systems must be comparable.

The different selectivities displayed by polar (HCl) and nonpolar (H_2) substrates for Zr–alkyl and Zr–silyl bonds appears to reflect relative bond polarities. On the basis of electronegativity differences, Zr–C bonds are predicted to be more polar than Zr–Si bonds. The enhanced reactivity of HCl toward a more nucleophilic carbon center is consistent with this explanation. For hydrogenolysis a simple interpretation is not so straightforward, since both M–ligand bond strengths and development of charge

---

[25] (a) Jordan, R. F.; Dasher, W. E.; Echols, S. F. *J. Am. Chem. Soc.* **1986**, *108*, 1718. (b) Jordan, R. F.; LaPointe, R. E.; Bajgur, C. S.; Echols, S. F.; Willett, R. *J. Am. Chem. Soc.* **1987**, *109*, 4111.

[26] (a) Baxter, S. G.; Mislow, K.; Blount, J. F. *Tetrahedron* **1980**, *36*, 605. (b) Weidenbruch, M.; Schäfer, A.; Rankers, R. *J. Organomet. Chem.* **1980**, *195*, 171.

distributions in a four-center transition state may be important.[27] We anticipate a better understanding of relative M–alkyl and M–silyl bonding behavior to be forthcoming from further studies of mixed alkyl/silyl compounds.

Experimental Section

All manipulations were performed under an inert atmosphere of nitrogen or argon. Dry, oxygen-free solvents were employed throughout. Elemental analyses were performed by Schwartzkopf microanalytical laboratories. Infrared spectra were recorded on a Perkin-Elmer 1330 infrared spectrometer. NMR spectra were recorded on a GE QE-300 instrument at 300 MHz (^{1}H), 75.5 MHz (^{13}C), and 59.6 MHz (^{29}Si). An INEPT sequence[28] was employed to enhance signals in the ^{29}Si spectra. The compounds Mes$_2$SiHCl,[29] Cp$_2$Zr(Me)Cl,[30] Cp*$_2$Zr(Me)Br,[31] and Cp*$_2$ZrMe$_2$[22] were prepared according to literature procedures. The literature procedure, with minor modifications, was also used to obtain Cp*$_2$ZrCl$_2$.[32] The yield of the latter zirconium compound is improved (to 81%) by using isolated LiCp* as a reagent and by conducting the reaction in refluxing toluene.

(THF)$_2$LiSiHMes$_2$ (1). Over the course of 1 h, a solution of Mes$_2$SiHCl (8.57 g, 28.3 mmol) in 50 mL of tetrahydrofuran was added dropwise to a rapidly stirred slurry of lithium dispersion (1% Na content, 2.00 g, 288 mmol) in 10 mL of tetrahydrofuran at 0 °C. After an additional hour of stirring at 0 °C the solvent was removed (at 0 °C) and the residue was taken up in toluene (50 mL) and filtered. Removal of toluene under vacuum and addition of pentane (40 mL) to the resulting oily brown residue gave an off-white precipitate which was washed several times with pentane and dried in vacuo. This gives reasonably pure 1 (by ^{1}H NMR) in 71% yield (8.43 g). Pure 1 (mp 124–126 °C) was obtained by recrystallization from diethyl ether (−60 °C). 1 can be exhaustively dried to a stoichiometry of (THF)$_{1.5}$LiSiHMes$_2$. Anal. Calcd for C$_{26}$H$_{39}$LiO$_2$Si: C, 74.6; H, 9.39. Found: C, 71.0; H, 8.72. Although this compound gave C and H analyses that were variable and somewhat low, spectroscopic data show that it is pure and correctly formulated. IR (Nujol, CsI, cm^{-1}): 2722 w, 1910 s br (Si–H), 1596, 1046, 890, 848, 810 m br, 709.

Cp$_2$Zr(SiHMes$_2$)Me (2). A solution of Cp$_2$Zr(Me)Cl (0.489 g, 1.80 mmol) and 1 (0.818 g, 1.95 mmol) in toluene (25 mL) was stirred at ambient temperature. Initially colorless, after several minutes the solution became deep orange. After 30 min the solvent was removed and the oily residue was dissolved in pentane (30 mL) and filtered. The solution was concentrated to 15 mL and cooled to −78 °C, resulting in precipitation of a yellow-orange solid that was isolated by filtration and dried in vacuo to yield 0.655 g (72%) of crude 2, >90% pure by ^{1}H NMR. Compound 2 decomposes at ambient temperature in the solid state but may be stored below 0 °C indefinitely. IR (Nujol, CsI, cm^{-1}): 2725 w, 2025 s (Si–H), 1601, 1016, 848, 803, 752, 705.

Cp*$_2$Zr(SiHMes$_2$)Me (3). A solution of Cp*$_2$Zr(Me)Br (0.984 g, 2.15 mmol) and 1 (1.12 g, 2.68 mmol) in toluene (40 mL) was stirred for 12 h at ambient temperature. The volatiles were removed, 40 mL of toluene was added, and the solution was filtered while warm (ca. 40 °C). The solvent was removed and the oily orange residue was slurred in pentane (20 mL), filtered, washed thoroughly with pentane, and dried in vacuo to give 1.17 g (84%) of orange product. 3 was recrystallized (mp 150–153 °C) from toluene/pentane in low to moderate yield. Anal. Calcd for C$_{39}$H$_{56}$SiZr: C, 72.7; H, 8.76. Found: C, 71.1; H, 8.75. IR (Nujol, CsI, cm^{-1}): 2060 s (Si–H), 1597, 1021, 843, 767.

Cp*$_2$Zr(SiHMes$_2$)Cl (4). To a rapidly stirred solution of 3 (0.200 g, 0.310 mmol) in toluene (10 mL) at −78 °C was carefully added HCl (0.310 mmol) via a gas addition bulb. An immediate evolution of gas was observed, and the solution became a deeper orange. After 30 min the solution was allowed to warm to ambient temperature and the solvent was removed. The orange solid residue was slurried in pentane (10 mL), isolated by filtration, and dried in vacuo to give crude 4 (0.157 g, 76%) of >95% purity by ^{1}H NMR. Analytically pure 4 was obtained by recrystallization from toluene (mp 151–152 °C). Anal. Calcd for C$_{38}$H$_{53}$ClSiZr: C, 68.7; H, 8.04; Cl, 5.33. Found: C, 68.5; H, 8.16; Cl, 5.77. IR (Nujol, CsI, Cm^{-1}): 2715 w, 2061 s (Si–H), 1595, 1040, 842, 760 s, 703, 587, 560, 542, 395, 353, 323.

Reaction of 2 with ^{13}CO. Approximately 0.20 mmol of ^{13}CO (91.7 atom %, MSD Isotopes) was added via gas-tight syringe to an NMR tube containing 2 (0.065 g, 0.17 mmol) in toluene-d_8 (0.4 mL) at −78 °C, and the reaction was monitored by variable-temperature ^{1}H NMR. At 0 °C the resonances for 2 were slowly replaced by a new set of peaks that were assigned to the Zr–Me insertion product Cp$_2$Zr(η^2-^{13}COMe)SiHMes$_2$ (5). Compound 5 decomposed at 20 °C to an uncharacterized mixture of products.

Reaction of 3 with ^{13}CO. Approximately 0.20 mmol of ^{13}CO (91.7 atom %, MSD Isotopes) was added via gas-tight syringe to an NMR tube containing 3 (0.050 g, 0.08 mmol) in toluene-d_8 (0.40 mL), and the reaction was followed by ^{1}H NMR at 20 °C. After 20 min, 50% of 3 had been converted to Cp*$_2$Zr(η^2-^{13}COSiHMes$_2$)Me (6), with approximately 10% of the final product 7 also present.

Cp*$_2$Zr[OC(=CH$_2$)SiHMes$_2$]H (7). A pressure bottle was charged with 3 (0.557 g, 0.87 mmol), carbon monoxide (100 psi), and toluene (30 mL), and the resulting solution stirred at ambient temperature. Initially orange, after a few minutes the solution became maroon and after 20 h was light brown. The volatiles were removed at this point, and the oily residue was taken up in 20 mL of pentane and filtered to remove a small amount of tan solid. Evaporation of pentane yielded 0.459 g of 7 as a light brown solid contaminated by ca. 10% of a single, unidentified impurity. Attempts to further purify the extremely soluble 7 were not successful. IR (Nujol, CsI, cm^{-1}): 2718 w, 2045 s (Si–H), 1597, 1540 (Zr–H), 1195 s, 1058, 1004 s, 863, 840, 824, 678, 618, 457, 421, 360.

Reaction of 7 with MeI. The reaction of 7 with MeI was monitored by ^{1}H NMR. Addition of MeI (ca. 0.03 mmol) to 7 (0.015 g, 0.022 mmol) in benzene-d_6 (0.40 mL) at ambient temperature resulted in immediate evolution of CH$_4$ and the clean appearance of a new set of resonances only slightly shifted from those of 7, with the absence of any peaks attributable to Zr–H. The new peaks are assigned to Cp*$_2$Zr[OC(=CH$_2$)SiHMes$_2$]I (8). A similar reaction has been reported to give Cp$_2$(PMe$_3$)Zr=CHOZrCp$_2$(I) from Cp$_2$(PMe$_3$)Zr=CHOZrCp$_2$(H) and MeI.[33]

Reaction of 3 with H$_2$. Approximately 0.25 mmol of H$_2$ was added via gas-tight syringe to an NMR tube containing 3 (0.050 g, 0.08 mmol) in benzene-d_6 (0.40 mL), and the reaction was followed by ^{1}H NMR at 20 °C. After 10 min, quantitative conversion to Cp*$_2$Zr(Me)H and Mes$_2$SiH$_2$ was observed. Over the next hour, the Cp*$_2$Zr(Me)H[21] was observed to undergo further hydrogenolysis to Cp*$_2$ZrH$_2$[22] and CH$_4$.

Cp*$_2$Zr(Me)OSO$_2$CF$_3$ (9). (a) Toluene (30 mL) was added to a solid mixture of Cp*$_2$ZrMe$_2$ (1.52 g, 3.88 mmol) and AgOSO$_2$CF$_3$ (1.00 g, 3.89 mmol) at −78 °C, and the solution was allowed to warm to ambient temperature with stirring. At ca. 0 °C a gray precipitate (Ag^0) began to form. After 12 h the mixture was filtered, the residual solids were extracted by repeated toluene washings, and the pale yellow filtrate solution was concentrated to 10 mL. Cooling to −78 °C and slow addition of pentane (ca. 10 mL) followed by filtration and drying in vacuo afforded 1.79 g (88%) of pale green, crystalline 9 (mp 178–195 °C dec). Anal. Calcd for C$_{21}$H$_{33}$F$_3$O$_3$SZr: C, 49.1; H, 6.47. Found: C, 49.9; H, 6.72. IR (Nujol, CsI, cm^{-1}): 1333, 1230, 1190 sh, 1180 s, 1000 s, 718 w, 628 s. Monitoring the reaction by ^{1}H NMR (benzene-d_6) revealed the formation of 1 equiv of ethane, identified by com-

---

(27) (a) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203. (b) Gell, K. I.; Posin, B.; Schwartz, J.; Williams, G. M. *J. Am. Chem. Soc.* **1982**, *104*, 1846. (c) Lin, Z.; Marks, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 7979.

(28) Blinka, T. A.; Helmer, B. J.; West, R. *Adv. Organomet. Chem.* **1984**, *23*, 193.

(29) Weidenbruch, M.; Schäfer, A.; Rankers, R. *J. Organomet. Chem.* **1980**, *195*, 171.

(30) Wailes, P. C.; Weigold, H.; Bell, A. P. *J. Organomet. Chem.* **1971**, *33*, 181.

(31) Straus, D. A. Ph.D. Thesis, California Institute of Technology, 1982.

(32) Manriquez, J. M.; McAlister, D. R.; Rosenberg, E.; Shiller, A. M.; Williamson, K. L.; Chan, S. I.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 3078.

(33) Barger, P. T.; Santarsiero, B. D.; Armantrout, J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 5178.

Organometallics 1989, *8*, 330–336

parison to an authentic sample.

(b) Compound **3** (0.010 g, 0.016 mmol), $AgOSO_2CF_3$ (0.004 g, 0.016 mmol), and benzene-d_6 (0.4 mL) were combined in an NMR tube. As determined by ^1H NMR, immediate reaction occurred with precipitation of Ag^0 to afford **9** and other Si–H compounds (see Results and Discussion).

$Mes_2SiH(OSO_2CF_3)$. Toluene (15 mL) was added to a solid mixture of Mes_2SiHCl (0.975 g, 3.22 mmol) and $AgOSO_2CF_3$ (0.834 g, 3.24 mmol) in an Al-foil-covered flask at –78 °C. The resulting white heterogeneous mixture was warmed to ambient temperature and stirred for 1 h. The volatiles were removed in vacuo, and the pink solid was extracted three times with diethyl ether and filtered. Concentration of the colorless filtrate to 10 mL followed by cooling to –78 °C and filtration gave 0.953 g (71%) of $Mes_2SiH(OSO_2CF_3)$ as an off-white powder. Recrystallization from diethyl ether afforded white crystals (mp 122–124 °C). Mass spectrum: exact mass calcd for $C_{19}H_{23}F_3O_3SSi$, 416.1089; found, 416.1093. IR (Nujol, CsI, cm^{-1}): 3030, 2239 (Si–H), 1607, 1547, 1263 sh, 1248, 1209 s, 1155 s, 1083, 1070 sh, 1035, 958 s, 924, 850 s, 772, 717, 683, 639, 624, 604 sh, 562 sh, 547, 509, 432, 410, 387. ^1H NMR (benzene-d_6, 300 MHz, 23 °C): δ 1.98 (s, 6 H, p-$C_6H_2(CH_3)_3)_2$, 2.32 (s, 12 H, o-$C_6H_2(CH_3)_3$), 6.32 (s, 1 H, Si*H*), 6.56 (s, 4 H), $C_6H_2(CH_3)_3$).

$Mes_2SiH(Me)$. MeLi (2.4 mL of a 1.4 M solution in diethyl ether, 3.36 mmol) was added to a solution of Mes_2SiHCl (1.04 g, 3.43 mmol) in tetrahydrofuran (10 mL). After the solution was stirred for 1 h at room temperature, volatiles were removed by vacuum transfer, leaving a white solid. The product was extracted into pentane (15 mL) and crystallized from that solvent at –78 °C. Yield of $Mes_2SiH(Me)$ was 0.658 g (68%). ^1H NMR (benzene-d_6, 300 MHz, 23 °C): δ 0.61 (d, 3 H, $SiCH_3$), 2.08 (s, 6 H, p-$C_6H_2(CH_3)_3$), 2.34 (s, 12 H, o-$C_6H_2(CH_3)_3$), 5.50 (q, 1 H, Si*H*), 6.70 (s, 4 H, $C_6H_2(CH_3)_3$).

$Cp^*_2\underline{ZrCH_2\overline{CCHCMeCHCMeC}}SiHMes$ (10). (a) A solution of Cp^*ZrCl_2 (0.375 g, 0.87 mmol) and **1** (0.875 g, 2.1 mmol) in toluene (20 mL) was stirred at ambient temperature for 5 h. Volatiles were removed, and the orange residue was taken up in warm toluene (30 mL, ca. 50 °C) and filtered. Toluene was removed, the resulting deep orange solid was slurried in 10 mL of diethyl ether, and the mixture was filtered. The isolated product was washed thoroughly with diethyl ether and dried in vacuo (mp 234–236 °C). By ^1H NMR the purity of **10** was >95%. Yield of **10**: 0.391 g, 72%. Anal. Calcd for $C_{38}H_{52}ZrSi$: C, 72.66; H, 8.34. Found: C, 72.28; H, 8.29. IR (Nujol, CsI, cm^{-1}): 2060 s (Si–H), 1583, 1018, 878, 845, 751, 720, 698.

Acknowledgment is made to the Air Force Office of Scientific Research, Air Force Systems Command, USAF, for support of this work under Grant AFOSR-85-0228. The U.S. Government is authorized to reproduce and distribute reprints for Governmental purposes notwithstanding any copyright notation thereon. T.D.T. thanks the Alfred P. Sloan Foundation for a research fellowship (1988–1990). We thank Dr. Howard Turner for information regarding $Cp^*_2Zr(Me)OSO_2CF_3$.

Registry No. 1, 117940-80-4; **2**, 117940-81-5; **3**, 117940-82-6; **4**, 117940-83-7; **5**, 117940-84-8; **6**, 117940-85-9; **7**, 117940-86-0; 8, 117940-87-1; **9**, 111287-33-3; **10**, 117940-88-2; Mes_2SiHCl, 50490-74-9; $Cp_2Zr(Me)Cl$, 1291-45-8; $Cp^*_2Zr(Me)Br$, 84987-21-3; $Cp^*_2Zr(Me)H$, 117940-89-3; $Cp^*_2ZrH_2$, 61396-34-7; $Cp^*_2ZrMe_2$, 67108-80-9; $AgOSO_2CF_3$, 2923-28-6; $Mes_2SiH(OSo_2CF_3)$, 117940-79-1; $Mes_2SiH(Me)$, 50490-58-9; $Cp^*_2ZrCl_2$, 54039-38-2.

Synthesis and Reactivity toward Nucleophiles of Bis(isocyanide)(porphyrinato)rhodium(III) Complexes. Crystal and Molecular Structure of a Novel Carbene Complex: $\{(TPP)Rh(PhCH_2NC)[:C(NHCH_2Ph)_2]PF_6\}$

Tristano Boschi,* Silvia Licoccia, Roberto Paolesse, and Pietro Tagliatesta

Dipartimento di Scienze e Tecnologie Chimiche, II Università di Roma Tor Vergata, Via O. Raimondo, 00173 Rome, Italy

Giancarlo Pelizzi and Francesca Vitali

Istituto di Chimica Generale, Università di Parma, Centro di Studio per la Strutturistica Diffrattometrica del CNR, Viale delle Scienze, 43100 Parma, Italy

Received April 12, 1988

Bis(isocyanide)(octaethylporphyrinato)- and bis(isocyanide)(tetraphenylporphyrinato)rhodium(III) hexafluorophosphates undergo nucleophilic attack leading to the formation of cationic carbene derivatives or neutral carboxymethyl, amido, and alkyl complexes. The formation of the various products is related to the strength of the nucleophile. The crystal and molecular structure of the title compound has been determined by X-ray diffraction methods. The crystals are triclinic, space group $P\bar{1}$, with unit cell dimensions a = 16.427 (7) Å, b = 14.386 (7) Å, c = 13.268 (5) Å, α = 107.83 (4)°, β = 99.51 (4)°, γ = 77.31 (3)°, and Z = 2. The structure was solved by the heavy-atom technique and refined to R = 0.0773 for 3991 independent reflections. The rhodium atom is at the center of a slightly distorted octahedral environment.

Introduction

Rhodium porphyrinates have been the subject of many studies because of the versatile redox behavior of the central metal atom and their possible applications as photocatalysts and as models for biological systems.[1-6] During our studies of the influence of monodentate axial ligands on the redox behavior and reactivity of metalloporphyrinates, we have synthesized and characterized some hexacoordinated rhodium(III) derivatives of octaethyl- (OEP) and *meso*-tetraphenylporphyrin (TPP).[7,8] These

---

(1) Wayland, B. B.; Woods, B. A. *J. Chem. Soc., Chem. Commun.* **1983**, 142.

(2) Kadish, K. M.; Yao, C. L.; Anderson, J. E.; Cocolios, P. *Inorg. Chem.* **1985**, *24*, 4515.

(3) Lever, A. B. P.; Ramaswamy, B. S.; Licoccia, S. *J. Photochem.* **1982**, *19*, 173.

(4) Wayland, B. B.; Woods, B. A. *J. Chem. Soc., Chem. Commun.* **1982**, 634.

(5) Aoyama, Y.; Watanabe, T.; Onda, H.; Ogoshi, H. *Tetrahedron Lett.* **1983**, *24*, 1183.

(6) Setsune, J.; Yoshida, Z.; Ogoshi, H. *J. Chem. Soc., Perkin Trans. 1* **1982**, 983.

0276-7333/89/2308-0330$01.50/0