Organometallics 1987, *6*, 473–479

Preparation and Reaction Chemistry of Trimethylsilyl Derivatives of Niobium. Redox Chemistry of $(\eta^5\text{-}C_5H_5)_2Nb(SiMe_3)Cl$ and X-ray Structures of $(\eta^5\text{-}C_5H_5)_2Nb(SiMe_3)(\eta^2\text{-}C_2H_4)$ and $[(\eta^5\text{-}C_5H_5)_2Nb(CH_2SiMe_3)Cl]PF_6$

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Received July 30, 1986

The purple niobium(IV) silyl complex $(\eta^5\text{-}C_5H_5)_2Nb(SiMe_3)Cl$ (1) is prepared from reaction of $(\eta^5\text{-}C_5H_5)_2NbCl_2$ with $Hg(SiMe_3)_2$. Reduction of 1 in the presence of ligands (L) affords niobium(III) silyl complexes $(\eta^5\text{-}C_5H_5)_2Nb(SiMe_3)(L)$, where L = CO, PMe_3, and C_2H_4. $(\eta^5\text{-}C_5H_5)_2Nb(SiMe_3)(\eta^2\text{-}C_2H_4)$ (4) crystallizes in the orthorhombic space group *Pnma* with $a = 13.756$ (3) Å, $b = 12.819$ (3) Å, $c = 8.541$ (2) Å, $Z = 4$, and $R_F = 2.26\%$. A crystallographic mirror plane in 4 contains the niobium atom, the ethylene ligand, Si, and C(9). The Nb–Si distance is 2.669 (1) Å. Oxidation of 1 in dichloromethane with ferrocenium hexafluorophosphate results in a complex reaction that produces Me_3SiCl, Me_3SiF, $[(\eta^5\text{-}C_5H_5)_2Nb(CH_2SiMe_3)Cl]PF_6$ (5), and $[(\eta^5\text{-}C_5H_5)_2NbCl_2]PF_6$ (6). The methylene group in 5 originates from the dichloromethane solvent. The mechanism of this reaction is discussed. Crystals of 5 are orthorhombic, space group $P2_12_12_1$, with $a = 10.542$ (2) Å, $b = 12.546$ (2) Å, $c = 14.712$ (2) Å, $Z = 4$, and $R_F = 4.11\%$. The Nb–C σ bond distance in 5 is 2.208 (8) Å.

Introduction

Early-transition-metal silyl chemistry is a rather undeveloped field that shows promise for providing unusual and useful transformations in organosilicon and transition-metal compounds.[1] Early-transition-metal silyl compounds may also serve as organometallic precursors to advanced materials such as refractory metal silicides (e.g., $TiSi_2$, $NbSi_2$, $TaSi_2$, and WSi_2), which are used in integrated-circuit technology.[2] A broader application of this chemistry must be preceded by a better understanding of reactivity and bonding in these silyl derivatives.

Two previous reports describe niobium silyl compounds. Ol'dekop and Knizhnikov have prepared violet $Cp_2Nb(SiPh_3)_2$ (Cp = $\eta^5\text{-}C_5H_5$), which is oxidized by ferrocenium tetrafluoroborate to diamagnetic $[Cp_2Nb(SiPh_3)_2]BF_4$.[3] Curtis et al. have reported that Cp_2NbH_3 reacts readily with $PhMe_2SiH$ to give yellow $Cp_2Nb(SiMe_2Ph)H_2$.[4] In this paper we describe the preparation of $Cp_2Nb(SiMe_3)Cl$ (1) and some of its reaction chemistry. Reduction of 1 provides niobium(III) silyls, including the ethylene complex $Cp_2Nb(SiMe_3)(\eta^2\text{-}C_2H_4)$ (4) for which the crystal structure has been determined. Oxidation of 1 leads to more complex reactions. In dichloromethane, oxidation results in a series of steps that transfer the methylene group from the solvent to niobium in producing the alkyl $[Cp_2Nb(CH_2SiMe_3)Cl]PF_6$ (5).

Results

Preparation and Properties of $Cp_2Nb(SiMe_3)Cl$ (1). Initial attempts to synthesize niobium silyl compounds from Cp_2NbCl_2 and the silylating reagents $LiSiMe_3$,[5] $Al(SiMe_3)_3{\cdot}OEt_2$,[6] and $LiSi(SiMe_3)_3{\cdot}3THF$[7] were unsuccessful. Although rapid reactions occurred at −78 °C to produce dark red solutions, the paramagnetic oils obtained could not be characterized. The milder silylating agent $Hg(SiMe_3)_2$[8] does not react with Cp_2NbCl_2 in benzene at room temperature (24 h), but refluxing for 4 h produces a dark purple solution and a deposit of metallic mercury. The product $Cp_2Nb(SiMe_3)Cl$ (1) is isolated as large purple flakes from diethyl ether (eq 1). The Me_3SiCl was identified as an additional product by GC. We assume that the reaction proceeds by metathesis of a chlorine ligand in Cp_2NbCl_2 to produce 1 and $Hg(SiMe_3)Cl$, which then decomposes to Hg and Me_3SiCl.[9] Use of pure (sublimed) Cp_2NbCl_2 is critical to the success of the reaction.

$$Cp_2NbCl_2 + Hg(SiMe_3)_2 \xrightarrow[C_6H_6]{\text{reflux, 4 h}} \underset{1}{Cp_2Nb(SiMe_3)Cl} + Me_3SiCl + Hg \quad (1)$$

Complex 1 is stable indefinitely at room temperature, as a solid or in hydrocarbon and ether solvents. It is, however, extremely sensitive to air and moisture, yielding $HSiMe_3$ quantitatively upon hydrolysis (^1H NMR). The infrared spectrum of 1 is similar to those of the group 4 analogues $Cp_2M(SiMe_3)Cl$, where M = Ti,[10] Zr,[11] and Hf.[11]

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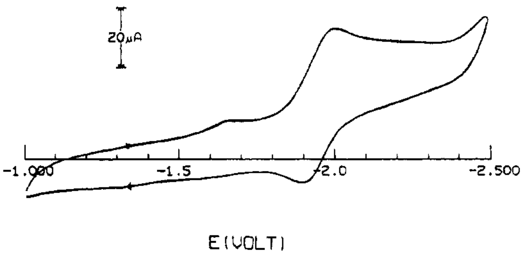


Figure 1. Cyclic voltammogram of $Cp_2Nb(SiMe_3)Cl$ (1 mM) (reduction wave from −1.0 to −2.5 V at 400 mV/s in tetrahydrofuran with 0.1 M $[(n\text{-}C_4H_9)_4N]PF_6$ at Pt-disk electrode; referenced to Ag/Ag^+ (0.1 M)).

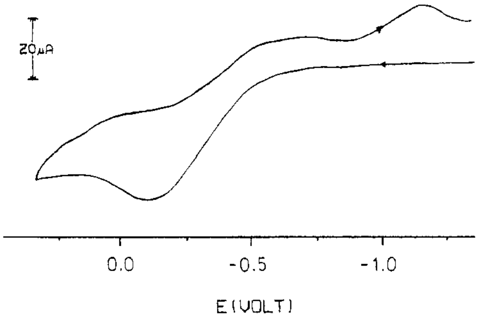


Figure 2. Cyclic voltammogram of $Cp_2Nb(SiMe_3)Cl$ (1 mM) (oxidation wave from −1.4 to +0.3 V at 300 mV/s in tetrahydrofuran with 0.1 M $[(n\text{-}C_4H_9)_4N]PF_6$ at Pt-disk electrode; referenced to Ag/Ag^+ (0.1 M)).

The magnetic moment of 1 measured by the Evans method[12] at 34 °C is 1.55 μ_B. In benzene-d_6 solution at room temperature, the ESR spectrum exhibits a 10-line pattern due to ^{93}Nb ($I = {}^9/_2$, 100%) coupling, with $g = 2.00$ and $a = 87$ G. These values are closer to those of dialkyls of the type Cp_2NbR_2 than to those of niobocene chloroalkyls $Cp_2Nb(R)Cl$.[13-15]

Cyclic voltammograms of 1 in tetrahydrofuran with 0.1 M $[(n\text{-}C_4H_9)_4N]PF_6$ as supporting electrolyte are shown in Figures 1 and 2. Under these conditions, reduction of 17-electron 1 is reversible with $E_{1/2} = -1.95$ V (Figure 1). In contrast, oxidation of 1 is irreversible (Figure 2, $E = -0.12$ V). For comparison, $Cp_2Nb(CH_2Ph)_2$ exhibits reversible redox potentials at −2.08 and −0.62 V relative to the Ag/Ag^+ electrode.[13]

Reduction of 1. Attempts to chemically reduce 1 with sodium, sodium naphthalenide, or sodium–mercury amalgam under a variety of conditions failed to give pure niobium(III) compounds. In the presence of suitable donor ligands, however, reduction yields the thermally stable, crystalline complexes $Cp_2Nb(SiMe_3)(L)$ (eq 2). Compounds 2–4 are diamagnetic and have been characterized by IR, NMR, and elemental analyses and, for 4, by X-ray crystallography.

$$1 + \text{Na/Hg} \xrightarrow[\text{THF}]{\text{L}} \begin{array}{c} \text{Cp}_2\text{Nb(SiMe}_3\text{)(L)} \\ \mathbf{2},\ \text{L} = \text{CO} \\ \mathbf{3},\ \text{L} = \text{PMe}_3 \\ \mathbf{4},\ \text{L} = \text{C}_2\text{H}_4 \end{array} + \text{NaCl} \qquad (2)$$

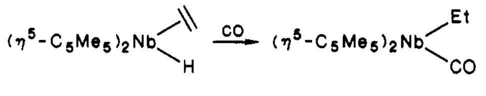
Table I. Crystal, Data Collection, and Refinement Parameters for 4 and 5

	4	**5**
formula	$C_{15}H_{23}NbSi$	$C_{13}H_{19}NbSiClPF_6$
crystal system	orthorhombic	orthorhombic
space group	*Pnma*	$P2_12_12_1$
a, Å	13.756 (3)	10.542 (2)
b, Å	12.819 (3)	12.546 (2)
c, Å	8.541 (2)	14.712 (2)
V, Å^3	1506.0 (5)	1945.7 (5)
Z	4	4
ρ(calcd), g cm^{-3}	1.43	1.63
μ, cm^{-1} (Mo Kα)	8.3	9.3
temp, °C	24	24
cryst dimens, mm	0.18 × 0.22 × 0.33	0.14 × 0.36 × 0.38
radiation	graphite-monochromated Mo Kα (λ = 0.71073 Å)	
diffractometer	Nicolet R3m/μ	
scan speed, deg/min	variable, 5–20	variable, 7–20
2θ scan range, deg	$4 \leqslant 2\theta \leqslant 60$	$4 \leqslant 2\theta \leqslant 52$
scan technique	$\theta/2\theta$	Wyckoff
data collected	$+h,+k,+l$	$+h,+k,+l$
weighting factor, g^a	0.0007	0.0010
unique data	2294 (2530 collected)	2183 (2204 collected)
unique data with $(F_0) \geq 5\sigma(F_0)$	1886	1658
std rflns	3 stds/197 rflns (<1% decay)	3 stds/197 rflns (<1% decay)
R_F, %	2.26	4.11
R_{wF}, %	2.60	4.33
GOF	0.891	1.089
maximum peak, e$^-$/Å^3	0.31	0.39
data/param	1886 rflns/133 least squares param	1658 rflns/224 least square param
Δ/σ	0.003	0.038

[a] $w^{-1} = \sigma^2(F_o) + gF_o^2$.

Spectroscopic features of the ethylene ligand in complex 4 are similar to those found in $Cp_2Nb(H)(\eta^2\text{-}C_2H_4)$ and $Cp_2Nb(Et)(\eta^2\text{-}C_2H_4)$.[16] The ^{1}H NMR spectrum of 4 shows that at 23 °C the ethylene ligand is static on the NMR time scale since two sets of resonances are observed for the inequivalent protons of the C_2H_4 group (pseudotriplets at δ 0.61 and 0.76, AA′BB′ pattern). In addition, the ^{13}C resonances of the two ethylenic carbon atoms (δ 13.04 and 13.48) suggest significant π-backbonding from the metal and a metallocyclopropane-type structure (cf. the ^{13}C NMR shift of 123.3 for free ethylene[17]).

Hydride migration to alkenes in complexes of the type $(\eta^5\text{-}C_5R_5)_2MH(\eta^2\text{-alkene})$ (R = Me, M = Nb; R = H, M = Ta) has been observed[18] by trapping of the migration product by carbon monoxide or isocyanides to give alkyl derivatives (e.g. eq 3[18b]). To determine whether the



(3)

$-SiMe_3$ group can migrate to ethylene in the same manner, 4 was treated with CO (30 psi, benzene-d_6, 2 days, 23 °C) and $CNCMe_3$ (3 equiv, benzene-d_6, 1 day, 23 °C). In neither case was reaction observed by ^{1}H NMR; when heated to 90 °C, the reaction between 4 and $CNCMe_3$ led only to a complex mixture of paramagnetic products.

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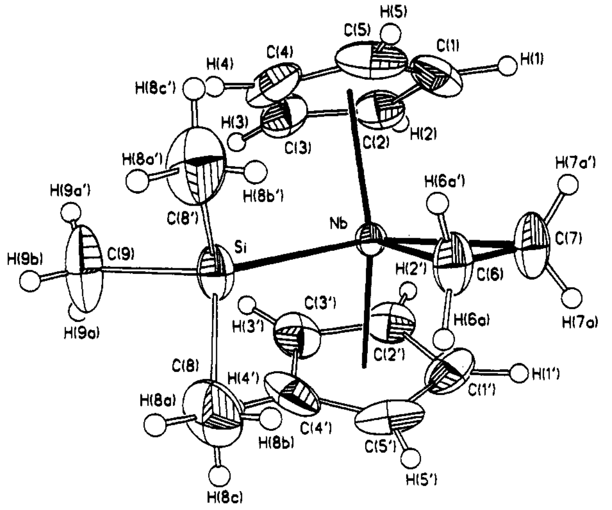

Figure 3. ORTEP view of 4 with atom-labeling scheme.

Table II. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for 4

	x	*y*	*z*	U^a
Nb	8419 (1)	2500	4181 (1)	28 (1)
Si	8839 (1)	2500	7232 (1)	48 (1)
C(1)	8296 (2)	4089 (2)	2686 (4)	67 (1)
C(2)	7355 (2)	3696 (2)	2845 (3)	56 (1)
C(3)	7103 (2)	3720 (2)	4436 (3)	62 (1)
C(4)	7879 (3)	4130 (2)	5261 (4)	72 (1)
C(5)	8628 (2)	4348 (2)	4204 (4)	76 (1)
C(6)	10093 (2)	2500	4448 (4)	55 (1)
C(7)	9869 (2)	2500	2801 (4)	62 (1)
C(8)	9571 (3)	1350 (3)	7989 (4)	87 (1)
C(9)	7723 (4)	2500	8536 (5)	100 (3)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table III. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for 5

	x	*y*	*z*	U^a
Nb	1714.4 (6)	1353.5 (5)	2241.8 (5)	40.9 (2)*
P	6890 (2)	429 (2)	346 (2)	60 (1)*
Cl	1765 (3)	7 (2)	3364 (2)	84 (1)*
Si	4664 (2)	1531 (2)	3318 (2)	51 (1)*
F(1)	6472 (1)	255 (9)	−648 (6)	185 (5)*
F(2)	5908 (7)	−409 (6)	688 (7)	146 (4)*
F(3)	7420 (9)	557 (9)	1313 (6)	154 (4)*
F(4)	7891 (7)	1244 (6)	11 (7)	152 (4)*
F(5)	5896 (6)	1327 (6)	490 (7)	150 (4)*
F(6)	7919 (6)	−480 (5)	203 (5)	109 (3)*
C(b)	3602 (7)	2101 (7)	2371 (6)	46 (3)*
Hcba	3528 (100)	2863 (77)	2542 (60)	93 (32)
Hcbb	4027 (68)	2056 (54)	1815 (51)	42 (20)
C(1)	−356 (10)	2034 (11)	2463 (11)	157 (8)*
C(2)	152 (17)	1996 (9)	3321 (10)	133 (7)*
C(3)	1137 (11)	2758 (9)	3288 (9)	95 (5)*
C(4)	1086 (13)	3165 (9)	2450 (9)	103 (5)*
C(5)	202 (12)	2739 (11)	1979 (9)	146 (7)*
C(6)	741 (9)	314 (7)	1084 (8)	78 (4)*
C(7)	1813 (10)	−271 (7)	1334 (7)	68 (3)*
C(8)	2883 (8)	309 (8)	1121 (6)	66 (3)*
C(9)	2494 (10)	1247 (8)	704 (5)	71 (3)*
C(10)	1185 (10)	1254 (9)	655 (6)	80 (4)*
C(11)	4003 (10)	1787 (8)	4461 (6)	74 (4)*
C(12)	6157 (9)	2353 (9)	3192 (9)	88 (4)*
C(13)	5086 (9)	98 (6)	3165 (7)	74 (4)*

[a] Numbers with an asterisk are equivalent isotropic *U*'s defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table IV. Selected Bond Distances (Å) and Angles (deg) for 4 and 5

(a) Bond Distances for 4			
Nb-CNT[a]	2.086 (3)	Nb-Si	2.669 (1)
Nb-C(6)	2.314 (3)	C(6)-C(7)	1.440 (5)
Nb-C(7)	2.317 (3)		
(b) Bond Angles for 4			
CNT-Nb-CNT′	133.8 (2)	C(6)-Nb-Si	71.8 (1)
CNT-Nb-Si	101.5 (1)	C(7)-Nb-Si	108.0 (1)
CNT-Nb-C(6)	112.5 (2)	C(6)-Nb-C(7)	36.2 (1)
CNT-Nb-C(7)	105.1 (2)		
(c) Bond Distances for 5			
Nb-CNT1	2.111 (7)	Nb-C(b)	2.208 (8)
Nb-CNT2	2.104 (7)	C(b)-Si	1.925 (8)
Nb-Cl	2.362 (3)	(av) P-F	1.557 (7)
(d) Bond Angles for 5			
CNT1-Nb-CNT2	130.2 (3)	CNT2-Nb-C(b)	102.9 (3)
CNT1-Nb-Cl	107.1 (2)	Cl-Nb-C(b)	102.9 (2)
CNT2-Nb-Cl	106.3 (2)	Nb-C(b)-Si	115.4 (4)
CNT1-Nb-C(b)	104.3 (3)		

[a] CNT = centroid of Cp ring.

Description of the Structure of 4. Compound 4 is the only structurally characterized niobium silyl compound. The molecular structure and atom-labeling scheme are shown in Figure 3. A crystallographic, molecular mirror plane containing the niobium atom, the ethylene ligand, Si, and C(9) requires eclipsing of the cyclopentadienyl ligands. The structure therefore very much resembles that of $Cp_2NbEt(\eta^2\text{-}C_2H_4)$.[16] Table IV lists some selected bond distances and intramolecular angles for 4. The Nb–C(ethylene) bond lengths in 4, 2.314 (3) and 2.317 (3) Å, are essentially identical with the corresponding bond lengths in $Cp_2NbEt(\eta^2\text{-}C_2H_4)$, which average to 2.299 (21) Å. Other geometrical parameters associated with ethylene ligation in 4 show that, as in $Cp_2NbEt(\eta^2\text{-}C_2H_4)$, the bonding involves considerable metal to ligand π donation.

Bonds between silicon and electron-rich (late) transition metals are often shorter than expected based on covalent radii.[19] In contrast, bonds between silicon and some heavy, early transition metals appear to be longer than expected,[11,20,21] although the Ta–Si bond length in $Cp_2Ta(SiMe_2Ph)H_2$, 2.651 (4) Å, is normal.[4] The Nb–Si distance in 4, 2.669 (1) Å, also corresponds to a single, covalent bond. The covalent radius of Nb(III) in $Cp_2Nb(\eta^2\text{-}C_2H_4)$ can be calculated from the $Cp_2NbEt(\eta^2\text{-}C_2H_4)$ structure by subtracting the radius of carbon (0.77 Å)[22] from the Nb–C(Et) bond length (2.316 (8) Å). This value, 1.55 Å, can then be combined with the Si radius of 1.12 Å[21] to give the expected, and observed, distance of 2.67 Å.

Oxidation of 1. Under the conditions of the cyclic voltammetry studies the oxidation of 1 is irreversible, perhaps due to rapid decomposition of an oxidized species. Accordingly, we found that preparative scale reactions between 1 and the oxidants $AgPF_6$ (in tetrahydrofuran) or $[Cp_2Fe]PF_6$ (in tetrahydrofuran or acetonitrile) gave uncharacterized mixtures of paramagnetic solids. These reactions appear to proceed with loss of the $-SiMe_3$ ligand, since the solid products contained no $-SiMe_3$ groups (by IR and by ^1H NMR of hydrolyzed samples).

Oxidation of 1 in dichloromethane (with $AgPF_6$ or $[Cp_2Fe]PF_6$) yields two niobium-containing products,

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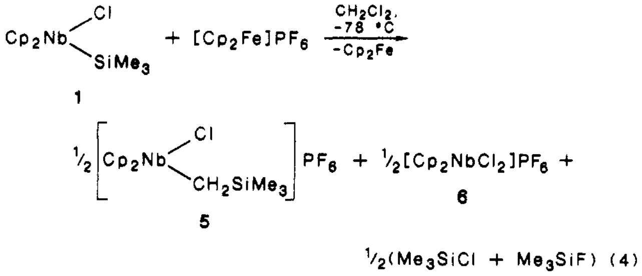
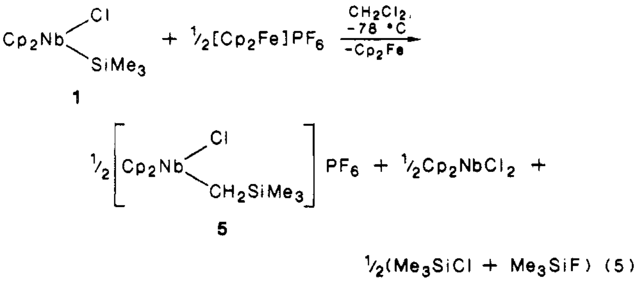
Table V. Structural Parameters in $Cp_2M(CH_2SiMe_3)L$ Complexes

compound	*d*(M–C), Å	*d*(C–Si), Å	∠(M–C–Si), deg	∠(C–M–L), deg	ref
$[Cp_2Nb(CH_2SiMe_3)Cl]PF_6$	2.208 (8)	1.925 (8)	115.4 (4)	102.9 (2)	this work
$Cp_2Nb(CH_2SiMe_3)_2$	2.285 (4), 2.288 (4)	1.861 (4), 1.850 (4)	127.4 (2), 127.5 (2)	83.1 (1)	30
$[Cp_2Y(CH_2SiMe_3)_2]^-$	2.402 (6), 2.445 (6)	1.836 (6), 1.824 (6)	134.3 (3), 130.1 (3)	97.8 (2)	31
$Cp_2Zr(CH_2SiMe_3)_2$	2.278 (4), 2.281 (4)	1.845 (4), 1.847 (4)	135.2 (2), 133.8 (2)	97.8 (1)	32
$Cp_2Lu(CH_2SiMe_3)(THF)$	2.376 (17)		130.7 (8)	95.8 (9)	34
$(\eta^5\text{-}C_5Me_5)_2Th(CH_2SiMe_3)_2$	2.46 (1), 2.51 (1)	1.86 (1), 1.87 (1)	132.0 (6), 148.0 (7)	96.8 (4)	35

$[Cp_2Nb(CH_2SiMe_3)Cl]PF_6$ (**5**) and $[Cp_2NbCl_2]PF_6$ (**6**) (eq 4). Yellow, crystalline **5** is isolated in relatively low yield (15–30%), and orange **6** is obtained in ca. 45% yield. The source of the methylene unit in **5** is the dichloromethane solvent, as determined by deuterium labeling. The resonance for these methylene protons in the ^1H NMR spectrum of **5** (δ 3.49) is absent when the reaction is carried out in dichloromethane-d_2. Analysis of the volatiles from the reaction by ^1H NMR and GC–MS identified Me_3SiCl and Me_3SiF (ca. 1:1) as additional products. The Me_3SiF may arise from halogen exchange between Me_3SiCl and PF_6^- in solution.[23] Consistent with the mechanism discussed below, $^1/_2$ equiv of the $[Cp_2Fe]PF_6$ oxidant consumes all of **1** to produce roughly equal amounts of **5** and Cp_2NbCl_2 (eq 5, see Experimental Section).



(4)



(5)

Although **6** was previously prepared by electrochemical oxidation of a tetrahydrofuran solution of Cp_2NbCl_2 in the presence of $[(n\text{-}C_4H_9)_4N]PF_6$, it was not fully characterized.[24] Though our elemental analyses and IR data are in accord with the proposed formulation of **6** as a niobium(V) cation, we do not observe the expected ^1H NMR spectrum (in nitromethane-d_3 or acetonitrile-d_3). Since **6** does not have a measurable magnetic moment ($\mu_{eff} \leq 0.3$ μ_B by Evans' method), we believe that the ^1H NMR spectrum of **6** was not observed due to line-broadening effects from traces of paramagnetic materials in solution. Similar difficulties have been encountered in related tungstenocene and molybdenocene systems.[25] Further evidence for the formulation of **6** as $[Cp_2NbCl_2]PF_6$ was obtained by an independent synthesis. Oxidation of Cp_2NbCl_2 with $[Cp_2Fe]PF_6$ in dichloromethane or acetonitrile yields **6** (by IR and melting point). Reduction of **6** with Na/Hg amalgam in tetrahydrofuran regenerates Cp_2NbCl_2 in high yield (eq 6).

$$Cp_2NbCl_2 \underset{Na/Hg}{\overset{[Cp_2Fe]PF_6}{\rightleftharpoons}} \underset{\mathbf{6}}{[Cp_2NbCl_2]PF_6} \qquad (6)$$

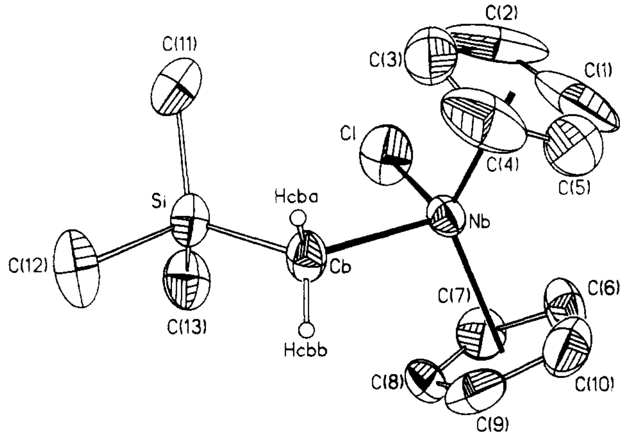


Figure 4. ORTEP view of the cation of **5** with atom-labeling scheme.

Description of the Structure of 5. Figure 4 provides a view of the cation in **5**, $[Cp_2Nb(CH_2SiMe_3)Cl]^+$, which adopts the familiar "bent sandwich" coordination geometry. Final atomic coordinates and isotropic thermal parameters are given in Table III. Selected bond lengths and angles are listed in Table IV.

As expected, the Nb(V)–C σ bond length, 2.208 (8) Å, is shorter than corresponding distances in Nb(III) alkyls ($Cp_2NbEt(\eta^2\text{-}C_2H_4)$,[16] 2.316 (8) Å; $Cp_2Nb(\eta^1\text{-}CH_2CH{=}CH_2)(\eta^2\text{-}CS_2)$,[26] 2.309 (3) Å) and Nb(IV) alkyls ($Cp_2Nb(CH_2Ph)_2$,[15] 2.304 (3) Å; $Cp_2Nb(CH_2SiMe_2CH_2)$,[27] 2.275 (3) Å; $(\eta^5\text{-}C_5H_4SiMe_3)_2Nb(o\text{-}CH_2C_6H_4CH_2)$,[28] 2.286 (9) Å; $(\eta^5\text{-}C_5H_4SiMe_3)_2Nb(CH_2SiMe_3)Cl$,[29] 2.28 (1) Å; $Cp_2Nb(CH_2SiMe_3)_2$,[30] 2.286 (4) Å). This bond is also shorter than metal–carbon σ bonds in closely related second-row d° metallocene dialkyls $[Cp_2Y(CH_2SiMe_3)_2]_2Li_2$(1,2-dimethoxyethane)$_2$(dioxane)[31] ($d$(Y–C) = 2.402 (6), 2.445 (6) Å) and $Cp_2Zr(CH_2SiMe_3)_2$[32] (d(Zr–C) = 2.278 (4), 2.281 (4) Å). Although we know of no pentavalent niobocene alkyl complexes that can be used for comparison, in $(Me_3SiCH_2)_2Nb(\mu\text{-}CSiMe_3)_2Nb(CH_2SiMe_3)_2$,[33] which can

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[23] A reaction between Me_3SiCl and NH_4PF_6 (1:1) in acetonitrile-d_3 gave ca. 40% conversion to Me_3SiF within 5 min (by ^1H NMR).

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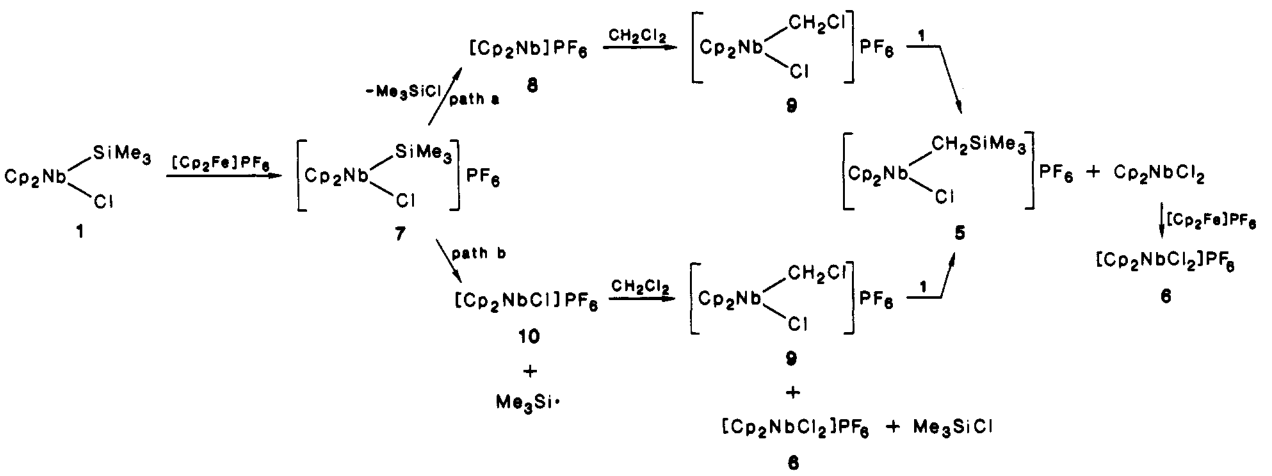
Scheme I



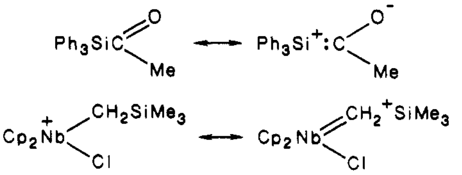
be considered to contain niobium(V) centers, the average value for the Nb–C σ bond lengths (2.16 Å) is in accord with the distance observed in **5**.

The metrical parameters associated with the $-CH_2SiMe_3$ ligation in **5** appear to be somewhat unusual (Table V). The C(b)–Si distance of 1.925 (8) Å is considerably longer than the corresponding distances in similar compounds (vida infra). Also, the Nb–C(b)–Si angle (115.4 (4)°) is smaller and the Cl–Nb–C(b) angle (102.9 (2)°) larger than values typically observed in related compounds. In d^0 "bent sandwich" complexes Cp_2ML_2, L–M–L angles normally range from 94 to 97°.[15,36] Although we are reluctant at this time to ascribe much significance to these observations, it seems likely that they result at least in part from differences in steric interactions in the Cp_2ML_2 "equatorial planes".

Discussion

Our investigations of niobocene silyl chemistry have allowed us to examine silyl derivatives of niobium(III), niobium(IV), and (presumably) niobium(V). Within these systems, our results point toward a general ordering of reactivity with respect to metal oxidation state and electron count of: Nb(V), 16 electron > Nb(IV), 17 electron > Nb(III), 18 electron. The niobium(IV) silyl **1** is readily reduced to niobium(III) silyls **2**–**4**, but oxidation leads to decomposition reactions that cleave the Nb–Si bond. With dichloromethane as solvent, the oxidation results in two niobium(V) compounds, the alkyl **5** and the niobocene dichloride cation **6**.

Other cationic alkyl complexes analogous to **5** are known, e.g. $[Cp_2Ta(CH_2SiMe_3)Me]Br$,[37] $[Cp_2Nb(Me)I]I$,[38] and $[Cp_2M(CHSiMe_3)(CH_2SiMe_3)]Y$ (M = Nb, Ta; Y = BF_4, SbF_6),[39] but none have been structurally characterized. A somewhat surprising feature of the structure of **5** is the Si–C(b) bond length, which is appreciably longer than the average of the remaining Si–C bond lengths, 1.868 (9) Å. A similar effect has been observed in acylsilanes such as $Ph_3SiCOMe$, for which the $Si-C_{acyl}$ distance (1.93 Å) is longer than the average $Si-C_{phenyl}$ distance (1.86 Å).[40] As in the latter case, these observations can be explained in terms of contributions from no-bond resonance forms:[40]



In support of this view, **5** reacts with water (1 equiv in acetone-d_6) to give $Me_3SiOSiMe_3$ (70% by ^1H NMR and GC) as the major silicon-containing product and no Me_4Si (<5% by ^1H NMR and GC). Other products in the reaction were not characterized.

Two possible mechanisms that account for the formation of products in eq 4 involve oxidatively induced reductive eliminations[41] (Scheme I, paths a and b). A likely first step in the reaction is oxidation of **1** to produce the niobium(V) silyl $[Cp_2Nb(SiMe_3)Cl]PF_6$ (**7**). This species may then undergo reductive elimination, either by a concerted, two-electron process (path a) or by homolytic cleavage of the Nb–Si bond (path b). We have previously observed reductive elimination of Me_3SiCl from d^0 silyl complexes of titanium[1g] and tantalum.[21] Further evidence that Me_3SiCl elimination can occur in **7** was obtained by carrying out the oxidation of **1** in chlorine-free solvents (acetonitrile-d_3 or benzene-d_6) with $AgOSO_2CF_3$. These reactions, which gave near-quantitative yields of Me_3SiCl (by ^1H NMR and GC), probably proceed by a concerted or two-step process analogous to path a or b, respectively.[42]

In path a the niobium(III) cation that is produced (**8**) oxidatively adds dichloromethane. Oxidative addition of dichloromethane has been reported for several metal complexes.[43] Here the product would be an α-chloroalkyl

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(42) We have found evidence for the participation of silyl radicals in reactions of zirconium silyl complexes with oxidants such as $AgOSO_2CF_3$ (ref 1h). Also, reaction of $Cp_2Zr(SiMe_3)Cl$[11] with $AgOSO_2CF_3$ in acetonitrile-d_3 gave 0.65 equiv of Me_3SiCl.

complex of niobium(V), $[Cp_2Nb(CH_2Cl)Cl]PF_6$, (**9**). Further reaction of **9** with a nucleophilic silylating agent such as **1** could give **5** and Cp_2NbCl_2,[44] which would be oxidized by remaining $[Cp_2Fe]PF_6$ to complete the observed quantitative oxidation of niobium(IV) to niobium(V). An attempt was made to trap an oxidative addition product analogous to **9** by employing chloromethane as solvent in the reaction. Although no products from this reaction could be characterized, it appeared that **6** was not formed (by IR).

In path b, the niobium(V) silyl **7** undergoes a one-electron reductive elimination by homolysis of the Nb–Si bond producing two odd-electron species, **10** and $Me_3Si^\bullet$. A precedent for this type of oxidatively induced reductive elimination is found in the formation of $[Cp_2M(SR)(NCMe)]^+$ and RSSR upon one-electron oxidation of $Cp_2M(SR)_2$ complexes (M = Mo, W; R = Me, Ph) in acetonitrile.[45] A similar reaction involving niobium has been observed electrochemically (eq 7).[23] The niobium(IV) intermediate **10** may react with dichloromethane by a one-electron oxidative addition,[46] affording **6** and **9**, which could proceed to products **5** and **6** as in path a. Alternatively, the $Me_3Si^\bullet$ radical may abstract chlorine from dichloromethane to give Me_3SiCl and $^\bullet CH_2Cl$, which could couple with **10** to produce **9**. No convincing evidence for the presence of silyl radicals was found. Only traces of $Me_3SiSiMe_3$ were detected by GC in reactions of **1** with $[Cp_2Fe]PF_6$ in dichloromethane and in reactions of **1** with $AgOSO_2CF_3$ in benzene-d_6 or acetonitrile-d_3. Attempts to use Me_3CBr or acetone as trapping reagents[47,48] for silyl radicals did not give conclusive results because of the reactivity of these reagents toward **1**.

$$Cp_2NbCl_2 \xrightarrow{-e^-} [Cp_2NbCl_2]^+ \rightarrow {}^1/_2Cl_2 + [Cp_2NbCl]^+ \qquad (7)$$

Although at this point we cannot exclude the possibility of other mechanisms, we prefer the relatively simple one outlined in Scheme I (particularly path a), which is consistent with the available data. We hope to gain further insight into this reactivity by our continuing studies of niobium silyl chemistry.

Experimental Section

Manipulations were performed under an inert atmosphere of nitrogen or argon by using standard Schlenk techniques or a Vacuum Atmospheres glovebox. Elemental analyses were performed by Galbraith or Schwartzkopf microanalytical laboratories. Infrared spectra were recorded on a Perkin-Elmer 1330 spectrometer. ^1H NMR spectra were recorded at 360 MHz with a spectrometer fabricated locally by Dr. John Wright, at 90 MHz with a Varian EM-390, or at 300 MHz with a GE QE-300 instrument. $^{13}C\{^1H\}$ NMR spectra were recorded at 50.3 MHz with a Nicolet WB-200 spectrometer or at 75.5 MHz on the GE QE-300. GC analyses were conducted on a Varian 3400 instrument coupled to a Varian 4290 integrator, using a 3 m × $^1/_8$ in. stainless steel column with 25% 1,2,3-tris(2-cyanoethoxy)propane as stationary phase. ESR spectra were obtained with a Varian E-3 spectrometer. Literature procedures were used to prepare $Hg(SiMe_3)_2$[8] and Cp_2NbCl_2.[15] Ferrocenium hexafluorophosphate was prepared by the addition of NH_4PF_6 to $[Cp_2Fe][FeCl_4]$ (Alfa) in water.

Cyclic voltammetry was performed on an IBM EC/225 voltammetric analyzer or on a BAS-100 electrochemical analyzer. The electrochemical cell, the platinum-disk working electrode, the platinum-wire auxiliary electrode, and the Ag/0.1 M $AgNO_3$ reference electrode (in acetonitrile) were also obtained from IBM Instruments. Working and auxiliary electrodes were cleaned with aqua regia before use. A blanket of argon, presaturated with solvent at the same temperature (21 ± 1 °C), was maintained in the cell by continuous purging. Experiments were run with 0.001 M $Cp_2Nb(SiMe_3)Cl$ (**1**) in tetrahydrofuran with 0.1 M$[(n\text{-}C_4H_9)_4N]PF_6$ as backing electrolyte.

$Cp_2Nb(SiMe_3)Cl$ (1). Benzene (100 mL), Cp_2NbCl_2 (5.50 g, 1.87 mmol), and $Hg(SiMe_3)_2$ (6.50 g, 1.87 mmol) were refluxed with stirring for 4 h. After the volatiles were removed in vacuo, the purple residue was extracted with diethyl ether (4 × 50 mL). The combined extracts were concentrated to ca. 40 mL and cooled to −45 °C to afford purple flakes (mp 135–137 °C dec) in 50% yield (3.11 g). Anal. Calcd for $C_{13}H_{19}ClNbSi$: C, 47.1; H, 5.73; Cl, 10.7. Found: C, 44.4; H, 5.76; Cl, 11.0. We have experienced difficulty in obtaining good elemental carbon (but not hydrogen or halogen) analyses for several silyl complexes, perhaps due to the formation of silicon carbide during combustion analysis. ESR (benzene-d_6, 23 °C): g = 2.00, 10 lines, a = 87 G. IR (Nujol, CsI, cm^{-1}): 3100 m, 1418 m, 1360 w, 1220 s, 1107 w, 1000 m, 908 w, 842 sh, 830 sh, 800 s, 727 m, 651 m, 599 m, 356 w, 315 m.

$Cp_2Nb(SiMe_3)(CO)$ (2). A solution of **1** (0.50 g, 1.5 mmol) in diethyl ether (20 mL) was added to a Na/Hg amalgam (0.035 g of Na, 1.5 mmol; 16 g of Hg) in a pressure bottle. The mixture was pressurized to 50 psi with carbon monoxide and stirred for 12 h. The dark red solution was filtered, concentrated to ca. 10 mL, and cooled to −15 °C. Green crystals of the product were isolated after 12 h (0.26 g, 53%). The compound sublimes at ca. 90 °C and 10^{-3} mm to give purple crystals (mp 137–139 °C dec) with spectroscopic properties identical with those of the crude, green product. Anal. Calcd for $C_{14}H_{19}NbOSi$: C, 51.9; H, 5.91; Si, 8.66. Found: C, 52.0; H, 6.03; Si, 8.46. IR (Nujol, CsI, cm^{-1}): 3118 w, 1919 s, 1883 s, 1228 s, 1013 m, 999 m, 821 s, 801 s, 735 s, 653 s, 607 s, 492 m, 448 w, 386 w, 307 w. IR (benzene-d_6 solution, CaF_2, cm^{-1}): ν_{CO} 1902. ^1H NMR (benzene-d_6, 360 MHz, 20 °C): δ 0.41 (s, 9 H, $SiMe_3$), 4.35 (s, 10 H, C_5H_5). $^{13}C\{^1H\}$ NMR (benzene-d_6, 50.3 MHz, 20 °C): δ 8.44 ($SiMe_3$), 86.6 (C_5H_5), 237.5 (NbCO).

$Cp_2Nb(SiMe_3)(PMe_3)$ (3). A cold (−78 °C) solution of **1** (0.30 g, 0.91 mmol) and trimethylphosphine (0.24 mL) in tetrahydrofuran (20 mL) was added to a cold (−78 °C) Na/Hg amalgam (0.021 g of Na, 0.91 mmol; 7 g of Hg). The cold bath was removed, and the purple solution began to develop a red color. After the solution was stirred for 30 min at room temperature, the volatiles were removed from the orange solution, and the residue was extracted with pentane (30 mL). Filtration, concentration (to ca. 10 mL), and cooling (−45 °C) overnight gave dark red crystals (mp 128–130 °C dec) in 65% yield (0.22 g). Anal. Calcd for $C_{16}H_{28}NbPSi$: C, 51.6; H, 7.58. Found: C, 51.4; H, 7.45. IR (Nujol, CsI, cm^{-1}): 3105 w, 1420 m, 1278 s, 1260 s, 1219 m, 1101 s, 1010 m, 996 m, 946 s, 825 s, 798 s, 717 m, 661 m, 635 m, 600 m, 384 m, 307 w. ^1H NMR (benzene-d_6, 360 MHz, 23 °C): δ 0.44 (s, 9 H, $SiMe_3$), 0.86 (d, J_{PH} = 7 Hz, 9 H, PMe_3), 4.21 (d, J_{PH} = 2 Hz, 10 H, C_5H_5). $^{13}C\{^1H\}$ NMR (benzene-d_6, 50.3 MHz, 23 °C): δ 10.2 ($SiMe_3$), 24.0 (d, J_{PC} = 21 Hz, PMe_3), 84.5 (C_5H_5).

$Cp_2Nb(SiMe_3)(\eta^2\text{-}C_2H_4)$ (4). A −78 °C solution of **1** (0.60 g, 1.8 mmol) in diethyl ether (20 mL) was added to a cold (−78 °C) Na/Hg amalgam (0.042 g of Na, 1.8 mmol; 5 g of Hg). The solution was pressurized with ethylene (100 psi) and then allowed to warm to room temperature with stirring. After 12 h the solution was filtered, concentrated to ca. 10 mL, and cooled to −45 °C to obtain pale brown crystals (mp 165–170 °C dec) of the product in 85% yield (0.50 g). Recrystallization from diethyl ether gave bright yellow crystals suitable for X-ray diffraction. Anal. Calcd for $C_{15}H_{23}NbSi$: C, 55.5; H, 7.15. Found: C, 55.5; H, 7.17. IR (Nujol, CsI, cm^{-1}): 3090 w, 3036 w, 1241 w, 1225 s, 1135 s, 1000 s, 838

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m, 822 s, 800 s, 728 s, 645 s, 601 s, 367 m, 303 m. ^{1}H NMR (benzene-d_6, 360 MHz, 25 °C): δ 0.49 (s, 9 H, SiMe$_3$), 0.61 (t, J = 11 Hz, 2 H, η^2-C$_2$H$_4$), 0.76 (t, J = 11 Hz, 2 H, η^2-C$_2$H$_4$), 4.23 (s, 10 H, C$_5$H$_5$). ^{13}C{^{1}H} NMR (benzene-d_6, 50.3 MHz, 23 °C): δ 7.24 (SiMe$_3$), 13.5 (η^2-C$_2$H$_4$), 14.0 (η^2-C$_2$H$_4$), 92.4 (C$_5$H$_5$).

[Cp$_2$Nb(CH$_2$SiMe$_3$)Cl]PF$_6$ (5). Addition of cold (–78 °C) dichloromethane (20 mL) to a mixture of 1 (0.30 g, 0.91 mmol) and [Cp$_2$Fe]PF$_6$ (0.30 g, 0.91 mmol) cooled to –78 °C resulted in formation of an orange solution and a brown precipitate. After the solution was allowed to warm to room temperature, the volatiles were removed under vacuum, and the residue was extracted with diethyl ether (2 × 30 mL). Evaporation of the diethyl ether solution to dryness gave a yellow crystalline material (0.15 g), identified as ferrocene by ^{1}H NMR and IR. The remaining residue in the reaction flask was then extracted with dichloromethane (2 × 20 mL) to give a yellow solution that was filtered, concentrated to ca. 20 mL, and cooled to –45 °C. Yellow crystals (mp 115–160 °C dec) of the product (0.12 g, 28%) were isolated by filtration. An orange residue (0.15 g, 45%) still remained in the reaction flask. This material was crystallized from acetonitrile (–15 °C) to give orange crystals of 6, whose IR spectrum and melting point were identical with those of an authentic sample prepared by the method below. Anal. Calcd for C$_{14}$H$_{21}$ClF$_6$NbPSi: C, 34.3; H, 4.31; Cl, 7.22; F, 23.2. Found: C, 33.6; H, 4.17; Cl, 8.07; F, 23.5. IR (Nujol, CsI, cm^{-1}): 3120 m, 1440 s, 1245 s, 1236 m, 1029 w, 1018 w, 830 br s, 650 s, 622 m, 553 s, 388 w, 315 m. ^{1}H NMR (dichloromethane-d_2, 300 MHz, 25 °C): δ 0.20 (s, 9 H, SiMe$_3$), 3.49 (s, 2 H, NbCH$_2$Si), 6.79 (s, 10 H, C$_5$H$_5$). ^{13}C{^{1}H} NMR (dichloromethane-d_2, 75.5 MHz, 25 °C): δ 2.08 (SiMe$_3$), 27.3 (NbCH$_2$Si), 117.1 (C$_5$H$_5$).

[Cp$_2$NbCl$_2$]PF$_6$ (6). (a) Dichloromethane (10 mL) at –78 °C was added to a cold (–78 °C) mixture of Cp$_2$NbCl$_2$ (0.30 g, 0.76 mmol) and [Cp$_2$Fe]PF$_6$ (0.25 g, 0.76 mmol). After the solution was allowed to warm to room temperature, the orange precipitate that had formed was isolated by filtration and dissolved in acetonitrile (20 mL). The solution was concentrated to ca. 10 mL and cooled to –15 °C. After 12 h orange crystals (0.31 g, 93%; mp 255–258 °C dec) were isolated by filtration. Anal. Calcd for C$_{10}$H$_{10}$Cl$_2$F$_6$NbP: C, 27.4; H, 2.30; Cl, 16.2; F, 26.0. Found: C, 27.8; H, 2.35; Cl, 16.0; F, 26.3. IR (Nujol, CsI, cm^{-1}): 3121 s, 1438 s, 1122 w, 1071 w, 1025 w, 1010 m, 830 s br, 740 w, 555 s, 369 m, 338 m, 304 m, 280 m.

(b) Acetonitrile (20 mL) was added to a mixture of Cp$_2$NbCl$_2$ (0.25 g, 0.85 mmol) and [Cp$_2$Fe]PF$_6$ (0.28 g, 0.85 mmol) at room temperature. After the solution was stirred for 30 min, the volatiles were removed under vacuum, and the resulting orange residue was washed with pentane (30 mL). The orange powder that remained was extracted with acetonitrile (20 mL). The extract was concentrated to 10 mL and cooled to –15 °C to yield orange crystals (0.25 g, 67%). The infrared spectrum and melting point of these crystals were identical with those in the above procedure.

Reduction of 6. A solution of 6 (0.25 g, 0.57 mmol) in tetrahydrofuran (30 mL) was vigorously stirred with Na/Hg amalgam (0.013 g of Na, 0.57 mmol; 13 g of Hg) for 3 h. After filtration, a brown powder and mercury remained in the flask. The mercury was removed by decantation to leave 0.13 g (76%) of Cp$_2$NbCl$_2$, identified by IR.

Reaction of 1 with $^1/_2$ equiv of [Cp$_2$Fe]PF$_6$. Dichloromethane (40 mL, –78 °C) was added to a cold (–78 °C) mixture of 1 (0.50 g, 1.5 mmol) and [Cp$_2$Fe]PF$_6$ (0.25 g, 0.75 mmol). The cold bath was removed, and the solution was allowed to stir for 3 h. The volatiles were removed from the orange solution, and the residue was extracted with diethyl ether (40 mL). Evaporation of this extract gave 0.12 g of Cp$_2$Fe (85% based on [Cp$_2$Fe]PF$_6$, identified by ^{1}H NMR). The residue in the flask was then extracted with acetone (40 mL). The acetone extract was quickly filtered and pumped to dryness to give a yellow solid that was washed with diethyl ether (10 mL). This yellow solid (0.31 g, 42% based on 1) was identified as 5 by ^{1}H NMR. A brown powder remaining in the reaction flask was shown to be Cp$_2$NbCl$_2$ (0.20 g, 40% based on 1) by IR.

Collection of Diffraction Data. The parameters used during the collection of diffraction data for 4 and 5 are summarized in Table I. Crystals of 4 and 5 were mounted in thin-walled glass capillaries in an inert-atmosphere glovebox, and the capillaries were flame-sealed.

Systematic absences in the intensity data determined that 4 crystallizes in either of the orthorhombic space groups $Pn2_1a$ or $Pnma$ and uniquely determined that 5 crystallizes in the orthorhombic space group $P2_12_12_1$. 4 was initially solved in the noncentrosymmetric space group $Pn2_1a$, but correlation phenomena quickly indicated the presence of mirror-plane symmetry confirming that $Pnma$ is the correct space group. Unit-cell dimensions were derived from the least-squares fit of the angular settings of 25 reflections with $20° \leq 2\theta \leq 30°$. Absorption corrections were not needed for either compound (regular crystal shapes, low absorption coefficients). No significant decay (<1%) occurred in three standard reflections for either compound. For 4, a profile fitting procedure was applied to all intensity data to improve the precision of the measurement of weak reflections.

Solution and Refinement of Structure. 4 was solved by using the direct methods program SOLV which located the Nb atom. The remaining atoms, including hydrogens, were located from subsequent difference Fourier syntheses. Non-hydrogen atoms were refined anisotropically. The molecule sits on a mirror plane with Nb, Si, C(6), C(7), and C(9) located on the mirror plane.

For 5, the Nb atom was located from a Patterson map. The remaining non-hydrogen atoms were located from subsequent difference Fourier syntheses. Additionally, the two hydrogen atoms of C(b) were located and refined isotropically. All non-hydrogen atoms were refined anisotropically. Idealized atom positions were calculated for the remaining hydrogen atoms (d(C–H) = 0.96 Å, thermal parameters 1.2 times the isotropic equivalent for the carbon atom to which it was attached).

For both compounds, final difference Fourier syntheses showed only diffuse backgrounds (maximum 0.31 e/Å^3, 4; maximum 0.39 e/Å^3, 5). An inspection of F_o vs. F_c values and trends based on sin θ, Miller index, or parity group failed to reveal any systematic errors in the data for either structure. All computer programs used in the data collections and refinements are contained in the Nicolet program packages P3 and SHELXTL (version 5.1).

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, to Research Corp., and to the Air Force Office of Scientific Research (Grant No. AFOSR-85-0228) for support of this work. We thank Prof. Jack Halpern and Prof. Jeff Petersen for helpful discussions and a reviewer for comments regarding the CV studies.

Registry No. 1, 106420-35-3; 2, 106420-36-4; 3, 106420-37-5; 4, 106420-38-6; 5, 106420-40-0; 6, 95615-07-9; Cp$_2$NbCl$_2$, 12793-14-5; [Cp$_2$Fe]PF$_6$, 11077-24-0; Cp$_2$Fe, 102-54-5; Hg(SiMe$_3$)$_2$, 4656-04-6.

Supplementary Material Available: Expanded tables of bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates for 4 and 5 (7 pages); listings of observed and calculated structure factors for 4 and 5 (22 pages). Ordering information is given on any current masthead page.