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Inorganic Chemistry Article

The Course of $(R_2R'SiO)_3TaCl_2$ (R = ^tBu, R′ = H, Me, Ph, ^tBu (silox); R = ^iPr, R′ = ^tBu, ^iPr) Reduction Is Dependent on Siloxide Size

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Various sized siloxides (Cy_3SiO > $^tBu_3SiO$ > $^tBu_2PhSiO$ > $^tBu_2MeSiO$ ~ $^iPr_2{}^tBuSiO$ > $^iPr_3SiO$ > $^tBu_2HSiO$) were used to make $(R_2R'SiO)_3TaCl_2$ (R = ^tBu, R′ = H (**1**-H), Me (**1**-Me), Ph (**1**-Ph), ^tBu (**1**); R = ^iPr, R′ = ^tBu (**1**-$^iPr_2$); R = R′ = ^iPr (**1**-$^iPr_3$); R = R′ = ^{c}Hex (Cy)). Product analyses of sodium amalgam reductions of several dichlorides suggest that $[(R_2R'SiO)_3Ta]_2(\mu\text{-}Cl)_2$ may be a common intermediate. When the siloxide is large (**1**-^tBu), formation of the Ta(III) species $(^tBu_3SiO)_3Ta$ (**6**) occurs via disproportionation. When the siloxide is small, the Ta(IV) intermediate is stable (e.g., $[(^iPr_3SiO)_3Ta]_2(\mu\text{-}Cl)_2$ (**2**)), and when intermediate sized siloxides are used, solvent bond activation via unstable Ta(III) tris-siloxides is proposed to occur. Under hydrogen, reductions of **1**-Me and **1**-Ph provide Ta(IV) and Ta(V) hydrides $[(^tBu_2MeSiO)_3Ta]_2(\mu\text{-}H)_2$ (**4**-Me) and $(^tBu_2PhSiO)_3TaH_2$ (**7**-Ph), respectively.

Introduction

The $^tBu_3SiO$ ligand (silox)[1−3] has been used with great success in the preparation of low coordinate, low valent, early transition metal compounds.[4−8] In particular, the generation of $(silox)_3Ta$[8] has led to investigations of CO cleavage[8−10] and a variety of other bond activations.[4−15] Despite extensive study of this unusual complex, including recent calculations testifying to the relatively low energy of its singlet ground state,[7] an understanding of its synthesis and kinetic stability is incomplete.

In a project originally designed to generate new metal−metal bonded derivatives of early transition metals, different siloxides were used to tune the tris-siloxide metal steric parameter, while keeping a similar electronic environment. By analysis of the reduction products of $(R_2R'SiO)_3TaCl_2$ (R = ^tBu, R′ = H, **1**-H; Me, **1**-Me; Ph, **1**-Ph; ^tBu, **1**; R = ^iPr, R′ = ^tBu, **1**-$^iPr_2$; R = R′ = ^iPr, **1**-$^iPr_3$; R = R′ = ^{c}Hex (Cy)), a greater insight into the synthesis of $(silox)_3Ta$ (**6**) was obtained. As a consequence, a uniform rationale for the distribution of reduction products in all of the cases is postulated, and the special nature of **6** was confirmed. Herein are reported these findings along with the syntheses and structures of two new Ta(IV) dimers, $[(^iPr_3SiO)_3Ta]_2(\mu\text{-}Cl)_2$ (**2**) and $[(^tBu_2MeSiO)_3Ta]_2(\mu\text{-}H)_2$ (**4**-Me).

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Results

Syntheses of $R_2R'SiH$, $R_2R'SiOH$, and $R_2R'SiONa$ ($R = {}^tBu$, $R' = H$, Me, Ph, ${}^tBu$; $R = R' = {}^iPr$). The syntheses of the various silanols started from readily available precursors: ${}^tBu_2SiHCl$, ${}^tBu_2SiH_2$, ${}^iPr_2SiHCl$, ${}^iPr_3SiH$, and Cy_3SiCl. In a modification of a Doyle and West procedure,[16] thermolysis of ${}^tBu_2SiHCl$ and methyllithium in Et_2O at 67 °C in a bomb reactor afforded the colorless oil ${}^tBu_2SiHMe$ in 94% yield (eq 1). Treatment of ${}^iPr_2SiHCl$ with 1 equiv of ${}^tBuLi$ in a 3:4 mixture of pentane/heptane at 23 °C generated ${}^iPr_2{}^tBuSiH$ in 43% yield (eq 2) upon distillation. A lower boiling fraction accounted for 30% of the crude mass, and spectroscopic analysis of this material failed to discern an Si−H functionality. A pathway involving silylene formation via deprotonation may be operable, and the generation of silylenes via electron transfer is also well documented.[17] A related thermolysis of ${}^tBu_2SiH_2$ and phenyllithium in heptane at 98 °C led to the elimination of LiH and the ultimate isolation of ${}^tBu_2SiHPh$ as a colorless oil (63%, eq 3).[18]

$$ {}^tBu_2SiHCl + MeLi \xrightarrow[67\ ^\circ C,\ 20\ h]{Et_2O} {}^tBu_2MeSiH + LiCl \qquad (1)$$

$$ {}^iPr_2SiHCl + {}^tBuLi \xrightarrow[23\ ^\circ C,\ 16\ h]{pentane/heptane} {}^iPr_2{}^tBuSiH + LiCl \qquad (2)$$

$$ {}^tBu_2SiH_2 + PhLi \xrightarrow[98\ ^\circ C,\ 14\ h]{heptane} {}^tBu_2PhSiH + LiH \qquad (3)$$

Exposure of the silanes to KOH/EtOH provided the silanols ${}^tBu_2RSiOH$ (R = Me (84%),[19] Ph (87%)) and ${}^iPr_2RSiOH$ ($R = {}^iPr$ (98%), ${}^tBu$ (75%)) in excellent yields (eq 4).

$$ R_2R'SiH \xrightarrow[78\ ^\circ C,\ 20-36\ h]{KOH,\ EtOH} R_2R'SiOH \qquad (4)$$

$R = {}^tBu$, $R' = Me$, Ph;
$R = {}^iPr$, $R' = {}^tBu$;
$R = R' = {}^iPr$

${}^tBu_2PhSiOH$, ${}^iPr_2{}^tBuSiOH$, and ${}^iPr_3SiOH$ are colorless oils, but sublimed ${}^tBu_2MeSiOH$ is a waxy, crystalline, white solid. ${}^tBu_2HSiOH$ was prepared according to a literature procedure[20] utilizing KOH/EtOH treatment of the chloride ${}^tBu_2SiHCl$. A related literature method was used to synthesize Cy_3SiOH from Cy_3SiCl.[21] Preparations[1,2] of ${}^tBu_3SiOH$ are related to eqs 1−4, since 2 equiv of ${}^tBuLi$ reacts with ${}^tBu_2SiF_2$, or 1 equiv of ${}^tBuLi$ reacts with ${}^tBu_2SiHF$, to generate ${}^tBu_3SiH$, and it is subsequently hydrolyzed with base.

A convenient preparation of ${}^tBu_3SiONa$ involves thermolysis of the silanol with sodium metal,[22] and this method was extended to the new species (eq 5).

$$ R_2R'SiOH \xrightarrow[111\ ^\circ C,\ 4-24\ h]{Na^0,\ toluene} R_2R'SiONa \qquad (5)$$

$R = {}^tBu$, $R' = H$, Me, Ph;
$R = {}^iPr$, $R' = {}^tBu$;
$R = R' = {}^iPr$, Cy

The sodium siloxides ranged from an amorphous, colorless solid (${}^iPr_3SiONa$, 87%)[23] to white, crystalline materials (${}^iPr_2{}^tBuSiONa$ (59%), Cy_3SiONa (>90%), and ${}^tBu_2RSiONa$ (R = H (47%), Me (79%), Ph (69%)). Spectral data for the silanes, silanols, and sodium siloxides are compiled in Table 1. Recent crystal structures of ${}^tBu_3SiONa$ and ${}^tBu_2PhSiONa$—prepared via N_2O treatment of the respective sodium silicides—reveal these species to be tetramers, with Na and O atoms occupying alternate corners of a cube.[24] A related structure of ${}^tBu_2MeSiONa$ has also been determined.[25]

Syntheses of $(R_2R'SiO)_3TaCl_2$ ($R = {}^tBu$, $R' = H$, Me, Ph, ${}^tBu$; $R = {}^iPr_2$, $R' = {}^tBu$; $R = R' = {}^iPr$). The tris-siloxide tantalum dichlorides were synthesized via treatment of $TaCl_5$ with the sodium siloxides in benzene or toluene, typically under thermolysis conditions (eq 6).

$$ TaCl_5 + 3R_2R'SiONa \rightarrow (R_2R'SiO)_3TaCl_2 + 3NaCl \qquad (6)$$

$R = {}^tBu$, $R' = H$ (**1**-H), Me (**1**-Me),
Ph (**1**-Ph);
$R = {}^iPr$, $R' = {}^tBu$ (**1**-${}^iPr_2$)
$R = R' = {}^iPr$ (**1**-${}^iPr_3$), Cy (**1**-Cy_3)

Although formation of $({}^tBu_2HSiO)_3TaCl_2$ (**1**-H, 55%) occurred in benzene at 23 °C after only 4 h of stirring, $({}^tBu_2MeSiO)_3TaCl_2$ (**1**-Me, 63%) required 16 h at 55 °C, and $({}^tBu_2PhSiO)_3TaCl_2$ (**1**-Ph, 69%), $({}^iPr_2{}^tBuSiO)_3TaCl_2$ (**1**-${}^iPr_2$, 51%), $({}^iPr_3SiO)_3TaCl_2$ (**1**-${}^iPr_3$, 42%), and $(Cy_3SiO)_3TaCl_2$ (**1**-Cy_3) were prepared by refluxing the reagents in toluene (>110 °C) for 20, 16, 12, and 20 h, respectively. $(silox)_3TaCl_2$ (**1**) was also prepared in refluxing toluene during a 15 h period.[8] All of the dichlorides are white, crystalline complexes, although **1**-H is quite waxy.

Dichloride Reductions. 1. $({}^iPr_3SiO)_3TaCl_2$ (1-${}^iPr_3$). Sodium amalgam reduction of $({}^iPr_3SiO)_3TaCl_2$ (**1**-${}^iPr_3$) in THF or DME resulted in a blue-purple solution whose color faded over the course of 1 h. Amidst several products, $({}^iPr_3SiO)_3TaO$ was tentatively identified on the basis of spectral characteristics and comparison to related reactions, but isolation was not attempted. Instead, Na/Hg reduction of **1**-${}^iPr_3$ in Et_2O afforded the Ta(IV) dimer $[({}^iPr_3SiO)_3Ta]_2(\mu\text{-}Cl)_2$ (**2**, eq 7), and excess Na^0 failed to further reduce the complex.

$$ 2\ \underset{\mathbf{1}\text{-}{}^iPr_3}{({}^iPr_3SiO)_3TaCl_2} \xrightarrow[Et_2O,\ 36-48\ h]{Na/Hg,\ -2NaCl} \underset{\mathbf{2}}{[({}^iPr_3SiO)_3Ta]_2(\mu\text{-}Cl)_2} \qquad (7)$$

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Table 1. ^{1}H and $^{13}C\{^{1}H\}$ NMR Spectral Assignments[a] for $R_2R'SiX$ (X = H, OH, or ONa), $(R_2R'SiO)_3TaCl_2$, and Its Reduction Products

	^{1}H NMR (δ (*J*, Hz), assignt)		$^{13}C\{^{1}H\}$ NMR (δ, assignt)	
compound	^{t}Bu	R/R′/other	$SiCMe_3$, $SiC(CH_3)_3$	R/R′/other
$^{t}Bu_2MeSiH$[b]	0.99	−0.01 (d, 4), Me		
$^{t}Bu_2PhSiH$[c]	1.02	3.63 (q, 4), SiH		
$^{i}Pr_2{}^{t}BuSiH$[d]	1.02	1.11 (d, 7.5), Me		
		1.13 (d, 7.5), Me		
		3.54, SiH		
$^{t}Bu_2MeSiOH$[e]	0.97	−0.03, Me		
$^{t}Bu_2PhSiOH$	1.02	7.21 (dd, 2, 5), *p*-Ph	21.14, 30.09	128.31, Ph
		7.44 (dd, 2, 8.5), *m*-Ph		133.94, Ph
		7.64 (m, 2), *o*-Ph		144.28, Ph
$^{i}Pr_2{}^{t}BuSiOH$[d]	0.99	1.07 (d, 5.6)		
$^{i}Pr_3SiOH$[d]		1.03 (d, 7.5), Me		12.15, CH
		3.59 (q, 2), OH		18.28, Me
$^{t}Bu_2HSiONa$	1.03	4.37 (SiH)		
$^{t}Bu_2MeSiONa$	1.02	−0.06, Me		
$^{t}Bu_2PhSiONa$	1.11	7.11 (m, 4.8), *m*-Ph		
		7.71 (dd, 1.6), *o*,*p*-Ph		
$^{i}Pr_2{}^{t}BuSiONa$	1.06	1.14 (d, 7), Me		
		1.15 (d, 7), Me		
$^{i}Pr_3SiONa$		1.08 (d, 7), Me		
		0.91 (sep, 7), CH		
$(^{t}Bu_2HSiO)_3TaCl_2$ (**1**-H)				
$(^{t}Bu_2MeSiO)_3TaCl_2$ (**1**-Me)	1.15	0.31, Me	21.54, 27.86	−7.07, Me
$(^{t}Bu_2PhSiO)_3TaCl_2$ (**1**-Ph)	1.31	7.19 (m, 2, 8), *m*-Ph	22.60, 28.70	127.87, Ph
		8.03 (m, 7), *o*/*p*-Ph		129.85, Ph
				133.80, Ph
				135.30, Ph
$(^{i}Pr_2{}^{t}BuSiO)_3TaCl_2$ (**1**-$^{i}Pr_2$)	1.22	1.26 (d, 8), Me	22.00, 28.21	14.20, CH
		1.29 (d, 8), Me		18.89, Me
		1.40 (m, 8), CH		
$(^{i}Pr_3SiO)_3TaCl_2$ (**1**-$^{i}Pr_3$)		1.22 (d, 5.6)		13.29, CH
				7.95, Me
$(Cy_3SiO)_3TaCl_2$ (**1**-Cy_3)		1.25 (dt, 2, 13)		25.75
		1.36 (q, 8.5)		27.49
		1.61 (q, 12.5)		28.07
		1.76 (br s)		28.85
		1.86 (d, 10.5)		
		2.07 (d, 13.5)		
$[(^{i}Pr_3SiO)_3Ta]_2(\mu\text{-}Cl)_2$ (**2**) (23 °C)		1.26 (br m, 7.2), CH		15.15, CH
		1.36 (br d, 6.8), Me		15.23, CH
				18.82, Me
				19.19, Me
(70°C)		1.29 (br s), Me		
		1.42 (br m), CH		
$[(^{t}Bu_2MeSiO)_3Ta]_2(\mu\text{-}O)_2$ (**3**-Me)	1.22	0.35		
$[(^{i}Pr_2{}^{t}BuSiO)_3Ta]_2(\mu\text{-}O)_2$ (**3**-$^{i}Pr_2$)	1.26	1.31 (d, 7.2), Me		
		1.32 (d, 6.8), Me		
		1.38 (sep, 7.6), CH		
$[(^{t}Bu_2MeSiO)_3Ta]_2(\mu\text{-}H)_2$ (**4**-Me)	1.21	0.47, Me		
		8.54, TaH		
$[(^{i}Pr_2{}^{t}BuSiO)_3Ta]_2(\mu\text{-}H)_2$ (**4**-$^{i}Pr_2$)	1.24	1.32 (d, 7.2), Me		
		1.33 (d, 7.2), Me		
		1.43 (sep, 7.6), CH		
		7.73, TaH		
$[(^{t}Bu_2MeSiO)_3TaH]_2(\mu\text{-}O)$ (**5**-Me)	1.22	0.36, Me		
		10.97, TaH		
$[(^{i}Pr_2{}^{t}BuSiO)_3TaH]_2(\mu\text{-}O)$ (**5**-$^{i}Pr_2$)[d]	1.26	1.14 (d, 11.2), Me		
		1.22 (d, 9.6), Me		
$(^{t}Bu_2PhSiO)_3TaH_2$ (**7**-Ph)	1.20	7.11 (m, 5.7), *o*/*p*-Ph		
		7.90 (dd, 1.8,5.7), *m*-Ph		
		22.72, TaH		
$(^{t}Bu_2PhSiO)_3Ta(\eta\text{-}C_2H_4)$ (**8**-Ph)	1.15	2.61, C_2H_4		
		7.20 (m, 5.5), *o*/*p*-Ph		
		7.84 (m, 7), *m*-Ph		
$(^{t}Bu_2MeSiO)_3TaCH_2(CH_2)_2CH_2$ (**9**-Me)	1.11	0.22, Me		
		2.13 (q, 3), $(CH_2)_2$		
		2.83 (q, 3), $(CH_2)_2$		
$(^{i}Pr_3SiO)_3TaCH_2(CH_2)_2CH_2$ (**9**-$^{i}Pr_3$)[d]		1.17, (d, 3), Me		
		2.12, (m, 1.5), $(CH_2)_2$		
		2.84, (m, 2.5), $(CH_2)_2$		
$(^{t}Bu_2MeSiO)_3Ta(\eta\text{-}C_2Me_2)$ (**10**-Me)	1.09	0.21, SiMe		
		2.58, C_2Me_2		
$(^{t}Bu_2PhSiO)_3Ta(\eta\text{-}C_2Me_2)$ (**10**-Ph)	1.17	2.59, C_2Me_2		
		7.21 (m, 1.2, 4.8), *o*/*p*-Ph		
		7.87 (m, 2), *m*-Ph		
$(^{i}Pr_3SiO)_3Ta(\eta\text{-}C_2Me_2)$ (**10**-$^{i}Pr_3$)[d]		1.17 (d, 3), Me		
		2.60, C_2Me_2		
$(^{t}Bu_2PhSiO)_3TaMe_2$ (**11**-Ph)	1.21	1.48, $TaMe_2$		
		7.19 (m, 3), *o*/*p*-Ph		
		7.92 (m, 1.5), *m*-Ph		

[a] Benzene-d_6 unless otherwise noted. [b] Reference 16. [c] Reference 18. [d] Methine is obscured. [e] Reference 19.

Table 2. Crystallographic Data for $[(^iPr_3SiO)_3Ta]_2(\mu\text{-}Cl)_2$ (**2**) and $[(^tBu_2MeSiO)_3Ta]_2(\mu\text{-}H)_2$ (**4**-Me)

	2	**4**-Me
formula	$C_{54}H_{126}Cl_2O_6Si_6Ta_2$	$C_{54}H_{126}O_6Si_6Ta_2$
fw	1472.89	1401.99
space group	$C2/c$	$P\bar{1}$
Z	4	2
a, Å	13.9922(8)	12.9177(16)
b, Å	25.2621(14)	13.4760(17)
c, Å	21.2191(11)	23.148(3)
α, deg	90	82.096(3)
β, deg	101.9680(10)	74.402(3
γ, deg	90	64.714(3)
V, Å^3	7337.3(7)	3508.2(8)
ρ_{calc}, g·cm^{-3}	1.333	1.327
μ, mm^{-1}	3.190	3.258
temp, K	173(2)	173(2)
λ, Å	0.71073	0.71073
R indices $[I > 2\sigma(I)]^{a,b}$	$R_1 = 0.0402$	$R_1 = 0.0577$
	$wR_2 = 0.0740$	$wR_2 = 0.1570$
R indices (all data)^{a,b}	$R_1 = 0.0680$	$R_1 = 0.0829$
	$wR_2 = 0.0810$	$wR_2 = 0.1689$
GOF^c	1.020	1.146

[a] $R_1 = S||F_o| - |F_c||/S|F_o|$. [b] $wR_2 = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$. [c] GOF (all data) $= [\sum w(|F_o| - |F_c|)^2/(n - p)]^{1/2}$, n = number of independent reflections, p = number of parameters.

The dimer was obtained as purple crystals from pentane in 40% yield. At 23 °C, the ^1H NMR spectrum C_6D_6 of **2** consists of three broad asymmetric resonances in the methyl region that overlap with a very broad feature whose integration is roughly consistent with the methine protons. At 70 °C, the spectrum simplifies immensely and the signals coalesce to a broad singlet at δ 1.29 accompanied by a broad multiplet at δ 1.42 corresponding to a single isopropyl group; the original spectrum was reconstituted upon cooling. Further heating (>70 °C) induced decomposition and a change in color from purple to brown.

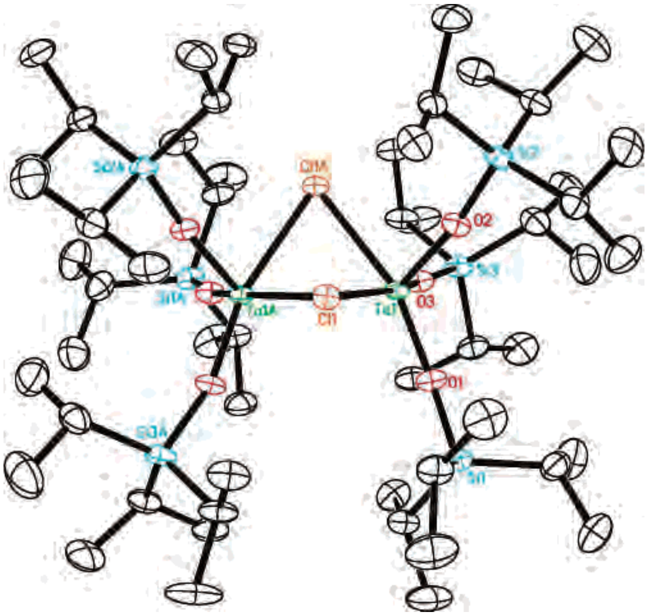

Figure 1. Molecular view of $[(^iPr_3SiO)_3Ta]_2(\mu\text{-}Cl)_2$ (**2**).

2. Structure of $[(^iPr_3SiO)_3Ta]_2(\mu\text{-}Cl)_2$ (2). A single crystal X-ray diffraction study of $[(^iPr_3SiO)_3Ta]_2(\mu\text{-}Cl)_2$ (**2**) confirmed its dimeric nature and permitted rationalization of the aforementioned ^1H NMR spectrum. The crystallographic information is given in Table 2, pertinent geometric data are presented in Table 3, and a molecular view is presented in Figure 1. The tantalum atoms are bridged by two chlorides, and the compound possesses C_2 symmetry, which distinguishes each of the $^iPr_3SiO$ ligands on one metal. A somewhat long Ta−Ta single bond[26−33] of 2.9773 Å is present, presumably because the μ-Cl ligands must adopt a severe angle (∠Ta−Cl1−Ta = 70.47(2)°) to accommodate the metal−metal interaction. The overall geometry is best described as two edge-shared square pyramids, whose apical siloxides are elongated (d(Ta−O2) = 1.989(2) Å) relative to the basal ligands (d(Ta−O1) = 1.864(2) Å, d(Ta−O3) = 1.859(2) Å). The basal siloxides are splayed (∠O1−Ta−O3 = 98.81(11)°, ∠O1−Ta−Cl1 = 89.46(8)°, ∠O3−Ta−Cl1A = 88.17(8)°) relative to the μ-chlorides (∠Cl1−Ta−Cl1A = 80.62(3)°, ∠Cl−Ta−O3 = 164.80(9)°, ∠Cl1A−Ta−O1 = 163.18(9)°), but the sum of the basal angles is 357.1°; hence, there is only minor deviation from the plane, and it is steric in origin. The apical−basal angles (∠O1−Ta−O2 = 107.63(11)°, ∠O3−Ta−O2 = 105.79(11)°, ∠Cl−Ta−O2 = 83.54(8)°, ∠Cl1A−Ta−O2 = 84.87(8)°) are a testament to the regular nature of the square pyramids and the interplay of the sterically encumbered $^iPr_3SiO$ ligands. The C_2 symmetry of the dimer is a consequence of a subtle twist of the siloxide groups to minimize steric interactions between the ligands on adjacent metals.

3. Reductions of $(R_2R'SiO)_3TaCl_2$ ($R = {}^tBu$, $R' = H$ (1-H), Me, (1-Me); $R = {}^iPr$, $R' = {}^tBu$ (1-^{i}Pr$_2$)). Reduction of $(^tBu_2HSiO)_3TaCl_2$ (**1**-H) led to intractable material, and evidence of C−O bond activation was obtained when $(^tBu_2MeSiO)_3TaCl_2$ (**1**-Me) was reduced with Na/Hg in ethereal solvents. In THF, Na/Hg reductions led to numerous products according to ^1H NMR spectral analysis, including $[(^tBu_2MeSiO)_3Ta]_2(\mu\text{-}O)_2$ (**3**-Me) and species containing resonances consistent with $-O(CH_2)CH_2-$ fragments.[5,9] In Et_2O, after ∼24 h, **1**-Me was converted (Na/Hg or K/C_8) to a roughly 1:1 mixture of **3**-Me and $[(^tBu_2MeSiO)_3Ta]_2(\mu\text{-}H)_2$ (**4**-Me), as indicated in Scheme 1. The compounds cocrystallize as a dark red-brown material. A single crystal X-ray

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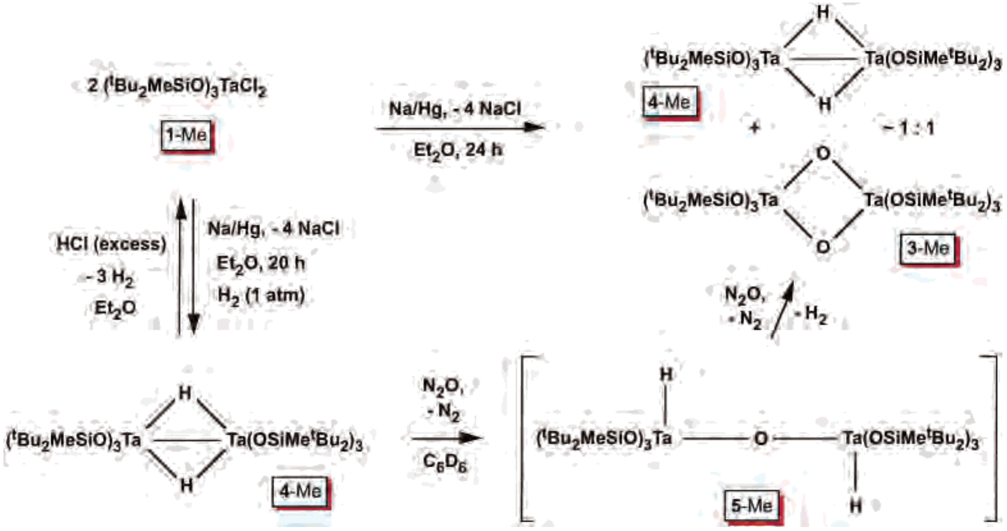
Table 3. Bond Distances (Å) and Angles (deg) in $[(^iPr_3SiO)_3Ta]_2(\mu\text{-}Cl)_2$ (**2**)

Ta−Ta	2.9773(3)	Ta−O1	1.864(2)	Ta−O2	1.989(2)
Ta−O3	1.859(2)	Ta−Cl1	2.5907(8)	Ta−Cl1A	2.5702(9)
Si1−O1	1.670(3)	Si2−O2	1.657(3)	Si3−O3	1.675 (3)
$Si−C_{av}$	1.877(7)	$C−C_{av}$	1.536(11)		
O1−Ta−O2	107.63(11)	O1−Ta−O3	98.81(11)	O2−Ta−O3	105.79(11)
O1−Ta−Cl1	89.46(8)	O1−Ta−Cl1A	163.18(9)	O2−Ta−Cl1	83.54(8)
O2−Ta−Cl1A	84.87(8)	O3−Ta−Cl1	164.80(9)	O3−Ta−Cl1A	88.17(8)
Cl1−Ta−Cl1A	80.62(3)	Ta−Cl1−Ta	70.47(2)	O1−Ta−Ta	108.09(9)
O2−Ta−Ta	123.21(8)	O3−Ta−Ta	110.57(8)	Cl1−Ta−Ta	54.45(2)
Cl1A-Ta−Ta	55.09(2)	Ta−O1−Si1	169.74(16)	Ta−O2−Si2	171.35(18)
Ta−O3−Si3	164.14(18)	$O−Si−C_{av}$	105.9(15)	$C−Si−C_{av}$	112.8(14)
$Si−C−C_{av}$	114.0(19)	$C−C−C_{av}$	110.4(8)		

Scheme 1



structure determination of a representative crystal generated geometric parameters and electron densities inconsistent with a single compound. Spectroscopic investigations and fractional crystallizations led to partial and then eventual separation of the yellow dioxo (**3**-Me) and black dihydride (**4**-Me) dimers. Assignment of **3**-Me as a dimer is based on the cocrystallization with **4**-Me, its yellow color in comparison to monomeric, colorless $(silox)_3TaO$,[8] and solubility properties.

Dihydride **4**-Me was more conveniently prepared via Na/Hg reduction in Et_2O under 1 atm of dihydrogen and isolated from pentane as black crystals in 52% yield. A diagnostic resonance at δ 8.54 that is absent in **4**-Me-d_2 is attributed to the bridging hydrides, but IR spectra are less informative. A shoulder present in **4**-Me at ~1350 cm^{-1} is lost upon deuteration, but the expected position (~960 cm^{-1}) of the corresponding Ta−D absorption in **4**-Me-d_2 is obscured by ligand vibrations. Since the hydrides were not observed crystallographically (vide infra), additional evidence for the Ta(IV) formulation was obtained via treatment with excess HCl. Toepler pump measurements of the gas evolved indicated 2.8 equiv per dimer, consistent with a Ta(IV) dihydride; two hydrides are protonated to give 2 equiv of H_2, and 2 equiv of HCl oxidizes two Ta(IV) centers to Ta(V), releasing 1 equiv of H_2.

When $[(^tBu_2MeSiO)_3Ta]_2(\mu\text{-}H)_2$ (**4**-Me) was exposed to excess N_2O in C_6D_6, a new set of hydride resonances were observed to grow in at δ 10.97 along with new siloxide signals. These gradually dissipated over 2 weeks, and resonances attributable to $[(^tBu_2MeSiO)_3Ta]_2(\mu\text{-}O)_2$ (**3**-Me) grew in concomitantly with the evolution of H_2, which was observed at δ 4.46. Thermolysis at 100 °C for 4 h completed the conversion. Apparently, nitrous oxide oxidized Ta(IV) to Ta(V), formulated as $[(^tBu_2MeSiO)_3TaH]_2(\mu\text{-}O)$ (**5**-Me), and then formally oxidized hydride to dihydrogen as **3**-Me was generated.

The reduction chemistry of $(^iPr_2{}^tBuSiO)_3TaCl_2$ (**1**-$^iPr_2$) paralleled that of $(^tBu_2MeSiO)_3TaCl_2$ (**1**-Me), but it was not pursued in detail because of the difficult isolations of the silane and silanol. However, a small scale reduction of **1**-$^iPr_2$ under dihydrogen in Et_2O afforded $[(^iPr_2{}^tBuSiO)_3Ta]_2(\mu\text{-}H)_2$ (**4**-$^iPr_2$) on the basis of its black appearance and a hydride resonance at δ 7.73 that integrates properly versus the siloxide ligands. Addition of 2 equiv of N_2O to **4**-$^iPr_2$ generated a new hydride resonance at δ 9.77, and thermolysis at 160 °C (24 h) produced H_2 and, presumably, dioxo $[(^iPr_2{}^tBuSiO)_3Ta]_2(\mu\text{-}O)_2$ (**3**-$^iPr_2$). The hydride resonance of the intermediate suggests that it belongs to $[(^iPr_2{}^tBuSiO)_3TaH]_2(\mu\text{-}O)_2$ (**5**-$^iPr_2$), given the related chemistry of **5**-Me.

4. Structure of $[(^tBu_2MeSiO)_3Ta]_2(\mu\text{-}H)_2$ (4-Me). A single crystal X-ray structure determination of $[(^tBu_2MeSiO)_3Ta]_2(\mu\text{-}H)_2$ (**4**-Me) was conducted, and the crystallographic data (Table 2) and geometric features (Table 4) are independently tabulated. Figure 2 illustrates the pseudo-D_{3d} symmetry that describes the dimer, whose hydrides were not located. The d(Ta−Ta) value is 2.8713(4) Å, which is

Table 4. Bond Distances (Å) and Angles (deg) in $[(^tBu_2MeSiO)_3Ta]_2(\mu\text{-}H)_2$ (**4**-Me)

Ta−Ta	2.8710(5)	Ta1−O1	1.894(8)	Ta1−O2	1.898(8)
Ta1−O3	1.934(7)	Ta2−O4	1.910(8)	Ta2−O5	1.917(8)
Ta2−O6	1.929(8)	O1−Si1	1.663(8)	O2−Si2	1.669(8)
O3−Si3	1.653(7)	O4−Si4	1.649(8)	O5−Si5	1.648(8)
O6−Si6	1.657(8)	Si−C_{av}	1.894(17)	C−C_{av}	1.540(10)
O1−Ta1−O2	102.9(4)	O1−Ta1−O3	106.5(3)	O2−Ta1−O3	104.5(4)
O4−Ta2−O5	105.0(4)	O4−Ta2−O6	104.5(4)	O5−Ta2−O6	103.8(4)
O1−Ta1−Ta2	113.0(3)	O2−Ta1−Ta2	112.5(3)	O3−Ta1−Ta2	116.1(3)
O4−Ta2−Ta1	113.5(3)	O5−Ta2−Ta1	112.2(3)	O6−Ta2−Ta1	116.7(2)
Ta1−O1−Si1	175.6(6)	Ta1−O2−Si2	166.6(6)	Ta1−O3−Si3	173.8(6)
Ta2−O4−Si4	175.4(6)	Ta2−O5−Si5	168.3(6)	Ta2−O6−Si6	171.3(5)
O−Si−C_{av}	108.2(14)	C−Si−C_{av}	110.7(30)	Si−C−C_{av}	110.7(23)
C−C−C_{av}	108.2(8)				

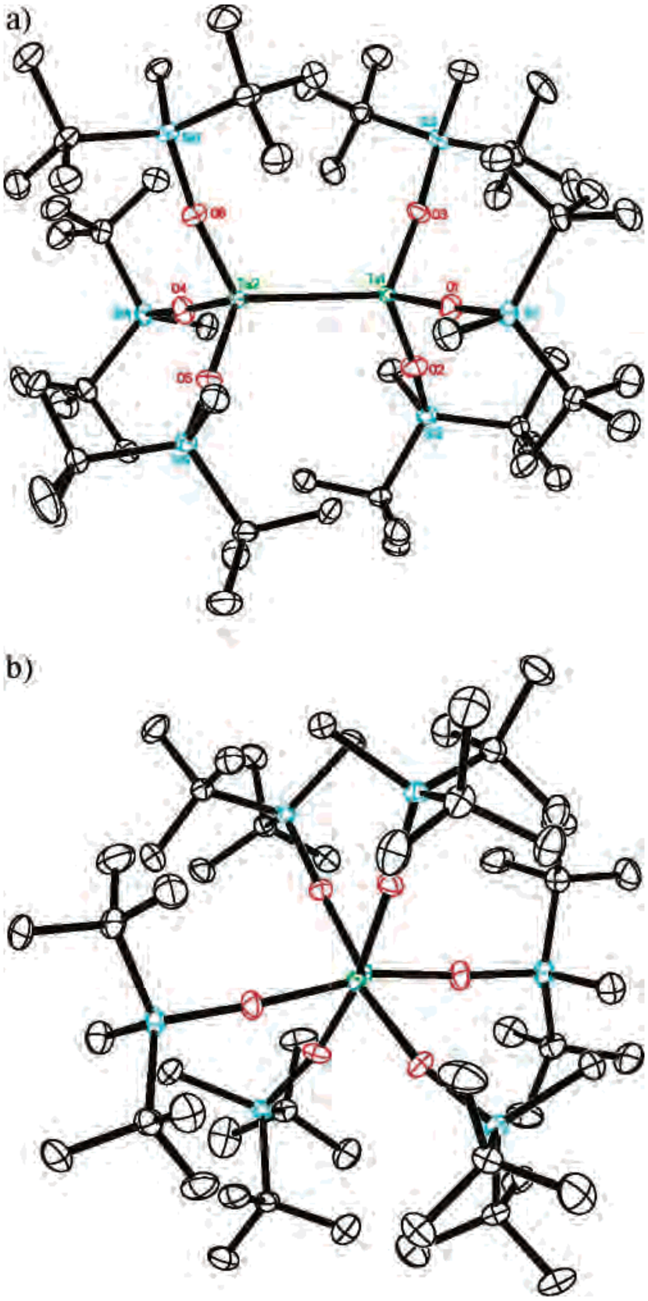


Figure 2. Molecular views of $[(^tBu_2MeSiO)_3Ta]_2(\mu\text{-}H)_2$ (**4**-Me): (a) from the side (hydrides not located) and (b) down the Ta−Ta axis.

shorter than that of $[(^iPr_3SiO)_3Ta]_2(\mu\text{-}Cl)_2$ (**2**) but longer than the sum of covalent radii and longer than that of the unbridged Ta(IV) dimers (e.g., $[(silox)_2TaH_2]_2$, d(Ta−Ta) = 2.720(4) Å).[9,26−34] Two tantalum oxygen distances are marginally longer (d(Ta1−O3) = 1.926(4) Å, d(Ta2−O6) = 1.924(4) Å) than the remaining four ($d(\text{Ta−O})_{av}$ = 1.901(7) Å). The O−Ta−O angles are statistically the same ($\angle$O−Ta−O_{av} = 104.4(10)°), but $\angle$Ta1−Ta2−O6 (116.55(12)°) and $\angle$Ta2−Ta1−O3 (116.18(13)°) were marginally larger than the remaining Ta−Ta−O angles (113.1(6)° (av)). Perhaps the hydrides are more oriented toward O3 and O6, but the deviations about the ditantalum unit are so minimal that it is difficult to assign their positions with any confidence.

5. Reductions of $(^tBu_2R'SiO)_3TaCl_2$ (R′ = Ph, 1-Ph; ^{t}Bu, 1). The Na/Hg reduction of $(silox)_3TaCl_2$ (**1**) has previously been reported to afford $(silox)_3Ta$ (**6**).[8] Reduction in the presence of H_2 or simple exposure of **6** to dihydrogen provides $(silox)_3TaH_2$ (**7**, δ(TaH) 21.99).[9] By comparison, reduction of $(^tBu_2PhSiO)_3TaCl_2$ (**1**-Ph) afforded a multitude of products that constituted a tan oil; identification proved unfeasible, but cyclometalation to various Ta(V) isomers is likely. In the presence of dihydrogen, reduction provided the dihydride $(^tBu_2PhSiO)_3TaH_2$ (**7**-Ph) in 80% yield as a colorless oil (eq 8).

$$\underset{\mathbf{1}\text{-Ph}}{(^tBu_2PhSiO)_3TaCl_2} \xrightarrow[Et_2O]{Na/Hg,\ -2NaCl,\ H_2\ (1\ atm)} \underset{\mathbf{7}\text{-Ph}}{(^tBu_2PhSiO)_3TaH_2} \tag{8}$$

The ^1H NMR spectrum of **7**-Ph, whose TaH_2 resonance is observed at δ 22.72, is diagnostic for a terminal dihydride,[9,27] and its IR spectrum contains a peak at a frequency of ν(TaH(D)) = 1751(1262) cm^{-1} and a corresponding wag ($\delta(TaH_2(D_2))$ at 783(533) cm^{-1}.[9] Cundari has calculated that the lowest energy structure of $(HO)_3TaH_2$ (**7′**) is a trigonal bipyramid with diequatorial hydrides; an isomer with axial and equatorial hydrides is a few kilocalories per mole higher, and the diaxial dihydride is not a minimum energy configuration.[35,36] The infrared spectrum is also consistent with the predicted diequatorial hydride structure.

Further Probes of Siloxide Steric Environment. It appears that the size of the siloxide significantly affects the

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reduction chemistry of the various dichlorides. To help provide further evidence of the size order in the siloxides, small scale reactions were used to probe the formation of olefin adducts versus metalacycles derived from ethylene and 2-butyne. ^1H NMR spectroscopic assays of the crude reaction mixture were used to ascertain the major product composition, but no purification or isolation was attempted. Examples of metalacyclopentanes[5,14,37] and ethylene and 2-butyne adducts[11] in these systems are documented. For the cases of $(^tBu_3SiO)_3Ta$ (**6**) and the reduction of $(^tBu_2PhSiO)_3TaCl_2$ (**1**-Ph), only the olefin adducts $(^tBu_3SiO)_3Ta(\eta\text{-}C_2H_4)$ (**8**-^{t}Bu)[11] and $(^tBu_2PhSiO)_3Ta(\eta\text{-}C_2H_4)$ (**8**-Ph) were obtained (eq 9), but for $(^tBu_2MeSiO)_3TaCl_2$ (**1**-Me) and $(^iPr_3SiO)_3TaCl_2$ (**1**-^{i}Pr$_3$), metalacycles $(^tBu_2MeSiO)_3Ta(-CH_2(CH_2)_2CH_2-)$ (**9**-Me) and $(^iPr_3SiO)_3Ta(-CH_2(CH_2)_2CH_2-)$ (**9**-^{i}Pr$_3$) were the observed products (eq 10). Reductions in the presence of 2-butyne led to the monoadducts in all cases (eq 11), just as exposure of **6** to 2-butyne afforded $(silox)_3Ta(\eta\text{-}C_2Me_2)$ (**10**).[11]

$$\underset{\mathbf{1}\text{-Ph}}{(^tBu_2PhSiO)_3TaCl_2} \xrightarrow[Et_2O]{Na/Hg,\ -2NaCl,\ C_2H_4\ (1\ atm)} \underset{\mathbf{8}\text{-Ph}}{(^tBu_2PhSiO)_3Ta(\eta\text{-}C_2H_4)} \quad (9)$$

$$\begin{array}{c}(R_2R'SiO)_3TaCl_2\\ R = {}^tBu,\ R' = Me\ (\mathbf{1}\text{-Me});\\ R = R' = {}^iPr\ (\mathbf{1}\text{-}{}^iPr_3)\end{array} \xrightarrow{Na/Hg,\ -2NaCl,\ C_2H_4\ (1\ atm)} \begin{array}{c}(R_2R'SiO)_3Ta(-CH_2(CH_2)_2CH_2-)\\ R = {}^tBu,\ R' = Me\ (\mathbf{9}\text{-Me});\\ R = R' = {}^iPr\ (\mathbf{9}\text{-}{}^iPr_3)\end{array} \quad (10)$$

$$\begin{array}{c}(R_2R'SiO)_3TaCl_2\\ R = {}^tBu,\ R' = Ph\ (\mathbf{1}\text{-Ph});\\ R = {}^tBu,\ R' = Me\ (\mathbf{1}\text{-Me});\\ R = R' = {}^iPr\ (\mathbf{1}\text{-}{}^iPr_3)\end{array} \xrightarrow{Na/Hg,\ -2NaCl,\ C_2Me_2\ (1\ atm)} \begin{array}{c}(R_2R'SiO)_3Ta(\eta\text{-}C_2Me_2)\\ R = {}^tBu,\ R' = Ph\ (\mathbf{10}\text{-Ph});\\ R = {}^tBu,\ R' = Me\ (\mathbf{10}\text{-Me});\\ R = R' = {}^iPr\ (\mathbf{10}\text{-}{}^iPr_3)\end{array} \quad (11)$$

Additional NMR tube and small scale experiments were also informative. Treatment of the Ta(IV) dichloride dimer $[(^iPr_3SiO)_3Ta]_2(\mu\text{-}Cl)_2$ (**2**) with 1 equiv of ethylene swiftly afforded the metalacycle $(^iPr_3SiO)_3Ta(-CH_2(CH_2)_2CH_2-)$ (**9**-^{i}Pr$_3$) and the Ta(V) dichloride $(^iPr_3SiO)_3TaCl_2$ (**1**-^{i}Pr$_3$); some starting material remained, and thus, the reaction can be taken as a simple disproportionation (eq 12). In analogous fashion, treatment of **2** with 1 equiv of 2-butyne again gave the dichloride **1**-^{i}Pr$_3$ concomitantly with the alkyne adduct $(^iPr_3SiO)_3Ta(\eta\text{-}C_2Me_2)$ (**10**-^{i}Pr$_3$, eq 13).

$$\underset{\mathbf{2}}{[(^iPr_3SiO)_3Ta]_2(\mu\text{-}Cl)_2} + 2C_2H_4 \xrightarrow{C_6D_6} \underset{\mathbf{9}\text{-}{}^iPr_3}{(^iPr_3SiO)_3Ta(-CH_2(CH_2)_2CH_2-)} + \underset{\mathbf{1}\text{-}{}^iPr_3}{(^iPr_3SiO)_3TaCl_2} \quad (12)$$

$$\underset{\mathbf{2}}{[(^iPr_3SiO)_3Ta]_2(\mu\text{-}Cl)_2} + C_2Me_2 \xrightarrow{C_6D_6} \underset{\mathbf{10}\text{-}{}^iPr_3}{(^iPr_3SiO)_3Ta(\eta\text{-}C_2Me_2)} + \underset{\mathbf{1}\text{-}{}^iPr_3}{(^iPr_3SiO)_3TaCl_2} \quad (13)$$

Addition of 2 equiv of MeMgBr to $(^tBu_2PhSiO)_3TaCl_2$ (**1**-Ph) in Et_2O provided the dimethyl derivative $(^tBu_2PhSiO)_3TaMe_2$ (**11**-Ph) as a colorless, crystalline solid (eq 14).

$$\underset{\mathbf{1}\text{-Ph}}{(^tBu_2PhSiO)_3TaCl_2} + MeMgBr \xrightarrow[-78\ °C \rightarrow 23\ °C,\ 12\ h]{Et_2O} \underset{\mathbf{11}\text{-Ph}}{(^tBu_2PhSiO)_3TaMe_2} + MgBrCl \quad (14)$$

No reaction was observed when derivatization of $(silox)_3TaCl_2$ (**1**) was attempted with a variety of methyl anion equivalents. Dimethyl **11**-Ph was thermolyzed for several hours at 180 °C without noticeable decomposition.

Discussion

Background. Although the objective of creating metal–metal bonded species without bridging ligands has yet to be realized, this initial foray into attenuating the steric bulk of $(silox)_3Ta$ (**6**) has provided valuable insights into the reduction chemistry of $(R_2R'SiO)_3TaCl_2$. With the aid of calculations on the model $(HO)_3Ta$ (**6′**),[7] the stability of **6**, which has pseudo-D_{3h} symmetry, is now better understood. Its $^1A_1'$ ground state reflects a $(d_{z^2})^2$ configuration that is ~14 kcal/mol below that of the $^3E''$ state, which is the lowest lying triplet state. The pair of electrons in the d_{z^2} orbital serves as a potent repulsive interaction to any approaching ligands;[11] hence, the UV–vis spectrum of **6** is unchanged in nonpolar media like hexane versus polar media containing moderately strong donors for early metals such as THF. The pocket of three $(^tBu_3SiO)$ groups restricts the approach of any donor to be along the z axis and greatly hampers attack at the empty d_{xz} and d_{yx} (e″) orbitals. It is the combination of sterics and electronics that enables **6** to exist. Calculations reveal that "$(silox)_3Nb$" also possesses a singlet ground state, but its lowest triplet state is only ~2 kcal/mol away.[7] The triplet state is not repulsive to incoming ligands; hence, $(silox)_3Nb$ has never been directly observed, and it binds L in cases where **6** does not (e.g., PMe_3). When generated in the absence of L, cyclometalation to $(silox)_2H\overline{NbOSi^tBu_2CMe_2CH_2}$ is swift. The corresponding cyclometalation of **6** has a barrier

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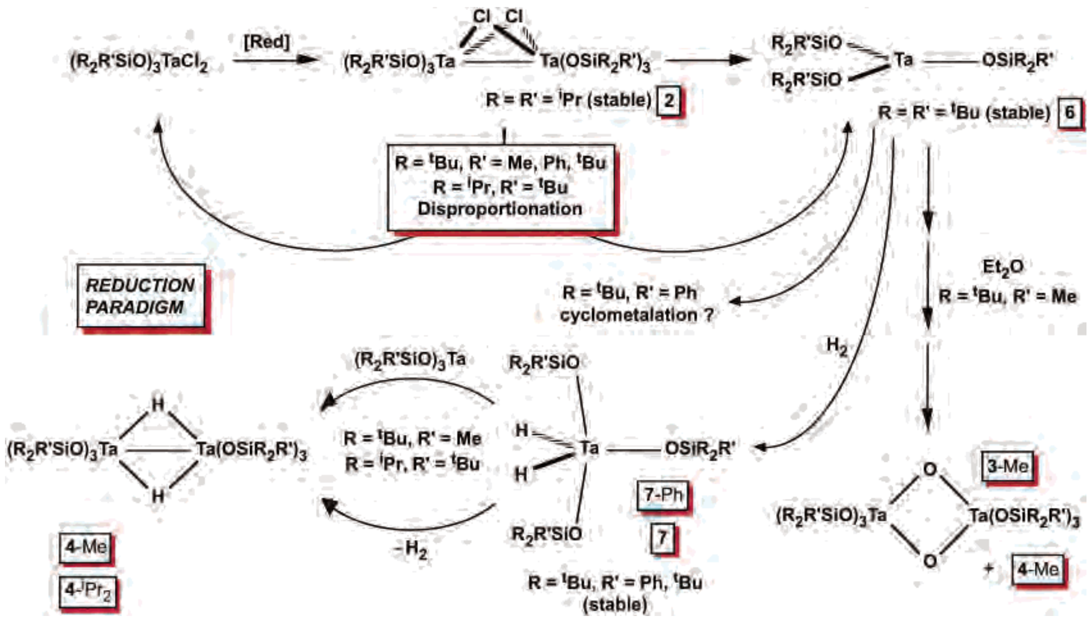
Scheme 2



of $\Delta G^{\ddagger} = 24.5$ (30) kcal/mol[38] because the pair of electrons in the d_{z^2} orbital prevents binding of a C−H bond of a ^{t}Bu "arm" prior to activation.

Reduction Paradigm. Previously, the $E°_{red}$ at −1.90 V (vs normal hydrogen electrode (NHE)) for (silox)$_3$TaCl$_2$ (**1**) to [(silox)$_3$TaCl$_2$]$^-$ was determined to be reversible.[6] Evidence of further reduction at more negative potentials was not observed, and it is plausible that, under Na/Hg conditions, direct generation of (silox)$_3$Ta (**6**) is not thermodynamically feasible. Assuming that all tris-siloxide tantalum dichlorides would behave similarly, the products derived from reduction fit the pattern based on siloxide sterics illustrated in Scheme 2. Reduction of the Ta(V) dichlorides affords the bridging dichloride Ta(IV) dimer, which is stable when the smallest siloxide is utilized, that is, [(^{i}Pr$_3$SiO)$_3$Ta]$_2$(μ-Cl)$_2$ (**2**). For all other cases, significant steric interactions of the adjacent metal centers encourage disproportionation to the respective Ta(V) dichlorides and tris-siloxide tantalum species. Note that even **2** disproportionates when ethylene or 2-butyne is present (eqs 11 and 12). Use of the most sterically encumbered siloxide, ^{t}Bu$_3$SiO, leads to the stable three coordinate complex (silox)$_3$Ta (**6**), but this species gradually cyclometalates to $(silox)_2H\overline{TaOSi^tBu_2CMe_2CH}$ over a period of days at room temperature. With a slightly less hindered siloxide, ^{t}Bu$_2$PhSiO, the (^{t}Bu$_2$PhSiO)$_3$Ta species is not stable, and while identification of the products was not possible, cyclometalation to a number of isomers is a plausible result. In the presence of H$_2$, the Ta(III) intermediate is trapped to afford (^{t}Bu$_2$PhSiO)$_3$TaH$_2$ (**7**-Ph), just as the addition of H$_2$ to **6** provides (silox)$_3$TaH$_2$ (**7**). In neither case is ether cleavage noted, although, upon standing in THF, trace amounts of (silox)$_3$TaO are produced as **6** cyclometalates. Whether the origin of the oxo-ligand is THF has not been determined, but **6** has been shown to deoxygenate epoxides and oxidatively add 2,3-dihydrofuran and 3,3-dimethyloxetane to give (silox)$_3$TaO(CH$_2$)$_2$CH=CH and (silox)$_3$TaOCH$_2$CMe$_2$CH$_2$, respectively.[13]

Under dihydrogen, reductions of (^{t}Bu$_2$MeSiO)$_3$TaCl$_2$ (**1**-Me) and (^{i}Pr$_2$^{t}BuSiO)$_3$TaCl$_2$ (**2**-^{t}Bu) may be construed as paralleling those of (silox)$_3$TaCl$_2$ (**1**-^{t}Bu) and (^{t}Bu$_2$PhSiO)$_3$TaCl$_2$ (**1**-Ph) to afford the tris-siloxide dihydrides, but these species are not stable. Either the Ta(V) dihydrides undergo a dinuclear reductive elimination to produce [(^{t}Bu$_2$MeSiO)$_3$Ta]$_2$(μ-H)$_2$ (**4**-Me) and [(^{i}Pr$_2$^{t}BuSiO)$_3$Ta]$_2$(μ-H)$_2$ (**4**-^{i}Pr$_2$) or the Ta(V) dihydrides scavenge the tris-siloxide Ta(III) species faster than dihydrogen. In either instance, the difference in products relative to (silox)$_3$TaH$_2$ (**7**) and (^{t}Bu$_2$PhSiO)$_3$TaH$_2$ (**7**-Ph) stems from the smaller size of the siloxides, which permits formation of the dinuclear Ta(IV) complexes. It should be noted that no conditions have been found to convert [(silox)$_2$TaH$_2$]$_2$ to a mononuclear Ta(V) hydride complex;[9] hence, there is precedent for tantalum−tantalum bond creation in preference to additional TaH bond formation.

Reduction of (^{t}Bu$_2$MeSiO)$_3$TaCl$_2$ (**1**-Me) in ethers provided evidence of C−O bond scission, and in the case of diethyl ether, the bis-μ-oxo [(^{t}Bu$_2$MeSiO)$_3$Ta]$_2$(μ-O)$_2$ (**3**-Me) and the bis-μ-hydrido [(^{t}Bu$_2$MeSiO)$_3$Ta]$_2$(μ-H)$_2$ (**4**-Me) are the products. The fate of the ethyl groups has not been determined, but no (^{t}Bu$_2$MeSiO)$_3$TaCH$_2$(CH$_2$)$_2$CH$_2$ (**9**-Me), which would be the expected product from a tris-siloxide Ta(III) species and ethylene, was detected. If disproportionation from the bis-μ-chloride dimer affords (^{t}Bu$_2$MeSiO)$_3$Ta, it is proposed that the smaller siloxide allows access to the d_{xz} and d_{yz} orbitals by the nucleophilic oxygen of an ether molecule. This juxtaposition of electrophilic (empty d_{xz} and d_{yz}) and nucleophilic (filled d_{z^2}) orbitals has previously been proposed as the key element in C−O, N−H, C−N, and C−H bond activations by (silox)$_3$Ta (**6**),[4−15] which can activate certain ethers, as mentioned above.[13] In the formation of **3**-Me and **4**-Me, C−O bond cleavage to yield (^{t}Bu$_2$MeSiO)$_3$EtTaOEt

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(38) Veige, A. S. Ph.D. Thesis, Cornell University, 2002.

is a logical start to numerous mechanisms; various binuclear scenarios involving C−O bond activation are also reasonable. While the reaction is clearly reproducible, the yields and the corresponding amount of byproduct do not foment optimism for further mechanistic evaluation.

Siloxide Steric Order. From the preceding discussion, the rough order of siloxide size is $^tBu_3SiO$ > $^tBu_2PhSiO$ > $^tBu_2MeSiO$ ∼ $^iPr_2{}^tBuSiO$ > $^iPr_3SiO$. Not enough information was obtained for $^tBu_2HSiO$ to accurately order it, but previous estimates of silicon steric factors indicate it as the smallest of this grouping.[39] Similarly, solubility difficulties pertaining to the chemistry of Cy_3SiO species precluded its inclusion in this paper, and the same estimates show it as the largest.[39] The ability to alkylate $(^tBu_2PhSiO)_3TaCl_2$ (**1**-Ph) under conditions that failed for $(silox)_3TaCl_2$ (**1**-^{t}Bu) supports its ordering. Since **1**-Ph is the only dichloride other than **1**-^{t}Bu to give an ethylene adduct when reduced in the presence of C_2H_4, it certainly contains the next most bulky siloxide investigated.

Conclusions

The paradigm for the reduction of $(siloxide)_3TaCl_2$ satisfactorily explains the experiments on this project to date and aids in rationalizing 20 years of observations pertaining to $(silox)_3Ta$ (**6**). Now that the sterics of the siloxides have been assessed, it is hoped that the designed synthesis of unsupported metal−metal bonded complexes will ultimately be realized through the extension of this chemistry to other early metals.

Experimental Section

General Considerations. All manipulations were performed using either glovebox or high vacuum line techniques. Hydrocarbon solvents, containing 1−2 mL of added tetraglyme, and ethereal solvents were distilled under nitrogen from purple benzophenone ketyl and vacuum transferred from the same. All glassware was oven dried prior to use. NMR tubes and glassware that was used in reductions were additionally flame dried under active vacuum prior to use. Gaseous reagents (H_2 (Matheson) and D_2 (Cambridge Isotope Laboratories) were slowly passed through a 77 K trap prior to use; N_2O and ethylene (Matheson) were passed through a −78 °C trap prior to use. $TaCl_5$ (99.9%, Strem) was sublimed (115 °C, 10^{-4} Torr) prior to use. Unless otherwise specified, all reagents were purchased from Aldrich. $^tBu_2SiH_2$ was purchased from FMC Lithium and used as received. $(C_6H_{11})_3SiX$ (X = Cl)[21] and $^tBu_2Si(H)OH$[20] were prepared via literature methods.

NMR spectra were obtained using Varian XL-400, INOVA-400, and Unity-500 spectromenters. Chemical shifts are reported relative to benzene-d_6 (^{1}H, s 7.15; ^{13}C, t 128.0). Infrared spectra were recorded on a Nicolet Impact 410 spectrophotometer interfaced to a Gateway PC. Elemental analyses were performed by Oneida Research Services, Whitesboro, NY, or Robertson Microlit Laboratories, Madison, NJ.

Procedures. 1. ^{t}Bu$_2$PhSiH. Into a 500 mL three-neck flask charged with $^tBu_2SiH_2$ (12.60 g, 87.4 mmol) and 200 mL of heptane at −78 °C was syringe-transferred (under Ar purge) 1.05 equiv of phenyllithium (1.9 M, 48.3 mL, 91.8 mmol). The solution was allowed to warm to 23 °C and brought to reflux. After 14 h, precipitation of LiH from the red-purple solution was noted. It was first cooled to 23 °C and subsequently cooled to 4 °C prior to dropwise addition of 2-propanol, which led to vigorous bubbling (H_2) and the evolution of heat. After the solid had dissipated and no further gas evolved, the amber solution was transferred to a separatory funnel and washed (3 × 100 mL) with water. The aqueous residues were then extracted once with 100 mL of hexanes. The combined organic layers were dried with $MgSO_4$, and the solvent was removed via rotary evaporation to provide an amber oil, from which was subsequently distilled (T = 60−90 °C, 10^{-4} Torr) 16.7 g of a clear, colorless oil (85% yield).

2. ^{t}Bu$_2$PhSiOH. Into a 100 mL three-neck flask charged with an ethanolic solution of $^tBu_2PhSiH$ (3.00 g, 13.1 mmol, 0.33 M in ethanol) was transferred KOH (3.00 g, 53.6 mmol). The reaction was brought to reflux for 36 h, cooled to 23 °C, and neutralized with NH_4Cl (satd). The resulting solution was then extracted (3 × 40 mL) with hexanes, and the combined organic layers were washed once with brine (40 mL), dried over $MgSO_4$, and concentrated to afford a yellow oil. From the crude yellow oil was distilled (60−70 °C, 10^{-3} Torr) 2.8 g of a clear, colorless oil (87% yield).

3. ^{t}Bu$_2$PhSiONa. Into a 50 mL flask containing $^tBu_2PhSiOH$ (2.00 g, 8.18 mmol) and sodium metal (339 mg, 14.7 mmol) was distilled 25 mL of toluene. The vessel was filled with an Ar atmosphere and brought to reflux for 24 h. The toluene was removed in vacuo to afford a yellow solid and residual sodium metal. The resulting mixture was filtered through a glass frit and then extracted five times with hexanes. The hexane filtrate was slowly concentrated until precipitation began. This volume was then gently heated with a warm water bath while stirring to resolubilize the material. The solution was then allowed to stand at room temperature for 4 h to initiate crystallization, subsequently cooled to −78 °C for 2 h, and then filtered to collect 1.5 g of a white, crystalline solid (69% yield).

4. (^{t}Bu$_2$PhSiO)$_3$TaCl$_2$ (1-Ph). To a 50 mL flask charged with $TaCl_5$ (1.50 g, 4.18 mmol) and $^tBu_2PhSiONa$ (3.24 g, 12.5 mmol) was distilled 20 mL of benzene. The resulting solution was brought to reflux for 20 h. The amber slurry was cooled to 23 °C, and the solvent was removed in vacuo to yield a tan solid. Pentane was added, and the resulting suspension was filtered. The salt cake was extracted (3 × 10 mL) with pentane, and the filtrate was then concentrated to 3 mL. The concentrate was then cooled to −78 °C for 4 h and filtered to yield 3.10 g of colorless crystals (78% yield). Anal. Calcd for $C_{42}H_{69}O_3Si_3Cl_2Ta$: C, 52.65; H, 7.26. Found: C, 52.25; H, 7.40.

5. (^{t}Bu$_2$PhSiO)$_3$TaH$_2$ (7-Ph). To a 25 mL flask charged with **1**-Ph (1.00 g, 1.04 mmol) and 2.2 equiv of Na/Hg (5.86 g, 2.29 mmol, 0.9% Na^0) was distilled 15 mL of ether. While the ether was kept frozen at 77 K, excess H_2 was slowly admitted to the reaction vessel until the pressure was 1 atm. The ether was allowed to thaw, and the reaction was stirred for 16 h, resulting in a colorless solution with a visible precipitate. The solvent was removed in vacuo, and the resulting mixture was triturated (3 × 5 mL) with pentane, suspended in 5 mL of pentane, and filtered through Celite. The solvent was removed in vacuo to afford 800 mg of a clear, colorless oil (87% yield).

6. ^{t}Bu$_2$MeSiH. Into a 100 mL bomb reactor charged with $^tBu_2SiHCl$ (10.00 g, 46.9 mmol) was syringe-transferred (under Ar purge) methyllithium (1.5 M in Et_2O, 50 mL, 49.2 mmol). The resulting solution was degassed, and the vessel was sealed and heated to 67 °C for 20 h, resulting in a white precipitate. The solution was cooled, and the excess methyllithium was quenched by slow addition of 20 mL of 2-propanol. The contents were then

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[39] Hwu, R. J.-R.; Tsay, S.-C.; Cheng, B.-L. In *The Chemistry of Organosilicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley & Sons: New York, 1934; Vol. 2, pp 431−494.

transferred to a separatory funnel and washed (3 × 10 mL) with distilled water. The organic layer was separated, and the aqueous residues were extracted three times with hexanes. The combined organic layers were then dried over $MgSO_4$ and concentrated to a yellow oil, and distillation (90 °C, 100 Torr) afforded 7.00 g of a clear, colorless oil (94% yield).

7. ^{t}Bu$_2$MeSiOH. Into a 100 mL three-neck flask charged with 40 mL of an ethanolic solution of ^{t}Bu$_2$MeSiH (13.50 g, 85.3 mmol, 2.1 M) was transferred, under ambient conditions, KOH (19.1 g, 0.341 mol). The reaction was brought to reflux for 20 h, then cooled to room temperature, and neutralized with a saturated solution of NH_4Cl. The resulting solution was then extracted (3 × 20 mL) with hexanes, and the combined organic layers were washed once with brine (30 mL), dried over $MgSO_4$, and then concentrated to afford a yellow, waxy solid. Sublimation (80 °C, 10^{-4} Torr) yielded 12.5 g of white crystals (84%).

8. ^{t}Bu$_2$MeSiONa. Into a 250 mL flask containing ^{t}Bu$_2$MeSiOH (12.30 g, 70.6 mmol) and sodium metal (1.95 g, 84.7 mmol) was distilled 125 mL of toluene. The vessel was placed under an Ar atmosphere and brought to reflux for 24 h. The toluene was removed in vacuo to afford a white solid amidst the residual sodium. A 50 mL portion of hexanes was added, the resulting mixture was filtered, and the insoluble material was extracted (5 × 5 mL) with hexanes. The hexane filtrate was concentrated until precipitation began, cooled to −78 °C for 2 h, and filtered to collect 11.0 g of a white, crystalline solid (79% yield).

9. (^{t}Bu$_2$CH$_3$SiO)$_3$TaCl$_2$ (1-Me). To a 50 mL flask charged with ^{t}Bu$_2$MeSiONa (2.00 g, 10.2 mmol) and $TaCl_5$ (1.22 g, 3.40 mmol) was distilled 25 mL of benzene. The resulting solution was stirred at 55 °C for 16 h, and the solvent was removed in vacuo. The resulting solid was triturated (3 × 10 mL) with pentane, suspended in pentane, and filtered. The salt cake was extracted with pentane (3 × 5 mL), and the combined filtrate was concentrated to 3 mL. The concentrate was then cooled to −78 °C for 4 h and filtered to yield 1.60 g of off-white microcrystals (63% yield). Anal. Calcd for $C_{27}H_{63}O_3Si_3Cl_2Ta$: C, 42.01; H, 8.23. Found: C, 42.00; H, 8.39.

10. [(^{t}Bu$_2$MeSiO)$_3$TaH]$_2$ (4-Me). a. Synthesis. Into a 50 mL flask charged with **1**-Me (1.00 g, 1.30 mmol) and 2.1 equiv of Na/Hg (6.95 g, 0.9% Na^0) was distilled 25 mL of diethyl ether. At 77 K, excess H_2 (1 atm) was slowly added, after passing it first through a liquid nitrogen trap. The ether was allowed to thaw, and the solution was stirred under 1 atm of H_2 for 20 h, resulting in an black mixture with visible precipitate. The solvent was removed in vacuo, and the resulting black solid was suspended in 10 mL of pentane and filtered. The insoluble material was extracted with pentane (3 × 10 mL), and the extracts were condensed to 5 mL and cooled to −78 °C for 2 h, after which 0.92 g of black crystals were collected by filtration (52% yield). Anal. Calcd for $C_{27}H_{64}O_3Si_3Ta$: C, 46.20; H, 9.19. Found: C, 46.27; H, 8.81. **b. Toepler Pump Analysis.** Into a 25 mL flask containing **4**-Me (118 mg, 0.0839 mmol) was added ∼10 mL of Et_2O at 77 K. Excess HCl (202 Torr, 3.02 mmol) was admitted via a gas bulb. Gas evolved while the solution was allowed to warm to 24 °C (20 min), and the black solution turned colorless. After the solution was stirred for 1 h, the gases were passed through a series of three liquid nitrogen traps and collected via a Toepler pump (0.240 mmol). The collected hydrogen was converted to water by cycling over CuO (300 °C), and the remaining volatiles were re-collected (0.0199 mmol, 0.238 equiv). By difference, 0.220 mmol of H_2 was produced (2.62 equiv with respect to **4**-Me, 87% of that expected).

11. (C$_6$H$_{11}$)$_3$SiOH. To a boiling ethanolic solution of $(C_6H_{11})_3SiCl$ (3.0 g, 9.6 mmol, 0.19 M) and trace phenylphthalein was added dropwise 10% aqueous KOH until the pink color persisted. The solvent was removed by rotary evaporation. The white solid was dissolved in 100 mL of boiling hexanes and cooled to −78 °C to afford 13.5 g of colorless crystals that were collected in three crops (85% yield).

12. (C$_6$H$_{11}$)$_3$SiONa. To a 250 mL flask charged with $(C_6H_{11})_3SiOH$ (9.2 g, 31.0 mmol) and sodium metal (1.30 g, 56 mmol) was distilled 100 mL of toluene. The resulting suspension was brought to reflux and the silanol dissolved. Heating for 1 h resulted in the formation of a white precipitate. The reflux was continued for an additional 12 h, and the toluene was removed in vacuo. The resulting white powder was washed (5 × 5 mL) with toluene and used without further purification (8.41 g, 90% yield). NMR spectral characterization was not possible due to low solubility.

13. ((C$_6$H$_{11}$)$_3$SiO)$_3$TaCl$_2$ (1-Cy$_3$). To a 100 mL flask charged with $(C_6H_{11})_3SiONa$ (4.00 g, 13.3 mmol) and $TaCl_5$ (1.59 g, 4.44 mmol) was distilled 45 mL of toluene. The resulting suspension was refluxed for 12 h, and the solvent was removed in vacuo. The resulting white powder was suspended in toluene and filtered. The insoluble solid was extracted (10 × 20 mL) with toluene. The extracts were concentrated to 10 mL, cooled to −78 °C for 4 h, and filtered to afford clear, colorless crystals (2.61 g, 52% yield). Anal. Calcd for $C_{54}H_{99}O_3Si_3Cl_2Ta$: C, 57.27; H, 8.81. Found: C, 57.02; H, 9.01.

14. ^{i}Pr$_3$SiOH. Into a 500 mL flask charged with 200 mL of an ethanolic solution of ^{i}Pr$_3$SiH (50.0 g, 0.316 mol, 1.58 M) was added KOH (71.0 g, 1.26 mol). The solution was brought to reflux for 24 h and cooled to 23 °C. To the solution was added aqueous HCl (1 M) until it was neutral by pH paper. The solution was extracted (3 × 50 mL) with hexanes. The combined extracts were concentrated in vacuo to afford a yellow oil. Distillation (110 °C, 50 Torr) afforded 54.0 g of a clear, colorless oil (98% yield).

15. ^{i}Pr$_3$SiONa. Into a 100 mL flask charged with ^{i}Pr$_3$SiOH (9.65 g, 55.4 mmol) and sodium metal (2.3 g, 99.6 mmol) was distilled 50 mL of toluene. The resulting solution was brought to reflux for 12 h, and the solvent was removed in vacuo. The resulting material was triturated (3 × 10 mL) with hexanes, dissolved in 20 mL of hexanes, and filtered. The solvent was removed to yield 9.5 g of a clear, colorless, amorphous solid (87% yield).

16. (^{i}Pr$_3$SiO)$_3$TaCl$_2$ (1-^{i}Pr$_3$). Into a 100 mL flask charged with ^{i}Pr$_3$SiONa (4.00 g, 20.4 mmol) and $TaCl_5$ (2.23 g, 6.79 mmol) was distilled 50 mL of toluene. The resulting solution was brought to reflux for 12 h, after which time the solvent was removed in vacuo, and the resulting material was triturated three times with 10 mL portions of hexanes, dissolved in 10 mL of hexanes, and filtered. The filtrate was concentrated to 5 mL, cooled to −78 °C for 2 h, and filtered to collect 2.20 g of an off-white, microcrystalline solid (42% yield). Anal. Calcd for $C_{27}H_{63}O_3Si_3Cl_2Ta$: C, 42.01; H, 8.23. Found: C, 40.72; H, 7.96.

17. [(^{i}Pr$_3$SiO)$_3$TaCl]$_2$ (2). Into a 50 mL flask charged with **1**-^{i}Pr$_3$ (250 mg, 0.32 mmol) and Na/Hg (1.74 g of 0.9% Na/Hg, 0.68 mmol of Na^0) was distilled 20 mL of ether. The solution took on a faint pink color after stirring for 45 min and then became purple over 12 h as a precipitate formed. The solution was stirred for 38 h, and the solvent was removed. The residual amalgam was decanted, and the remaining solid was suspended in pentane and filtered. The insoluble material was washed with (3 × 10 mL) pentane, and the filtrate was allowed to evaporate at −35 °C in a nitrogen atmosphere. After 24 h, the soluble material was removed by pipet and 200 mg of purple crystals were collected (40% yield). Anal. Calcd for $C_{27}H_{63}O_3Si_3ClTa$: C, 44.04; H, 8.62. Found: C, 43.84; H, 8.84.

18. ^{i}Pr$_2$^{t}BuSiH. Into a 100 mL flask charged with ^{i}Pr$_2$SiHCl was distilled 40 mL of heptane. The resulting solution was cooled to

−78 °C, and ^{t}BuLi (26 mL, 0.043 mol, 1.7 M in pentane) was syringe-transferred. A white precipitate formed while the solution was allowed to warm while stirring. The solution was stirred for 12 h, cooled to 4 °C, and quenched by dropwise addition of 10 mL of 2-propanol. The resulting mixture was added to 40 mL of water. The organic layer was separated, washed once with 20 mL of distilled water, and dried over $MgSO_4$. It was filtered and concentrated to afford a yellow oil. Distillation (65−80 °C, $\sim 10^{-4}$ Torr) afforded 2.7 g of a clear, colorless oil (43% yield).

19. $^{i}Pr_2{}^{t}BuSiOH$. Into a 100 mL three-neck flask charged with 20 mL of an ethanolic solution of $^{i}Pr_2{}^{t}BuSiH$ (2.70 g, 15.7 mmol, 0.78 M in ethanol) was transferred KOH (3.50 g, 62.6 mmol). The reaction was brought to reflux for 22 h, cooled to 23 °C, and neutralized with NH_4Cl (satd). The resulting solution was then extracted (3 × 40 mL) with hexanes. The resulting organic layer was washed once with brine (40 mL), dried over $MgSO_4$, and concentrated to afford a yellow oil. From the crude yellow oil was distilled (115−130 °C, 10^{-4} Torr) 2.2 g of a clear, colorless oil (75% yield).

20. $^{i}Pr_2{}^{t}BuSiONa$. Into a 50 mL flask charged with $^{i}Pr_2{}^{t}BuSiOH$ (1.97 g, 10.5 mmol) and sodium metal (0.480 g, 99.6 mmol) was distilled 30 mL of toluene. The resulting solution was refluxed for 21 h and cooled to 23 °C, and the solvent was removed in vacuo. The resulting solid was triturated with pentane (3 × 5 mL), dissolved in 10 mL of hexanes, and filtered. Residual insoluble material was extracted (3 × 5 mL) with hexanes, and the combined extracts were concentrated to 5 mL, cooled to −78 °C for 2 h, and filtered to provide 1.30 g of white crystals (59% yield).

21. $(^{i}Pr_2{}^{t}BuSiO)_3TaCl_2$ (1-$^{i}Pr_2$). Into a 50 mL flask charged with $^{i}Pr_2{}^{t}BuSiONa$ (1.27 g, 6.04 mmol) and $TaCl_5$ (0.720 g, 2.01 mmol) was distilled 25 mL of toluene. The solution was brought to reflux for 16 h, and the solvent was removed in vacuo. The resulting solid was triturated (3 × 10 mL) with pentane, suspended in 30 mL of pentane, and filtered. The salt cake was extracted (3 × 5 mL) with pentane, and the combined filtrates were concentrated to 3 mL. Upon cooling to −78 °C for 4 h, 748 mg of off-white microcrystals (51% yield) was isolated by filtration. Anal. Calcd for $C_{30}H_{69}O_3Si_3Cl_2Ta$: C, 44.27; H, 8.54. Found: C, 43.82; H, 8.69.

22. $^{t}Bu_2HSiONa$. Into a 50 mL flask charged with $^{t}Bu_2HSiOH$ (2.00 g, 12.5 mmol) and sodium metal (516 mg, 22.5 mmol) was distilled 30 mL of toluene. The resulting mixture was stirred for 4 h at 23 °C, and the solvent was removed in vacuo. The resulting white solid was triturated (3 × 5 mL) with pentane, taken up in 25 mL of pentane, and filtered to remove residual sodium. The filtrate was concentrated, cooled to −78 °C for 2 h, and filtered to collect 980 mg of white crystals (47% yield).

23. $(^{t}Bu_2HSiO)_3TaCl_2$ (1-H). Into a 25 mL flask charged with $^{t}Bu_2HSiONa$ (200 mg, 1.20 mmol) and $TaCl_5$ (144 mg, 0.402 mmol) was distilled 10 mL of benzene. The resulting solution was stirred for 4 h at 23 °C, and the solvent was removed in vacuo. The resulting material was triturated (3 × 5 mL) with pentane, dissolved in 5 mL of pentane, and filtered. The solvent was removed in vacuo to afford 150 mg of a waxy, white solid (55% yield).

NMR Tube Reactions. 24. $[(^{t}Bu_2MeSiO)_3TaH]_2$ (4-Me) with N_2O. To a flame dried NMR tube equipped with a 180° joint was added **4**-Me (30 mg, 0.021 mmol) and 0.6 mL of C_6D_6. The solution was then degassed, and N_2O (0.044 mmol, ~2.1 equiv) was added via a gas bulb. The NMR tube was then flame sealed, and the reaction was monitored by ^1H NMR spectroscopy. After 15 h at 23 °C, resonances tentatively assigned to $[(^{t}Bu_2MeSiO)_3TaH]_2(\mu\text{-}O)$ (**5**-Me) and those belonging to $[(^{t}Bu_2MeSiO)_3Ta]_2(\mu\text{-}O)_2$ (**3**-Me) were observed and continued to grow in over 48 h. Prolonged reaction times (1 week) or thermolysis (160 °C, 2 h) resulted in complete conversion to **3**-Me and observation of H_2 (δ 4.46 ppm). **25. $[(^{i}Pr_2{}^{t}BuSiO)_3TaH]_2$ (4-$^{i}Pr_2$) with N_2O.** Procedure 24 was used with 29 mg (0.020 mmol) of **4**-$^{i}Pr_2$ and 0.041 mmol (~2.1 equiv) of N_2O. After 12 h at 23 °C, the ^1H NMR spectrum displayed resonances tentatively assigned to $[(^{i}Pr_2{}^{t}BuSiO)_3TaH]_2(\mu\text{-}O)$ (**5**-$^{i}Pr_2$) and $[(^{i}Pr_2{}^{t}BuSiO)_3TaO]_2$ (**3**-$^{i}Pr_2$). Thermolysis (160 °C, 24 h) resulted in complete conversion to **3**-$^{i}Pr_2$ and observation of H_2.

Small Pot Reactions. Dichloride Reductions in the Presence of Ethylene. 26. From $(^{t}Bu_2CH_3SiO)_3TaCl_2$ (1-Me). Into a 100 mL flask containing **1**-Me (400 mg, 0.518 mmol) and 2.1 equiv of Na/Hg (2.8 g, 0.9% Na^0) was distilled 30 mL of 1,2-dimethoxyethane (DME). Ethylene (1 atm), which was passed through a −78 °C bath, was admitted to the flask. After stirring for 5 h at 23 °C, the solvent was removed and the residual solid was triturated three times with 5 mL of hexanes. A 15 mL portion of hexanes was added, and the solution was filtered and evaporated to dryness to afford 411 mg of $(^{t}Bu_2MeSiO)_3TaCH_2(CH_2)_2CH_2$ (**9**-Me). A ^1H NMR spectral assay indicated 85% purity. **27. From $(^{i}Pr_3SiO)_3TaCl_2$ (1-$^{i}Pr_3$).** Into a 50 mL flask charged with 200 mg (0.26 mmol) of **1**-$^{i}Pr_3$ and 1.4 g of Na/Hg (2.1 equiv, 0.9% Na^0) was distilled 20 mL of THF. Procedure 26 was followed to afford a colorless material assayed by ^1H NMR spectroscopy to be 80% $(^{i}Pr_3SiO)_3TaCH_2(CH_2)_2CH_2$ (**9**-$^{i}Pr_3$). **28. From $(^{t}Bu_2PhSiO)_3TaCl_2$ (1-Ph).** Into a 50 mL flask charged with **1**-Ph (250 mg, 0.26 mmol) and 1.4 g of Na/Hg (2.1 equiv, 0.9% Na^0) was distilled 20 mL of THF. Procedure 26 was followed except that the reaction was stirred for 2 h, during which time a color change from green to bright orange was noted. The final orange material was assayed by ^1H NMR spectroscopy to be 75% $(^{t}Bu_2PhSiO)_3Ta(\eta\text{-}C_2H_4)$ (**8**-Ph).

29. Reaction of $[(^{i}Pr_3SiO)_3TaCl]_2$ (2) with C_2H_4. A 25 mL flask equipped with a gas bulb was charged with **2** (100 mg, 0.068 mmol) and 5 mL of diethyl ether. Into the 77 K reaction mixture was condensed ethylene (0.075 mmol, 1.1 equiv) after passing through a −78 °C trap. The purple color of the solution faded over 24 h and became yellow after 48 h. The solvent was removed, and the products were determined by ^1H NMR spectroscopy to be a 1:1 mixture of **9**-$^{i}Pr_3$ and **1**-$^{i}Pr_3$.

Dichloride Reductions in the Presence of 2-Butyne. 30. From $(^{t}Bu_2CH_3SiO)_3TaCl_2$ (1-Me). To a 25 mL flask charged with 275 mg of **1**-Me (0.356 mmol) and 1.91 g of Na/Hg (2.1 equiv, 0.9% Na^0) was distilled 10 mL of THF at 77 K. To the frozen mixture was distilled 2-butyne (0.56 mL, 0.39 g, 7.1 mmol, 20 equiv). The reaction was allowed to stir for 2 h at 23 °C, and the solvent was removed. Pentane (10 mL) was added, the mixture was filtered, and the solvent was removed. A ^1H NMR assay of the colorless material indicated $(^{t}Bu_2MeSiO)_3Ta(\eta\text{-}C_2Me_2)$ (**10**-Me) in 90% purity. **31. From $(^{t}Bu_2PhSiO)_3TaCl_2$ (1-Ph).** To a 25 mL flask charged with 250 mg of **1**-Ph (0.261 mmol) and 1.4 g of Na/Hg (2.1 equiv, 0.9% Na^0) was distilled 6 mL of Et_2O at 77 K. Procedure 30 was followed, and $(^{t}Bu_2PhSiO)_3Ta(\eta\text{-}C_2Me_2)$ (**10**-Ph) was assayed by ^1H NMR spectroscopy as the product in 90% purity. **32. From $(^{i}Pr_3SiO)_3TaCl_2$ (1-$^{i}Pr_3$).** Into a 25 mL flask charged with 400 mg of **1**-$^{i}Pr_3$ (0.518 mmol) and 2.74 g of Na/Hg (0.68 mmol of 0.9% Na^0, 2.1 equiv) was distilled 10 mL of Et_2O at 77 K. Procedure 30 was followed except the reaction was allowed to stir for 24 h at 23 °C. A ^1H NMR assay confirmed the presence of $(^{i}Pr_3SiO)_3Ta(\eta\text{-}C_2Me_2)$ (**10**-$^{i}Pr_3$) in the colorless oil in 80% purity.

33. Reaction of $[(^{i}Pr_3SiO)_3TaCl]_2$ (2) with 2-Butyne. A 25 mL flask was charged with **2** (100 mg, 0.068 mmol) and 5 mL of Et_2O. Into the 77 K reaction mixture was condensed 2-butyne (0.075 mmol, 1.1 equiv) via a gas bulb. The reaction was allowed to stir for 24 h, culminating in a clear, yellow solution. The solvent was removed, and the products were determined by ^{1}H NMR spectral assay to be a 1:1 mixture of **1**-^{i}Pr$_3$ and **10**- ^{i}Pr$_3$.

34. Attempted Reduction of (^{t}Bu$_2$CH$_3$SiO)$_3$TaCl$_2$ (1-Me) in Et$_2$O. To a 50 mL flask charged with **1**-Me (1.00 g, 1.3 mmol) and K/C$_8$ (0.7 g, 5.2 mmol of K^0, 4 equiv) was distilled Et$_2$O. The reaction immediately became olive green in color and then faded to brown over the course of 1 h at 23 °C. After 2 h, the solvent was removed and the crude brown solid was taken up and filtered in hexanes. After concentration of the filtrate, 750 mg of brown solid was collected. The ^{1}H NMR spectrum for this material revealed a 1:1 mixture of [(^{t}Bu$_2$MeSiO)$_3$TaH]$_2$ (**4**-Me) and [(^{t}Bu$_2$MeSiO)$_3$Ta]$_2$(μ-O)$_2$ (**3**-Me).

Single-Crystal X-ray Diffraction Studies. 35. [(^{i}Pr$_3$SiO)$_3$TaCl]$_2$ (2). Purple crystals of **2** were grown by evaporating a concentrated pentane solution. Upon isolation, a suitable crystal (0.20 × 0.20 × 0.20 mm^3) was immersed in polyisobutylene and placed under a 173 K N$_2$ stream on the goniometer head of a Siemens P4 SMART CCD area detector system (graphite-monochromated Mo Kα radiation). Absorption corrections were performed using the SADABS program, and the structure was solved by direct methods (SHELXS), completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures (SHELXL).[40] After an initial refinement, all non-hydrogen atoms were treated and refined anisotropically and hydrogen atoms were treated as idealized contributions.

36. [(^{t}Bu$_2$MeSiO)$_3$TaH]$_2$ (4-Me). Dark brown-black crystals of **4**-Me were grown by evaporating a concentrated hexane solution. Upon isolation, a suitable crystal (0.40 × 0.20 × 0.15 mm^3) was immersed in polyisobutylene and placed under a 173 K N$_2$ stream on the goniometer head of a Siemens P4 SMART CCD area detector system (graphite-monochromated Mo Kα radiation). Modest quality data was indicated by high mosaicity and somewhat diffuse reflections. Absorption corrections were performed using the SADABS program, and the structure was solved by direct methods (SHELXS), completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures (SHELXL).[40] After an initial refinement, all non-hydrogen atoms were treated and refined anisotropically and hydrogen atoms were treated as idealized contributions. The tantalum hydrides were not located but assigned bridging positions based on their chemical shifts in the ^{1}H NMR spectrum and the absence of terminal hydride absorptions in the infrared spectrum.

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(40) SMART and SAINT (software reference manuals, version 5.042, Bruker Analytical X-ray Systems: Madison, WI, 1998) include SADABS (software for empirical absorption correction, Sheldrick, G. M. University of Gottingen, Germany, 2000), SHELXS, and SHELXTL (reference manuals, version 5.1, Sheldrick, G. M. University of Gottingen, Germany, 1997).