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Synthesis of Mono- and Bis(silyl) Complexes of Tantalum

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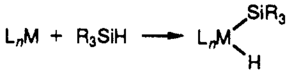
Thermal (ca. 110 °C) or photochemical (350 nm) reaction of $Cp_2Ta(H)_3$ (Cp ≡ η^5-C_5H_5) or $Cp_2Ta(L)(H)$ (L = CO, PMe_3, $CH_2{=}CH_2$) with hydrosilanes ($HSiR_3$) produces the tantalum(V) dihydride silyl complexes $Cp_2Ta(H)_2(SiR_3)$ (1–6; SiR_3 = SiH_3, $SiMeH_2$, $SiMe_2H$, $SiMe_3$, $SiMe_2Cl$, $Si(OMe)_3$) in good to excellent yields. Two structural isomers of the complexes are observed. The major isomer has a symmetrical structure, with the silyl group occupying the central position between two equivalent hydride positions. In contrast, the silyl occupies a lateral position in the minor isomer, giving rise to two unique hydride environments (central and lateral). The tantalum(V) bis(silyl) complexes $Cp_2Ta(H)(SiR_3)_2$ (7–11; SiR_3 = $SiMeH_2$, $SiMe_2H$, $SiMe_3$, $SiMe_2Cl$, $Si(OMe)_3$) can be prepared by treatment of the tantalum(III) methyl complexes $Cp_2Ta(L)(CH_3)$ with excess hydrosilane. In most cases, only the symmetrical isomer with both silyls in lateral positions is observed, although both isomers have been observed for $Cp_2Ta(SiMeH_2)_2(H)$. Thermolysis of the bis(silyl) complexes in the presence of excess PMe_3 leads to high yields of the corresponding tantalum(III) mono(silyl) complexes $Cp_2Ta(PMe_3)(SiR_3)$ (12–15; SiR_3 = $SiMeH_2$, $SiMe_3$, $SiMe_2Cl$, $Si(OMe)_3$). Carbonyl derivatives $Cp_2Ta(CO)(SiR_3)$ (17, 18; SiR_3 = $SiMe_3$, $Si(t\text{-}Bu)_2H$) were prepared by ligand displacement from the corresponding phosphine complexes. Compounds 8 and 13 have been characterized by single-crystal X-ray diffraction studies. 8: orthorhombic space group $P2_12_12_1$ ($Z = 4$) with $a = 7.989$ (1) Å, $b = 8.822$ (1) Å, $c = 23.100$ (3) Å, and $V = 1628.0$ (6) Å^3. 13: orthorhombic space group $P2_12_12_1$ ($Z = 4$) with $a = 8.131$ (1) Å, $b = 9.124$ (2) Å, $c = 25.004$ (2) Å, and $V = 1854.9$ (8) Å^3.

Silyl complexes of the early transition metals exhibit a wealth of reactivity that differs significantly from that of silyls of the less electropositive metals.[2] Recent examples include silane polymerization,[3] C–H bond activation,[4] and silyl migration to unsaturated organic substrates such as carbon monoxide,[5] olefins,[6] and isonitriles.[7,5e] Limitations of the synthetic methods used to prepare early metal–silicon bonds, however, have for the most part restricted study to trialkyl- or triarylsilyl derivatives. In general, the two most common methods for preparing metal–silicon bonds involve (1) salt elimination reactions, starting either from halosilanes and an anionic metal complex (eq 1) or from a metal halide and an anionic silyl derivative (eq 2), or (2) the oxidative addition of hydrosilanes to coordinatively unsaturated transition-metal complexes (eq 3). The first method is limited by the small number of readily available anionic early metal or silicon species. In addition, this route is not generally applicable to the synthesis of silyl complexes with halide or alkoxide substituents. On the other hand, Si–H addition reactions are generally high yield, and usually only volatile substances such as H_2, hydrocarbons, or HX are generated as byproducts, which simplifies the synthetic procedure. Although the oxidative addition route has been widely applied to the synthesis of late-transition-metal silyl complexes, this method has been used to prepare group 5 silyls in only a few instances.[8,9]

$$L_nMM' + XSiR_3 \longrightarrow L_nMSiR_3 + M'X \qquad (1)$$

$$L_nMX + M'SiR_3 \longrightarrow L_nMSiR_3 + M'X \qquad (2)$$



$$L_nM + R_3SiH \longrightarrow L_nM(SiR_3)(H) \qquad (3)$$

In a recent report we demonstrated that two tantalum silyl complexes react with benzene to yield equilibrium mixtures of the silyl and phenyl complexes.[4] A more complete study of this reactivity required a series of tantalum complexes in which steric and electronic effects of the silyl ligand were varied systematically. The ready availability of hydrosilanes made the oxidative addition route most attractive, although we were initially concerned that the electrophilic tantalum center would not be compatible with electronegative substituents such as halide or alkoxide on silicon. Surprisingly, substituted silyl complexes of Ta(III) and Ta(V) can be prepared quite generally and in high yield from hydrosilanes and convenient tantalum starting materials. This contribution describes the synthesis of three classes of tantalum silyl complexes: tantalum(V) silyl dihydride complexes $Cp_2Ta(H)_2(SiR_3)$,

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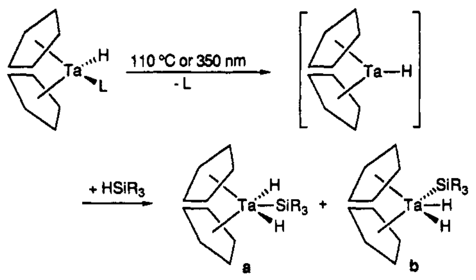
Scheme I



tantalum(V) bis(silyl) complexes $Cp_2Ta(H)(SiR_3)_2$, and tantalum(III) silyl complexes $Cp_2Ta(L)(SiR_3)$ (L = PMe_3, CO). Representative compounds from both of the latter two classes have been structurally characterized. In addition, both symmetrical and unsymmetrical isomers of the tantalum(V) silyl dihydride and bis(silyl) hydride complexes have been characterized.

Results and Discussion

Synthesis of Tantalum(V) Mono(silyl) Complexes $Cp_2Ta(H)_2(SiR_3)$. Organosilicon complexes of group 5 metals are among the most recently explored in the transition-metal series. The first vanadium silyl compound was reported in 1976,[10] whereas the first niobium and tantalum silyl complexes were not reported until 1985, when Curtis and co-workers described the synthesis of silyl dihydride complexes $Cp_2M(H)_2(SiMe_2Ph)$ (M = Ta, Nb) by reaction of $Cp_2M(H)_3$ with phenyldimethylsilane.[8] More recently, Harrod and co-workers described a similar compound, $Cp_2Ta(H)_2(SiH_2Ph)$, in the course of their investigation of the catalytic activity of $Cp_2Ta(H)_3$ toward silane dehydrogenation.[9] In addition, we have previously described another member of this class, $Cp_2Ta(H)_2(SiMe_2H)$, which was prepared by the net insertion of dimethylsilylene into a tantalum hydride bond.[11]

Direct reaction with hydrosilanes is clearly the most general route to these tantalum silyl dihydride complexes. Thermolysis (>100 °C) of $Cp_2Ta(H)_3$ or photolysis (350 nm) of $Cp_2Ta(L)(H)$ (L = CO, PMe_3, $CH_2{=}CH_2$) in the presence of hydrosilanes ($HSiR_3$) affords the corresponding tantalum silyl dihydrides $Cp_2Ta(H)_2(SiR_3)$ (1–6; SiR_3 = SiH_3, $SiMeH_2$, $SiMe_2H$, $SiMe_3$, $SiMe_2Cl$, $Si(OMe)_3$) in good to excellent yields (eq 4).

$$Cp_2Ta(L)(H) + HSiR_3 \xrightarrow{110\ ^\circ C \text{ or } 350\text{ nm}} \underset{1-6}{Cp_2Ta(H)_2(SiR_3)} + L \tag{4}$$

$L = CO, PMe_3, CH_2{=}CH_2, (H)_2$

$SiR_3 = SiH_3, SiMeH_2, SiMe_2H, SiMe_3, SiMe_2Cl, Si(OMe)_3$

Reaction of $Cp_2Ta(H)_3$ with hydrosilanes typically requires days at 110 °C and periodic removal of the hydrogen generated to drive the reaction to completion. The photochemical reaction of $Cp_2Ta(L)(H)$ with excess silane, however, is complete within a few hours. As suggested by Curtis,[8] the initial step is presumably formation of the coordinatively unsaturated "$Cp_2Ta(H)$" by either the thermolytic loss of H_2 or photolytic dissociation of L (Scheme I). Subsequent insertion of this reactive species into a hydrosilane Si–H bond leads to the observed products. Compounds 1–6 are white or off-white solids at room temperature, sublime readily at 60–80 °C under high vacuum, and are very sensitive to oxygen and moisture in both solution and the solid state.

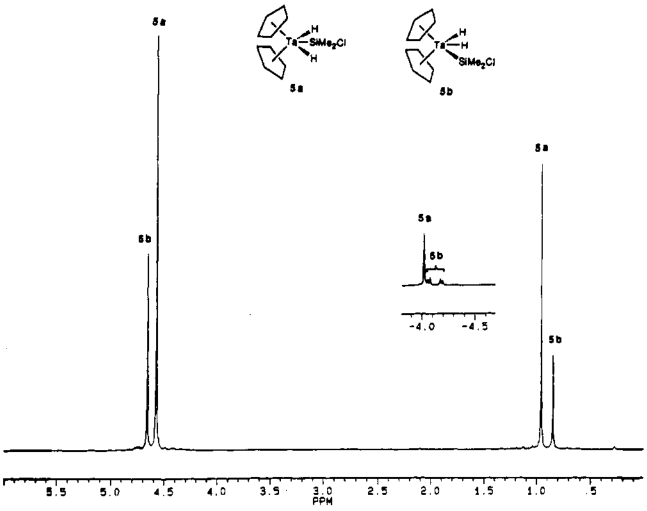


Figure 1. ^1H NMR spectrum of $Cp_2Ta(H)_2(SiMe_2Cl)$ (**5**), showing symmetrical (**5a**) and unsymmetrical (**5b**) isomers.

Table I. NMR Data (δ) for Tantalum(V) Mono(Silyl) Complexes $Cp_2Ta(H)_2(SiR_3)$[a]

compound	^1H NMR	^{29}Si NMR
$Cp_2Ta(H)_2(SiH_3)$ (**1a**)	4.52 (s, 10 H, C_5H_5) 4.21 (t, ^3J = 1.5, 3 H, SiH_3), –3.99 (b, 2 H, TaH)	-74.1
$Cp_2Ta(H)(SiH_3)(H)$ (**1b**)	4.50 (s, 10 H, C_5H_5) 4.46 (d, ^3J = 2.5, 3 H, SiH_3) –3.01 (d, ^2J = 6.1, 1 H, TaH) –4.32 (d, ^2J = 6.1, 1 H, TaH)	-40.1
$Cp_2Ta(H)_2(SiMeH_2)$ (**2a**)	4.93 (m, 2 H, SiH) 4.54 (s, 10 H, C_5H_5) 0.86 (t, ^3J = 4.3, 3 H, $SiCH_3$) –4.35 (b, 2 H, TaH)	-33.5
$Cp_2Ta(H)(SiMeH_2)(H)$ (**2b**)	5.33 (q, ^3J = 4.3, 2 H, SiH) 4.51 (s, 10 H, C_5H_5) 0.71 (t, ^3J = 4.3, 3 H, $SiCH_3$) –3.22 (d, ^2J = 6.7, 1 H, TaH) –4.51 (d, ^2J = 6.7, 1 H, TaH)	-7.0
$Cp_2Ta(H)_2(SiMe_2H)$ (**3a**)	5.38 (sept, ^3J = 4.1, 1 H, SiH) 4.52 (s, 10 H, C_5H_5) 0.79 (d, ^3J = 4.1, 6 H, $SiCH_3$) –4.50 (b, 2 H, TaH)	-5.2
$Cp_2Ta(H)(SiMe_2H)(H)$ (**3b**)	5.32 (sept, ^3J = 3.6, 1 H, SiH) 4.51 (s, 10 H, C_5H_5) 0.63 (d, ^3J = 3.6, 6 H, $SiCH_3$) –3.33 (d, ^2J = 7.5, 1 H, TaH) –4.72 (d, ^2J = 7.5, 1 H, TaH)	15.0
$Cp_2Ta(H)_2(SiMe_3)$ (**4a**)	4.52 (s, 10 H, C_5H_5) 0.61 (s, 9 H, $SiCH_3$) –4.52 (s, 2 H TaH)	10.4
$Cp_2Ta(H)(SiMe_3)(H)$ (**4b**)	4.47 (s, 10 H) 0.49 (s, 9 H, $SiCH_3$) –3.30 (d, ^2J = 7.3, 1 H, TaH) –4.88 (d, ^2J = 7.3, 1 H, TaH)	27.3
$Cp_2Ta(H)_2(SiMe_2Cl)$ (**5a**)	4.55 (s, 10 H, C_5H_5) 0.96 (s, 6 H, $SiCH_3$) –4.03 (s, 2 H, TaH)	76.2
$Cp_2Ta(H)(SiMe_2Cl)(H)$ (**5b**)	4.64 (s, 10 H, C_5H_5) 0.84 (s, 6 H, $SiCH_3$) –4.08 (d, ^2J = 6.0, 1 H, TaH) –4.18 (d, ^2J = 6.0, 1 H, TaH)	83.0
$Cp_2Ta(H)_2(Si(OMe)_3)$ (**6a**)	4.69 (s, 10 H, C_5H_5) 3.73 (s, 9 H, $SiOCH_3$) –4.78 (s, 2 H, TaH)	40.9
$Cp_2Ta(H)(Si(OMe)_3)(H)$ (**6b**)	4.76, (s, 10 H, C_5H_5) 3.70 (s, 9 H, $SiOCH_3$) –4.02, (d, ^2J = 6.0, 1 H, TaH) –4.66, (d, ^2J = 6.0, 1 H, TaH)	40.7

[a] J values in hertz.

The ^1H NMR spectra of these complexes clearly show that two isomers (**a** and **b**) are present in solution, as shown for **5** in Figure 1. The symmetrical isomer (**a**) exhibits one singlet for the two equivalent hydrides, whereas the unsymmetrical isomer (**b**) displays a pair of coupled doublets in the hydride region. Resonances for the Cp

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rings and silyl substituents of each isomer are also observed (Table I). Complexes containing hydrogens on the silyl group (**1**–**3**) also exhibit coupling between this proton and the tantalum hydrides. This three-bond coupling is fairly small (ca. 1–1.5 Hz) and can only be observed in the Si–H resonance by decoupling any additional spin–spin interactions (e.g., SiMe groups). For example, the SiH resonance in the symmetrical isomer **3a** is coupled to two equivalent tantalum hydrides and appears as a triplet (J = 1.5 Hz) when the SiMe resonance is decoupled. In contrast, the SiH resonance of the unsymmetrical isomer **3b** is coupled to only one of the tantalum hydrides and appears as a doublet (J = 1.5 Hz, SiMe decoupled). This coupling is not observed in the tantalum hydride resonances due to their relatively broad line widths.

The chemical shifts of the silyl groups in the ^{29}Si NMR spectra vary over a ca. 150 ppm range. In general, silyls with electron-withdrawing substituents tend to exhibit more downfield shifts, mirroring the trend observed in the parent silanes. In addition, in most of the compounds the resonance for the unsymmetrical isomer is found downfield of the symmetrical isomers ($\Delta\delta$ = 7–34 ppm). However, in the case of the trimethoxy derivative **6** the ^{29}Si chemical shifts of the isomers differ by only 0.2 ppm.

Although the means by which the two isomers interconvert will be the subject of a future publication, it is worth noting here that the rate of isomerization is strongly influenced by the nature of the silyl group. The qualitative ordering of isomerization rates is $SiMe_2Cl$ (**5**) $\approx$ SiH_3 (**1**) < $Si(OMe)_3$ (**6**) $\approx$ $SiMeH_2$ (**2**) < $SiMe_2H$ (**3**) < $SiMe_3$ (**4**). Isomerization occurs rapidly below 25 °C for **3** and **4** but requires hours at 80 °C in the case of **1** and **5**. It has also been shown that the isomerization is intramolecular; i.e., exchange with deuterated free silane does not occur during isomerization. Pure samples of the symmetrical isomers of **1**, **2**, and **5** have been obtained by recrystallization of the mixtures. Pure samples of the minor isomers of **1**–**6** have not yet been isolated, but mixtures containing nearly equal amounts of both isomers can be initially obtained from the relatively low temperature (−50 to 0 °C) photochemical synthetic procedure.

Synthesis of Tantalum(V) Bis(silyl) Complexes $Cp_2Ta(H)(SiR_3)_2$. Bis(silyl) complexes of Ta(V) with the formula $Cp_2Ta(H)(SiR_3)_2$ (**7**–**11**; SiR_3 = $SiMeH_2$, $SiMe_2H$, $SiMe_3$, $SiMe_2Cl$, $Si(OMe)_3$) can be prepared by the reaction of tantalum(III) methyl complexes $Cp_2Ta(L)(CH_3)$ (L = PMe_3, $CH_2{=}CH_2$) with excess $HSiR_3$ under photolytic (350 nm) or thermal (105–110 °C) conditions (eq 5). Methane is also produced in the reaction.

$$Cp_2Ta(L)(CH_3) + 2\ HSiR_3 \xrightarrow[-L]{110\ ^\circ C\ \text{or}\ 350\ \text{nm}} \underset{7-11}{Cp_2Ta(H)(SiR_3)_2} + CH_4 \qquad (5)$$

L = PMe_3, $CH_2{=}CH_2$

SiR_3 = $SiMeH_2$, $SiMe_2H$, $SiMe_3$, $SiMe_2Cl$, $Si(OMe)_3$

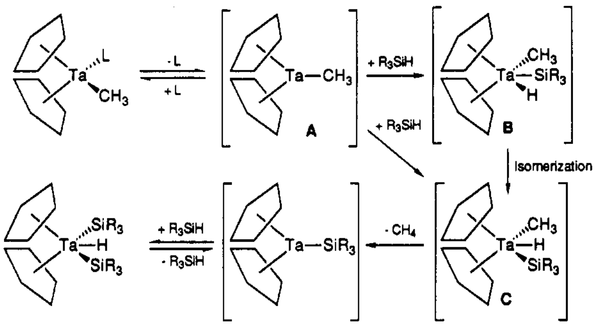
These bis(silyl) complexes are new members of the class of bent metallocene complexes containing three ligands in the equatorial wedge, and as in the case of the mono(silyl) complexes, there are two possible isomers of the bis(silyl) complexes. In this case, however, the symmetrical isomer (**a**) has both silyls in the two equivalent lateral positions and the hydride in the central position. The ^{1}H NMR spectra of the symmetrical isomers are straightforward (Table II). For example, the ^{1}H NMR spectrum of **8a** exhibits resonances consistent with a single environment for the two $SiMe_2H$ groups (δ 5.12, sept, Si*H*; δ 0.52, d, SiC*H*$_3$), along with the hydride resonance (δ −3.90, br). The symmetrical isomer of **8** has also been structurally characterized by a single-crystal X-ray diffraction study (vide infra).

Table II. NMR Data (δ) for Tantalum(V) Bis(Silyl) Complexes $Cp_2Ta(H)(SiR_3)_2$[a]

compound	^{1}H NMR	^{29}Si NMR
$Cp_2Ta(H)(SiMeH_2)_2$ (**7a**)	4.78 (q, ^3J = 3.9, 4 H, Si*H*)	-11.7
	4.35 (s, 10 H, C_5H_5)	
	0.60 (t, ^3J = 3.9, 6 H, SiC*H*$_3$),	
	−3.85 (s, 1 H, Ta*H*)	
$Cp_2Ta(H)(SiMeH_2)_2$ (**7b**)	4.45 (q, 2 H, Si*H*)	-5.9
	4.32 (s, 10 H, C_5H_5)	-23.4
	4.18 (q, 2 H, Si*H*)	
	0.64 (m, 6 H, SiC*H*$_3$)	
	−6.15 (s, 1 H, Ta*H*)	
$Cp_2Ta(H)(SiMe_2H)_2$ (**8**)	5.12 (sept, ^3J = 4.0, 2 H, Si*H*)	11.5
	4.33 (s, 10 H, C_5H_5)	
	0.52 (d, ^3J = 4.0, 12 H, SiC*H*$_3$)	
	−3.90 (s, 1 H, Ta*H*)	
$Cp_2Ta(H)(SiMe_3)_2$ (**9**)	4.32 (s, 10 H, C_5H_5)	24.7
	0.43 (s, 18 H, SiC*H*$_3$)	
	−3.75 (s, 1 H, Ta*H*)	
$Cp_2Ta(H)(SiMe_2Cl)_2$ (**10**)	4.63 (s, 10 H, C_5H_5)	81.0
	0.63 (s, 12 H, SiC*H*$_3$)	
	−5.01 (s, 1 H, Ta*H*)	
$Cp_2Ta(H)(Si(OMe)_3)_2$ (**11**)	4.85 9s, 10 H, C_5H_5)	36.6
	3.69 (s, 18 H, SiOC*H*$_3$)	
	−4.79 (s, 1 H, Ta*H*)	

[a] J values in hertz.

Scheme II



Only the symmetrical isomer is observed for the majority of the bis(silyl) derivatives prepared. In the case of **7**, however, a mixture of both symmetrical and unsymmetrical isomers (ca. 6:1) has been observed by ^{1}H and ^{29}Si NMR (Table II). It has not been determined whether this ratio represents a kinetic or a thermodynamic distribution.

The mechanism of bis(silyl) complex formation can be most easily explained in terms of simple oxidative addition and reductive elimination steps (Scheme II). Thermal or photochemical dissociation of L from $Cp_2Ta(L)(CH_3)$ leads to the 16e$^-$ intermediate A. Oxidative addition of $HSiR_3$ to A could lead to two isomeric Ta(V) complexes, B and C. Reductive elimination of methane from C and subsequent oxidative addition of a second silane would then yield the bis(silyl) product. In most cases, isomerization of B to C should be facile (cf. isomerization of silyl dihydride complexes **1**–**6**), and rapid elimination of methane would preclude observation of B.

However, an intermediate that may correspond to isomer B has been directly observed in photochemical reactions involving $HSiMe_2Cl$. Irradiation of a mixture of $Cp_2Ta(CH_2{=}CH_2)(CH_3)$ and $HSiMe_2Cl$ in benzene-d_6 at 25 °C for approximately 2 h yields a 1:1 mixture of the bis(silyl) product (**10**) and $Cp_2Ta(H)(SiMe_2Cl)(CH_3)$ (intermediate B). The ^{1}H NMR spectrum of the latter exhibits resonances at δ 4.55 (s, C_5H_5), 0.87 (s, SiC*H*$_3$), −0.14 (d, J = 3.2 Hz, TaC*H*$_3$), and −3.18 (q, J = 3.2 Hz, Ta*H*). The chemical shift of the tantalum methyl (δ −0.14) is in the range of values found for related tantalum compounds, e.g., $Cp_2Ta(PMe_3)(CH_3)$ (δ −0.41), $Cp_2Ta(CO)(CH_3)$ (δ −0.36), and $Cp_2Ta(CH_3)_3$ (δ 0.33, 0.30). The spin–spin

Table III. NMR Data (δ) for Tantalum(III) Silyl Complexes $Cp_2Ta(L)(SiR_3)$[a]

compound	^1H NMR	^{29}Si NMR	^{31}P
$Cp_2Ta(PMe_3)(SiMeH_2)$ (12)	4.60 (q, $^3J = 4.4$, 2 H, Si*H*) 4.14 (d, $^3J_{PH} = 2.1$, 10 H, C_5H_5) 0.96 (d, $^2J_{PH} = 7.4$, 9 H, PCH_3) 0.78 (t, $^3J = 4.4$, 3 H, SiC*H*)	-21.3 (d, $J_{PSi} = 15.1$)	-20.4
$Cp_2Ta(PMe_3)(SiMe_3)$ (13)	4.11 (d, $^3J_{PH} = 1.8$, 10 H, C_5H_5) 0.97 (d, $^2J_{PH} = 7.3$, 9 H, PCH_3) 0.49 (s, 9 H, SiC*H*)	9.7 (d, $J_{PSi} = 11.5$)	-20.7
$Cp_2Ta(PMe_3)(SiMe_2Cl)$ (14)	4.23 (d, $^3J_{PH} = 2.3$, 10 H, C_5H_5) 0.96 (d, $^2J_{PH} = 7.9$, 9 H, PCH_3) 0.94 (s, 6 H, SiC*H*)	89.7 (d, $J_{PSi} = 8.6$)	-19.1
$Cp_2Ta(PMe_3)(Si(OMe_3))$ (15)	4.36 (d, $^3J_{PH} = 1.9$, 10 H, C_5H_5) 3.77 (s, 9 H, OCH_3) 1.20 (d, $^2J_{PH} = 7.9$, 9 H, PCH_3)	30.4 (d, $J_{PSi} = 22.9$)	-17.1
$Cp_2Ta(PMe_3)(SiH(t\text{-}Bu)_2)$ (16)	4.26 (d, $^3J_{PH} = 2.4$, 10 H, C_5H_5) 4.06 (s, 1 H, Si*H*) 1.38 (s, 18 H, CCH_3) 0.85 (d, $^2J_{PH} = 6.0$, 9 H, PCH_3)	46.4 (d, $J_{PSi} = 8.9$)	-24.8
$Cp_2Ta(CO)(SiMe_3)$ (17)	4.28 (s, 10 H, C_5H_5) 0.45 (s, 9 H, $SiCH_3$)	7.5	
$Cp_2Ta(CO)(SiH(t\text{-}Bu)_2)$ (18)	4.46 (b, 5 H, C_5H_5) 4.37 (b, 5 H, C_5H_5) 4.03 (s, 1 H, Si*H*) 1.42 (b, 9 H, CCH_3) 1.19 (b, 9 H, CCH_3)	51.1	

[a] *J* values in hertz.

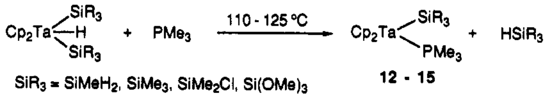
coupling between the hydride and methyl protons has been confirmed by decoupling experiments. Intermediate B is unstable and converts to **10** after 1 day at room temperature in the presence of silane, presumably via isomerization to C, elimination of CH_4, and addition of $HSiMe_2Cl$. The spectroscopic data do not eliminate the possibility that the observed intermediate is itself isomer C, although it is not clear why the $SiMe_2Cl$ derivative would be so stable to methane elimination. Isomerization of the $SiMe_2Cl$ derivative of B, on the other hand, could be expected to be relatively slow in analogy to the trend in isomerization rate of $Cp_2Ta(H)_2(SiR_3)$ complexes. In addition, an analogue, $Cp^*_2Ta(H)(SiH_3)(CH_3)$, has been characterized in solution and assigned structure B by Bercaw and co-workers, although subsequent formation of the bis(silyl) complex was not reported.[12]

Intermediate B has cis silyl and methyl ligands, and an alternate reductive elimination path could generate a new carbon–silicon bond and Cp_2TaH. The latter would react rapidly with hydrosilane to yield $Cp_2Ta(H)_2(SiR_3)$ (**1–6**). However, this pathway does not appear to be significant, as the mono(silyl) complexes and $MeSiR_3$ are not observed in most of the reactions. A trace amount (<2%) of Me_3SiH was observed in the formation of **8**, but this is comparable to the level of Me_3SiH contamination present in the starting Me_2SiH_2.

The extremely hindered bis(silyl) complex $Cp_2Ta(Si(t\text{-}Bu)_2H)_2(H)$ could not be prepared, presumably as a result of unfavorable steric interactions associated with addition of a second bulky silane to the metal center. The reaction of $Cp_2Ta(PMe_3)(CH_3)$ with $H_2Si(t\text{-}Bu)_2$ in cyclohexane or neat silane yields only the tantalum(III) mono(silyl) complex $Cp_2Ta(PMe_3)(Si(t\text{-}Bu)_2H)$, which will be discussed in more detail in the following section.

Synthesis of Tantalum(III) Mono(silyl) Complexes $Cp_2Ta(L)(SiR_3)$. Tilley and co-workers have previously described the synthesis of niobium(III) and tantalum(III) trimethylsilyl complexes by routes in which the metal–silicon bond is introduced with mercury[13] or aluminum silylating agents.[14] Tantalum(III) dimethylsilyl complexes $Cp_2Ta(L)(SiMe_2H)$ (L = CO, PMe_3) have also been prepared in high yield by dimethylsilylene insertion into Ta–H bonds.[11] Neither method, however, is particularly general in scope.

Bis(silyl) complexes **7–11** described above are excellent precursors for the preparation of the corresponding tantalum(III) silyl complexes. Reaction of these bis(silyl) complexes with trimethylphosphine at 110–125 °C produces $Cp_2Ta(PMe_3)(SiR_3)$ (**12–15**; SiR_3 = $SiMeH_2$, $SiMe_3$, $SiMe_2Cl$, $Si(OMe)_3$) as shown in eq 6. The reversibility



(6)

of the reaction requires the use of excess PMe_3 to drive the reaction to completion. In the cases of **14** and **15**, small amounts of $Cp_2Ta(PMe_3)(X)$ (X = Cl, OMe) are also detected, although the mechanism of their formation is unclear. ^1H and ^{29}Si NMR data for these compounds are listed in Table III. In addition, the crystal structure of the trimethylsilyl derivative **13** has been determined (vide infra).

In theory, tantalum(III) silyl phosphine complexes could be prepared directly from the reaction of $Cp_2Ta(PMe_3)(CH_3)$ with 1 equiv of silane. In practice, however, mixtures of $Cp_2Ta(PMe_3)(SiR_3)$, $Cp_2Ta(H)(SiR_3)_2$, and unreacted starting material result. Prolonged heating leads to decomposition. As a result, a one-pot, two-step method is recommended for the synthesis of $Cp_2Ta(PMe_3)(SiR_3)$ from $Cp_2Ta(L)(CH_3)$. Crude $Cp_2Ta(H)(SiR_3)_2$ is generated by the reaction of $Cp_2Ta(L)(CH_3)$ with excess $HSiR_3$, and then all volatiles are removed under vacuum. This residue is dissolved in fresh solvent, excess PMe_3 added, and the mixture maintained at 110–125 °C until conversion to $Cp_2Ta(PMe_3)(SiR_3)$ is complete. The complexes can be purified by recrystallization from toluene/hexanes or by sublimation.

As mentioned in the previous section, the tantalum di-*tert*-butylsilyl phosphine complex $Cp_2Ta(PMe_3)(Si(t\text{-}$

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Table IV. Summary of Structure Determinations of 8 and 13

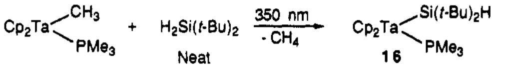
	8	13
formula	$TaSi_2C_{14}H_{25}$	$TaPSiC_{16}H_{28}$
formula weight	430.48	460.41
crystal dimensions, mm	0.60 × 0.45 × 0.15	0.50 × 0.32 × 0.26
crystal class	orthorhombic	orthorhombic
space group	$P2_12_12_1$ (No. 19)	$P2_12_12_1$ (No. 19)
Z	4	4
cell constants		
a, Å	7.989 (1)	8.131 (1)
b, Å	8.822 (1)	9.124 (2)
c, Å	23.100 (3)	25.004 (2)
V, Å^3	1628.0 (6)	1854.9 (8)
μ, cm^{-1}	67.99	59.94
D(calc), g/cm^3	1.76	1.65
F(000)	840	904
radiation	Mo Kα	Mo Kα (0.71073 Å)
θ range, deg	2.0–27.5	2.0–27.5
scan mode	ω–2θ	ω–2θ
h, *k*, *l*	10,11,±29	10,11,32
no. reflcns measd	4358	2473
no. unique reflcns	3728	2465
no. reflcns used in refinement	3557 (>3.0σ)	2252 (>3.0σ)
no. parameters	154	172
data parameter ratio	23.1	13.1
R_1	0.028	0.037
R_2	0.048	0.061
GOF	1.814	1.791

Table V. Bond Distances (Å) in 8[a]

Ta–Si1	2.633 (2)	Si1–C12	1.92 (1)
Ta–Si2	2.624 (2)	Si2–C13	1.91 (1)
Ta–C1	2.371 (9)	Si2–C14	1.888 (9)
Ta–C2	2.423 (9)	C1–C2	1.42 (1)
Ta–C3	2.386 (8)	C1–C5	1.42 (1)
Ta–C4	2.362 (9)	C2–C3	1.46 (1)
Ta–C5	2.37 (1)	C3–C4	1.43 (1)
Ta–C6	2.368 (9)	C4–C5	1.39 (1)
Ta–C7	2.389 (9)	C6–C7	1.40 (1)
Ta–C8	2.366 (9)	C6–C10	1.40 (1)
Ta–C9	2.384 (9)	C7–C8	1.41 (1)
Ta–C10	2.363 (9)	C8–C9	1.39 (1)
Si1–C11	1.89 (1)	C9–C10	1.42 (1)

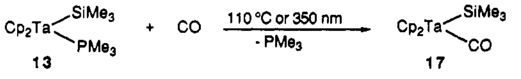
[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Bu)$_2$H) (16) can be prepared directly from Cp$_2$Ta(PMe$_3$)(CH$_3$) and the silane. Compound 16 is formed in high yield upon irradiation of a solution of Cp$_2$Ta(PMe$_3$)(CH$_3$) in neat di-*tert*-butylsilane at 350 nm for 20 h (eq 7). The silane can be separated under vacuum and reused. The resulting red crystalline product (16) reacts with arene C–H bonds at ambient temperature;[4] therefore, aromatic solvents can not be used during its preparation.

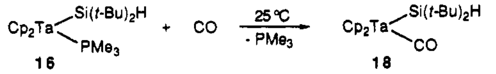


$$Cp_2Ta(CH_3)(PMe_3) + H_2Si(t\text{-}Bu)_2 \ (\text{Neat}) \xrightarrow[-\,CH_4]{350\ \text{nm}} Cp_2Ta(Si(t\text{-}Bu)_2H)(PMe_3)\ \mathbf{16} \qquad (7)$$

The PMe$_3$ ligand in tantalum(III) silyl complexes 13 and 16 can be readily replaced by CO. For example, photolysis of Cp$_2$Ta(PMe$_3$)(SiMe$_3$) under ca. 5 atm of carbon monoxide yields the carbonyl derivative Cp$_2$Ta(CO)(SiMe$_3$) (17) quantitatively (eq 8). Replacement of phosphine with CO in the sterically hindered silyl 16 occurs at room temperature without irradiation (eq 9), reflecting the unusual lability of PMe$_3$ in this complex.



$$Cp_2Ta(SiMe_3)(PMe_3)\ \mathbf{13} + CO \xrightarrow[-\,PMe_3]{110\,^\circ C \text{ or } 350\ \text{nm}} Cp_2Ta(SiMe_3)(CO)\ \mathbf{17} \qquad (8)$$



$$Cp_2Ta(Si(t\text{-}Bu)_2H)(PMe_3)\ \mathbf{16} + CO \xrightarrow[-\,PMe_3]{25\,^\circ C} Cp_2Ta(Si(t\text{-}Bu)_2H)(CO)\ \mathbf{18} \qquad (9)$$

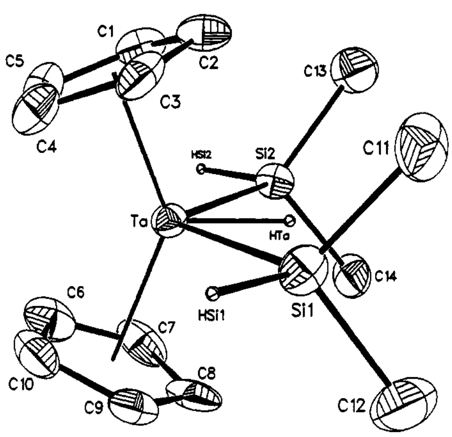


Figure 2. ORTEP drawing of Cp$_2$Ta(H)(SiMe$_2$H)$_2$ (8), showing 30% probability thermal ellipsoids.

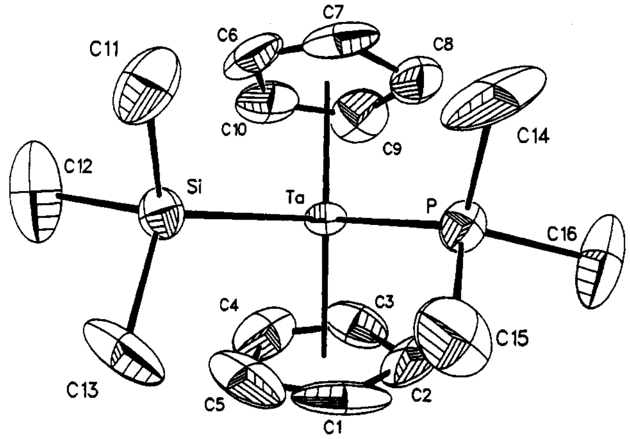


Figure 3. ORTEP drawing of Cp$_2$Ta(PMe$_3$)(SiMe$_3$) (13), showing 30% probability thermal ellipsoids.

Table VI. Selected Bond Angles (deg) in 8[a]

Cp1[b]–Ta–Cp2[b]	138.0	C1–C2–C3	106.8 (8)
Si1–Ta–Si2	109.90 (7)	C2–C3–C4	106.2 (8)
Ta–Si1–C11	114.5 (4)	C3–C4–C5	110.0 (8)
Ta–Si1–C12	116.4 (4)	C1–C5–C4	107.5 (8)
C11–Si1–C12	100.4 (5)	C7–C6–C10	109.8 (8)
Ta–Si2–C13	114.2 (3)	C6–C7–C8	105.4 (8)
Ta–Si2–C14	115.8 (3)	C7–C8–C9	110.5 (8)
C13–Si2–C14	105.0 (5)	C8–C9–C10	106.5 (8)
C2–C1–C5	109.4 (8)	C6–C10–C9	107.8 (8)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] Cp1 and Cp2 refer to the C$_5$H$_5$ centroids.

Table VII. Bond Distances (Å) in 13[a]

Ta–Si	2.639 (4)	Si–C13	1.91 (3)
Ta–P	2.516 (4)	P–C14	1.79 (2)
Ta–C1	2.33 (2)	P–C15	1.80 (3)
Ta–C2	2.32 (2)	P–C16	1.80 (2)
Ta–C3	2.32 (2)	C1–C2	1.33 (4)
Ta–C4	2.38 (2)	C1–C5	1.38 (4)
Ta–C5	2.38 (2)	C2–C3	1.38 (3)
Ta–C6	2.39 (2)	C3–C4	1.33 (4)
Ta–C7	2.33 (2)	C4–C5	1.34 (4)
Ta–C8	2.32 (2)	C6–C7	1.33 (3)
Ta–C9	2.33 (2)	C6–C10	1.32 (3)
Ta–C10	2.38 (2)	C7–C8	1.48 (3)
Si–C11	1.93 (2)	C8–C9	1.41 (3)
Si–C12	1.89 (3)	C9–C10	1.35 (3)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Structures of Cp$_2$Ta(H)(SiMe$_2$H)$_2$ (8) and Cp$_2$Ta(PMe$_3$)(SiMe$_3$) (13). The molecular structures of 8 and

Table VIII. Selected Bond Angles (deg) in 13[a]

Cp1[b]–Ta–Cp2[b]	134.9	C14–P–C16	100 (1)
Si–Ta–P	90.0 (1)	C15–P–C16	97 (1)
Ta–Si–C11	118.4 (7)	C2–C1–C5	113 (2)
Ta–Si–C12	113.1 (8)	C1–C2–C3	103 (2)
Ta–Si–C13	117.4 (7)	C2–C3–C4	112 (2)
C11–Si–C12	100 (1)	C3–C4–C5	108 (2)
C11–Si–C13	103 (1)	C1–C5–C4	105 (2)
C12–Si–C13	102 (1)	C7–C6–C10	111 (2)
Ta–P–C14	119.8 (9)	C6–C7–C8	108 (2)
Ta–P–C15	120.0 (9)	C7–C8–C9	102 (2)
Ta–P–C16	118.0 (8)	C8–C9–C10	109 (2)
C14–P–C15	98 (1)	C6–C10–C9	110 (2)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] Cp1 and Cp2 refer to the C_5H_5 centroids.

13 as determined by single-crystal X-ray diffraction studies are shown in Figures 2 and 3. Crystallographic details are summarized in Table IV, and selected bond distances and angles are listed in Tables V–VIII. Ignoring the tantalum hydride in 8 for the moment, both molecules adopt pseudotetrahedral geometries typical for bent metallocene complexes. The angles subtended by the two Cp ring centroids in the respective complexes (138.0° and 134.9°) are normal, and in each molecule the ligands lie in the "equatorial" plane, which bisects the dihedral formed by the two Cp ligands. In the case of 8, the symmetrical location of the silyls suggests the tantalum hydride lies between the two silicon groups, consistent with the spectroscopic data described above.

A peak that may correspond to the tantalum hydride in 8 was observed in the final difference Fourier map. Interestingly, although this peak was located at a reasonable Ta–H distance (1.60 Å) and was in the $TaSi_2$ plane, it was located asymmetrically between the two silyls (Si–Ta–H = 64°, 45°.) The asymmetrical position results in a fairly short contact with Si2 (1.83 vs 2.48 Å). This distance is comparable to the values observed in "nonclassical" η^2-$HSiR_3$ ligands.[15] In addition, the two silicon atoms subtend an angle of only 109.9 (7)° at tantalum, considerably smaller than the corresponding angle found in other Cp_2ML_3 complexes such as $Cp_2Ta(H)_3$ (125.8 (5)°) and $Cp_2Nb(H)_3$ (126 (3)°).[16] Although the small angle in 8 may reflect adverse steric interactions between the lateral silyls and Cp rings, it would also be consistent with a nonclassical structure in which the bonding interaction allows closer contact between the hydride and one of the silicon atoms. If the unsymmetrical position of the hydride in the solid state is correct, the equivalence of the silyl groups in the NMR spectra would then imply either that the classical and nonclassical silyl groups are rapidly exchanging or that a symmetrical structure is more stable in solution. Unfortunately, the positional parameters of the "hydride" could not be successfully refined, and given the uncertainties associated with locating hydrogen atoms in heavy atom structures, definitive assignment of a nonclassical solid-state structure in 8 will require more substantial evidence. A large crystal of 8 has been grown and a neutron diffraction study is pending.

Table IX. M–Si Bond Lengths in Niobium and Tantalum Silyl Complexes

compound	D(M–Si) (Å)	ref
$Cp_2Nb(C_2H_4)(SiMe_3)$	2.669 (1)	13
$Cp^*Ta(Cl)_3(SiMe_3)$	2.669 (4)	14
$Cp_2Ta(H)_2(SiMe_2Ph)$	2.651 (4)	8
$Cp^*Ta(PMe_3)(Cl)_2(SiMe_3)$	2.642 (1)	14
$Cp_2Ta(PMe_3)(SiMe_3)$	2.639 (4)	this work
$Cp_2Ta(H)(SiMe_2H)_2$	2.624 (2), 2.633 (2)	this work

The Ta–Si bond distances in 8 (2.624 (2), 2.633 (2) Å) and 13 (2.639 (4) Å) are by a small margin the shortest reported (Table IX). The short Ta–Si bond in 13 is consistent with the observation of an inverse correlation of d-electron count with M–Si bond length.[2,13,14] The phosphine ligand in 13 is a better donor and much poorer π acceptor than the ethylene ligand in $Cp_2Nb(CH_2{=}CH_2)(SiMe_3)$; thus, 13 should be substantially more electron rich. Unfortunately, 13 is also somewhat less sterically hindered than the niobium complex, which would also contribute to the shortening of the M–Si bond. The apparent role of steric factors is even more apparent in 8, which exhibits the shortest Ta–Si bonds of all, despite the formal Ta(V), d^0 configuration. This is likely due to the relatively small size and steric anisotropy of the dimethylsilyl groups and clearly points out the difficulty in distinguishing steric and electronic contributions to geometrical parameters.

Experimental Section

General Procedures. All reactions and manipulations were carried out with use of either high-vacuum line techniques or a glovebox under an atmosphere of prepurified N_2. Solvents were distilled from sodium benzophenone ketyl before use. All photolyses were carried out in a Rayonet photochemical reactor with low-pressure mercury arc lamps (350 nm). ^1H NMR spectra were recorded on an IBM AC-250 NMR spectrometer. ^{13}C NMR spectra were obtained at 125.76 MHz on a Bruker AM-500 spectrometer equipped with a $^1H/^{13}C$ dual probe. ^{31}P NMR spectra were obtained at 81.02 MHz on a Bruker AF-200 spectrometer equipped with a broad-band multinuclear probe. ^{29}Si spectra were obtained at 39.73 MHz on a Bruker AF-200 spectrometer with a broad-band multinuclear probe using the DEPT pulse sequence. Benzene-d_6 was used as NMR solvent unless otherwise indicated. The ^1H, ^{13}C, and ^{29}Si spectra are referenced to $SiMe_4$ and ^{31}P spectra are referenced to external standard 85% H_3PO_4. Elemental analyses were performed by Desert Analytics, Galbraith Laboratories, or Mikroanalytisches Labor Pascher (Germany). Infrared measurements were made on a Perkin-Elmer 1430 spectrophotometer, calibrated against polystyrene films, and were measured in benzene solution, unless noted otherwise. High-resolution mass spectra were obtained on a VG Instrument ZAB-E spectrometer using chemical ionization. $Cp_2Ta(H)_3$[17] and $Cp_2Ta(CH_3)(CH_2{=}CH_2)$[18] were prepared as previously described. $(t\text{-}Bu)_2SiH_2$ (Lithco), $HSiMe_2Cl$, and $HSi(OMe)_3$ (Aldrich Chemical) were dried over molecular sieves and degassed before use. All other silanes (SiH_4, $MeSiH_3$, Me_2SiH_2, Me_3SiH) were obtained by reaction of the corresponding chlorosilanes with lithium aluminum hydride and purified by vacuum fractionation.

Preparation of $Cp_2Ta(H)_2(SiH_3)$ (1). A solution of $Cp_2Ta(H)_3$ (320 mg, 1.02 mmol) and SiH_4 (2.5 mmol) in 10 mL of benzene was heated at 110 °C for 5 days with daily freeze–pump–thaw cycles to remove liberated H_2. The reaction was monitored by ^1H NMR. The resulting solution was filtered, and solvents were removed under vacuum. Sublimation of the residue at 85 °C (10^{-4} mmHg) yielded 280 mg of $Cp_2Ta(H)_2(SiH_3)$ (80%) as white solid. The symmetrical isomer of this compound can be obtained by recrystallization of the sublimate from toluene-

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(17) $Cp_2Ta(H)_3$ was prepared in 87% yield by the method reported for $Cp^*_2Ta(H)_3$: Gibson, V. C.; Bercaw, J. E.; Bruton, W. J.; Sanner, R. D. *Organometallics* **1986**, *5*, 976.

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/hexanes at −40 °C. IR: ν(Si–H) 2040, ν(Ta–H) 1776 cm^{-1}. HRMS: *m/e* calcd for $C_{10}H_{14}SiTa$ (M^+ − H), 343.0345; found, 343.0301.

Preparation of $Cp_2Ta(H)_2(SiMeH_2)$ (2). A solution of $Cp_2Ta(H)_3$ (314 mg, 1.0 mmol) and 5.0 mmol of H_3SiMe in 5 mL of toluene was heated at 110 °C for 4 days with daily freeze–pump–thaw cycles to remove liberated H_2. The reaction was monitored by ^{1}H NMR. The resulting solution was filtered, volatiles were removed in vacuo, and the residue was sublimed at 85 °C (10^{-4} mmHg) to yield 340 mg of **2** (99%). IR: ν(Si–H) 2036, ν(Ta–H) 1780 cm^{-1}. HRMS: *m/e* calcd for $C_{11}H_{16}SiTa$ (M^+ − H), 357.0502; found, 357.0465.

$Cp_2Ta(H)_2(SiMe_2H)$ (3). A sealed NMR tube containing $Cp_2Ta(H)(CO)$ (10 mg, 0.029 mmol) and 1.5 mmol of H_2SiMe_2 in 0.5 mL of benzene-d_6 was photolyzed and monitored periodically by ^{1}H NMR. Clean conversion to **3**, as determined by comparison with an authentic sample,[11] was complete within 2 h.

Preparation of $Cp_2Ta(H)_2(SiMe_3)$ (4). A solution of $Cp_2Ta(H)_3$ (314 mg, 1.0 mmol) and 10.0 mmol of $HSiMe_3$ in 5 mL of toluene was heated at 100 °C for 7 days with daily freeze–pump–thaw cycles to remove liberated H_2. The reaction was monitored by ^{1}H NMR. The resulting solution was filtered, volatiles were removed in vacuo, and the residue was sublimed at 70 °C (10^{-4} mmHg) to yield 333 mg of **4** (86%). IR: ν(Ta–H) 1764 cm^{-1}. HRMS: *m/e* calcd for $C_{13}H_{21}SiTa$ (M^+), 386.0893; found, 386.0914.

Preparation of $Cp_2Ta(H)_2(SiMe_2Cl)$ (5). A solution of $Cp_2Ta(H)_3$ (330 mg, 1.05 mmol) and $HSiMe_2Cl$ (190 mg, 2 mmol) in 7 mL of toluene was heated at 105 °C for 3 days with daily freeze–pump–thaw cycles to remove liberated H_2. The reaction was monitored by ^{1}H NMR. The resulting solution was filtered, volatiles were removed in vacuo, and the residue was sublimed at 70 °C (10^{-4} mmHg) to yield 280 mg of **5** (66%; 2:1 mixture of **5a** and **5b**). IR: ν(Ta–H) 1770, 1720 cm^{-1}. HRMS: *m/e* calcd for $C_{12}H_{18}SiTa$ (M^+ − Cl), 371.0658; found, 371.0646. Anal. Calcd for $C_{12}H_{18}ClSiTa$: C, 35.43; H, 4.46. Found: C, 35.13; H, 4.57.

Preparation of $Cp_2Ta(H)_2(Si(OMe)_3)$ (6). A solution containing $Cp_2Ta(H)(CO)$ (100 mg, 0.32 mmol) and $HSi(OMe)_3$ (300 mg, 2.5 mmol) in 10 mL of toluene was irradiated (350 nm) at 15 °C for 4 h. The resulting solution was filtered, solvents were removed under vacuum, and the residue was recrystallized from toluene/hexanes at −40 °C to yield 110 mg of **6** (86%). HRMS: *m/e* calcd for $C_{13}H_{21}O_3SiTa$, 434.0740; found, 434.0782. Anal. Calcd for $C_{13}H_{21}O_3SiTa$: C, 35.95; H, 4.87. Found: C, 35.66; H, 4.75.

Preparation of $Cp_2Ta(H)(SiMeH_2)_2$ (7). A solution of $Cp_2Ta(CH_2{=}CH_2)(CH_3)$ (62 mg, 0.18 mmol) and H_3SiMe (0.72 mmol) in 0.6 mL of benzene was heated at 105 °C for 15 h. The resulting solution was filtered, volatiles were removed by vacuum, and the yellow residue was recrystallized from toluene/hexanes at −40 °C to yield 58 mg of **7** (82%). HRMS: *m/e* calcd for $C_{12}H_{20}Si_2Ta$ (M^+ − H), 401.0584; found, 401.0557. Anal. Calcd for $C_{16}H_{29}Si_2Ta$: C, 35.82; H, 5.26. Found: C, 36.09; H, 5.10.

Preparation of $Cp_2Ta(H)(SiMe_2H)_2$ (8). A solution of $Cp_2Ta(CH_2{=}CH_2)(CH_3)$ (150 mg, 0.42 mmol) and H_2SiMe_2 (4.0 mmol) in 10 mL of benzene was irradiated (350 nm) at 40 °C for 3 h. The reaction was monitored by ^{1}H NMR. The resulting solution was filtered, solvents were removed under vacuum, and the residue was sublimed at 70 °C (10^{-4} mmHg) to yield 140 mg of **8** (77%). IR: ν(Si–H) 1985, ν(Ta–H) 1775 cm^{-1}. HRMS: *m/e* calcd for $C_{14}H_{24}Si_2Ta$ (M^+ − H), 429.0877; found, 429.0858. Anal. Calcd for $C_{14}H_{25}Si_2Ta$: C, 39.06; H, 5.85. Found: C, 37.92; H, 5.96.

Preparation of $Cp_2Ta(H)(SiMe_3)_2$ (9). A solution of $Cp_2Ta(CH_2{=}CH_2)(CH_3)$ (200 mg, 0.56 mmol) and $HSiMe_3$ (1.7 mmol) in 10 mL of benzene was irradiated (350 nm) at 40 °C for 4 h. The reaction was monitored by ^{1}H NMR. The resulting solution was filtered, volatiles were removed in vacuo, and the residue was recrystallized from toluene/hexanes at −40 °C to yield 230 mg of **9** (90%). IR: ν(Ta–H) 1792 cm^{-1}. HRMS: *m/e* calcd for $C_{16}H_{29}Si_2Ta$ (M^+), 458.1288; found, 458.1262. Anal. Calcd for $C_{16}H_{29}Si_2Ta$: C, 41.91; H, 6.37. Found: C, 41.89; H, 6.35.

Preparation of $Cp_2Ta(H)(SiMe_2Cl)_2$ (10). A solution of $Cp_2Ta(CH_2{=}CH_2)(CH_3)$ (360 mg, 1.02 mmol) and $HSiMe_2Cl$ (450 mg, 4.8 mmol) in 10 mL of benzene was heated at 115 °C for 15 h. The resulting solution was filtered, volatiles were removed by vacuum, and the reddish residue was recrystallized from toluene/hexanes at −40 °C to yield 392 mg of **10** (77%). IR: ν(Ta–H) 1760 cm^{-1}. HRMS: *m/e* calcd for $C_{14}H_{23}ClSi_2Ta$ (M^+ − Cl), 463.0507; found, 463.0507. Anal. Calcd for $C_{14}H_{23}Cl_2Si_2Ta$: C, 33.67; H, 4.64. Found: C, 34.37; H, 4.52.

Preparation of $Cp_2Ta(H)(Si(OMe)_3)_2$ (11). A solution of $Cp_2Ta(CH_2{=}CH_2)(CH_3)$ (213 mg, 0.60 mmol) and $HSi(OMe)_3$ (438 mg, 3.6 mmol) in 10 mL of benzene was irradiated (350 nm) at 15 °C for 2.5 h. The reaction was monitored by ^{1}H NMR. A first crop of **11** (178 mg) was separated by filtration of the reaction mixture and washed with toluene. A second crop (74 mg) was obtained by recrystallization of the residue from toluene/hexanes at −40 °C. A total of 252 mg of **11** was collected (76%). IR (Nujol mull): IR: ν(Ta–H) 1723 cm^{-1}.

Photolysis of $Cp_2Ta(CH_2{=}CH_2)(CH_3)$ with $HSiMe_2Cl$: Observation of $Cp_2Ta(CH_3)(SiMe_2Cl)(H)$. A sealed NMR tube containing $Cp_2Ta(CH_2{=}CH_2)(CH_3)$ (10 mg, 0.028 mmol) and $HSiMe_2Cl$ (10 μl, 0.10 mmol) in benzene-d_6 (0.5 mL) was irradiated (350 nm) at 10 °C for 2 h. ^{1}H and ^{13}C NMR spectra were recorded immediately after the photolysis and showed two products in ca. 1:1 ratio. One was the bis(silyl) complex **10** (see Table II). The other was assigned as $Cp_2Ta(CH_3)(SiMe_2Cl)H$. ^{1}H NMR: δ 4.55 (s, 10 H, C_5H_5), 0.87 (s, 6 H, $SiCH_3$), −0.14 (d, 3 H, $TaCH_3$, J = 3.2 Hz), −3.18 (q, 1 H, Ta*H*, J = 3.2 Hz). $^{13}C\{^1H\}$ NMR: δ 94.2 (C_5H_5), 13.1 ($SiCH_3$), −7.2 ($TaCH_3$).

Preparation of $Cp_2Ta(PMe_3)(SiMeH_2)$ (12). A solution of **7** (43 mg, 0.11 mmol) and PMe_3 (4.5 mmol) in 1 mL of benzene was heated at 105–110 °C for 7 days. The resulting solution was then filtered, volatiles were removed in vacuo, and the residue was recrystallized from toluene/hexanes to yield 38 mg of **12** (82%). IR: ν(Si–H) 1976 cm^{-1}. HRMS: *m/e* calcd for $C_{14}H_{24}SiPTa$ (M^+), 432.0865; found, 432.0897.

Preparation of $Cp_2Ta(PMe_3)(SiMe_3)$ (13). A solution of $Cp_2Ta(CH_2{=}CH_2)(CH_3)$ (300 mg, 0.85 mmol) and 5 equiv of $HSiMe_3$ in 10 mL of toluene was irradiated (350 nm) at 10 °C for 2 h. Excess silane was removed under vacuum, 3 mL of PMe_3 was added, and the reaction mixture was heated at 110 °C for 16 h. Volatiles were then removed under vacuum, and the residue sublimed at 75 °C (10^{-4} mmHg) to yield **13** (330 mg, 85% yield). HRMS: *m/e* calcd for $C_{16}H_{28}SiPTa$ (M^+), 460.1178; found, 460.1209.

Preparation of $Cp_2Ta(PMe_3)(SiMe_2Cl)$ (14). A solution of **10** (86 mg, 0.172 mmol) and PMe_3 (3 mL) in 10 mL of benzene was heated at 125 °C for 7 days. The resulting solution was filtered, volatiles were removed in vacuo, and the residue was recrystallized from toluene/hexanes to yield 72 mg of **14** (87%). HRMS: *m/e* calcd for $C_{15}H_{25}ClSiPTa$ (M^+), 480.0632; found, 480.0659. Anal. Calcd for $C_{15}H_{25}ClSiPTa$: C, 37.47; H, 5.24. Found: C, 37.56; H, 5.25.

Preparation of $Cp_2Ta(PMe_3)(Si(OMe)_3)$ (15). A solution of **11** (70 mg, 0.13 mmol) and PMe_3 (3 mL) in 5 mL of THF was heated at 125 °C for 6 days. The resulting solution was then filtered, volatiles were removed in vacuo, and the residue was recrystallized from toluene/hexanes to yield 41 mg of **15** (64%). HRMS: *m/e* calcd for $C_{16}H_{28}O_3SiPTa$ (M^+), 508.1026; found, 508.1003.

Preparation of $Cp_2Ta(PMe_3)(Si(t\text{-}Bu)_2H)$ (16). A solution containing 200 mg (0.50 mmol) of $Cp_2Ta(PMe_3)(CH_3)$ in 20 mL of $H_2Si(t\text{-}Bu)_2$ was irradiated at 350 nm at 10 °C for 20 h. The solution was filtered and the silane removed under vacuum to yield red microcrystalline $Cp_2Ta(PMe_3)(Si(t\text{-}Bu)_2H)$, which can be recrystallized from hexanes (92%). IR: ν(Si–H) 1933 cm^{-1}. Anal. Calcd for $C_{21}H_{38}PSiTa$: C, 47.54; H, 7.22. Found: C, 47.72; H, 7.21.

Preparation of $Cp_2Ta(CO)(SiMe_3)$ (17). A solution containing **13** (54 mg, 0.117 mmol) and CO (0.92 mmol) in 5 mL of toluene was irradiated (350 nm) at 25 °C for 5 h. The resulting solution was filtered, solvents were removed under vacuum, and the residue was recrystallized from toluene/hexanes at −40 °C to yield 43 mg of **17** (89%). ^{13}C NMR: δ 261.5 (*C*O), 84.3 (C_5H_5), 8.46 ($SiCH_3$). IR: ν(CO) 1872 cm^{-1}.

Preparation of $Cp_2Ta(CO)(Si(t\text{-}Bu)_2H)$ (18). A solution containing **16** (100 mg, 0.189 mmol) and CO (1.10 mmol) in 10 mL of cyclohexane was heated at 65 °C for 5 h. The resulting solution was filtered, solvents were removed under vacuum, and the residue was recrystallized from toluene/hexanes at −40 °C to yield 74 mg of 18 (81%). IR: ν(Si–H) 2034, ν(CO) 1880 cm^{-1}. HRMS: m/e calcd for $C_{19}H_{29}OSiTa$ (M^+), 482.1468; found, 482.1471. Anal. Calcd for $C_{19}H_{29}OSiTa$: C, 47.30; H, 6.06. Found: C, 47.20; H, 5.77.

Structure Determinations of 8 and 13. General Crystallographic Procedures. Single crystals of suitable size were grown from toluene/hexanes at −35 °C and sealed in 0.5-mm thin-walled Pyrex capillaries in the glovebox, and the capillaries were mounted on the diffractometer. Refined cell dimensions and their standard deviations were obtained from least-squares refinement of 25 accurately centered reflections with $2\theta > 25°$. Crystal data are summarized in Table IV.

Diffraction data were collected at 295 K on an Enraf-Nonius four-circle CAD-4 diffractometer employing Mo Kα radiation filtered through a highly oriented graphite crystal monochromator. The intensities of three standard reflections measured at intervals of ca. 80 reflections showed no systematic change during data collection. Data collection is summarized in Table IV. The raw intensities were corrected for Lorentz and polarization effects by using the program BEGIN from the SDP+ package.[19] Empirical absorption corrections based on ψ scans were also applied.

All calculations were performed on a VAX 11/785 computer with the SDP+ software package.[19] The full-matrix least-squares refinement was based on F, and the function minimized was $\sum w(|F_o| - |F_c|)^2$. The weights (w) were taken as $4F_o^2/(\sigma(F_o^2))^2$ where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes. Atomic scattering factors and complex anomalous dispersion corrections were taken from refs 20–22. Agreement factors are defined as $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = [\sum w||F_o| - |F_c||^2/\sum w|F_o|^2]^{1/2}$. The goodness of fit is defined as GOF = $[\sum w(|F_o| - |F_c|)^2/(N_o - N_p)]^{1/2}$, where N_o and N_p are the numbers of observations and parameters.

Solution and Refinement for 8. The coordinates of the tantalum and silicon atoms were obtained from three-dimensional Patterson maps. Analysis of subsequent difference Fourier maps led to location of the remaining heavy atoms. Refinement using anisotropic Gaussian amplitudes followed by difference Fourier synthesis resulted in the location of most of the Cp hydrogens and at least one hydrogen on each methyl group. The hydrogens on the silicon atoms were also located. The positions of all hydrogen atoms were optimized (D(C–H) = 0.95 Å, D(Si–H) = 1.45 Å) with use of the program HYDRO.[19] All remaining hydrogen atoms were placed at idealized locations. Final refinement included anisotropic Gaussian amplitudes for all non-hydrogen atoms and fixed positions and fixed isotropic parameters for the hydrogen atoms. A peak was observed in the final difference Fourier map at a distance of 1.604 Å from the metal, lying in the $TaSi_2$ plane and roughly between the silyl ligands. Attempts to refine the position of this peak as a hydrogen atom were not successful, and it was not included in the final structure factor calculation.

Choice of the acentric space group was confirmed by collection and examination of an entire octant of Bijvoet reflections ($hk\bar{l}$), which did not average satisfactorily with the original octant after absorption correction. The second octant was treated as unique data in the final refinement. Correct enantiomer assignment was confirmed by refinement of the other enantiomer to higher agreement factors (R_1 = 0.041, R_2 = 0.068). Final agreement factors for the correct enantiomer were determined as R_1 = 0.028 and R_2 = 0.048. Structure refinement is summarized in Table IV. Final positional parameters, Guassian amplitudes, and structure factor amplitudes for 8 are included in the supplementary material.

Solution and Refinement for 13. All heavy atoms were located by Patterson and difference Fourier methods as described above for 8. Refinement using anisotropic Gaussian amplitudes followed by difference Fourier synthesis resulted in the location of the most of the Cp hydrogens and at least one hydrogen on each methyl group. All remaining hydrogen atoms were placed at idealized locations (D(C–H) = 0.95 Å) with use of the program HYDRO.[19] Final refinement included anisotropic Gaussian amplitudes for all non-hydrogen atoms and fixed positions and fixed isotropic parameters for the hydrogen atoms. Choice of the acentric space group and correct enantiomer assignment was confirmed by refinement of the other enantiomer to higher agreement factors (R_1 = 0.041, R_2 = 0.066). Final agreement factors for the correct enantiomer were determined as R_1 = 0.037 and R_2 = 0.061. Structure refinement is summarized in Table IV. Final positional parameters, Gaussian amplitudes, and structure factor amplitudes for 13 are included in the supplementary material.

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Supplementary Material Available: Tables of positional parameters and anisotropic thermal parameters for 8 and 13 (6 pages); listings of observed and calculated structure factors for 8 and 13 (22 pages). Ordering information is given on any current masthead page.

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