

Four-Coordinate Mo(II) as (silox)₂Mo(PMe₃)₂ and Its W(IV) Congener (silox)₂HW(η^2 -CH₂PMe₂)(PMe₃) (silox = ^tBu₃SiO)

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The reduction of [(^tBu₃SiO)₂MoCl]₂ (**2**) provided the cyclometalated derivative, (silox)₂HMoMo(κ -O,C-OSi^tBu₂CMe₂CH₂)(silox) (**3**), and alkylation of **2** with MeMgBr afforded [(^tBu₃SiO)₂MoCH₃]₂ (**4**). The hydrogenation of **4** was ineffective, but the reduction of **2** under H₂ generated [(^tBu₃SiO)₂MoH]₂ (**5**), and the addition of 2-butyne to **3** gave [(silox)₂Mo]₂(μ : η^2 : η^2 -C₂Me₂) (**6**), thereby implicating the existence of [(silox)₂Mo]₂ (**1**₂). The addition of (silox)H to Mo(NMe₂)₄ led to (silox)₂Mo(NMe₂)₂ (**7**), but further elaboration of the core proved ineffective. The silanolysis of MoCl₅ afforded (silox)₂MoCl₄ (**8**) and (silox)₃MoCl₃ (**9**) as a mixture from which pure **8** could be isolated, and the addition of THF or PMe₃ resulted in derivatives of **9** as (silox)₂Cl₃MoL (L = THF, **10**; PMe₃, **11**). Reductions of **11** and (silox)₂WCl₄ (**15**) in the presence of excess PMe₃ provided (silox)₂Cl₂MPMe₃ (M = Mo, **12**; W, **16**) or (silox)₂HW(η^2 -CH₂PMe₂)PMe₃ (**14**). While “(silox)₂W(PMe₃)₂” was unstable with respect to W(IV) as **14**, a reduction of **12** led to the stable Mo(II) diphosphine, (silox)₂Mo(PMe₃)₂ (**17**). X-ray crystal structures of **10** (pseudo-O_h), **12** (square pyramidal), and **14** and **17** (distorted T_d) are reported. Calculations address the diamagnetism of **12** and **16**, and the distortion of **17** and its stability to cyclometalation in contrast to **14**.

Introduction

Recent investigations of group 5 niobium and tantalum species,^{1,2} and group 6 molybdenum and tungsten compounds,^{3,4} have focused on low-coordinate d² and d³ complexes that reveal the influence of nd_{z²}(n + 1)s mixing^{5,6} on structure and reactivity. Key syntheses of trigonal monoprismatic (silox)₃MoCl and squashed tetrahedral (silox)₃WCl³ led to the preparation of (silox)₃MPMe₃ (M = Mo, W; silox = ^tBu₃SiO), (silox)₃Mo, and related C_{3v} derivatives including (silox)₃MP (M = Mo, W).⁴ The M(III) complexes are particularly interesting because steric and

electronic features prevented generation of the typical metal–metal triply bonded compounds, whose chemistry comprises a significant fraction of the coordination chemistry of this oxidation state in group 6.^{7,8}

Similar to molybdenum and tungsten(III), low-coordinate, mononuclear Mo(II) and W(II) compounds are difficult to prepare due to their propensity to form metal–metal bonds. Quadruple-bonded complexes readily form, and these occupy a historically important niche in inorganic coordination chemistry due to the presence of δ -bonding.^{7,9} While the use of the silox (^tBu₃SiO) ligand has enabled the synthesis

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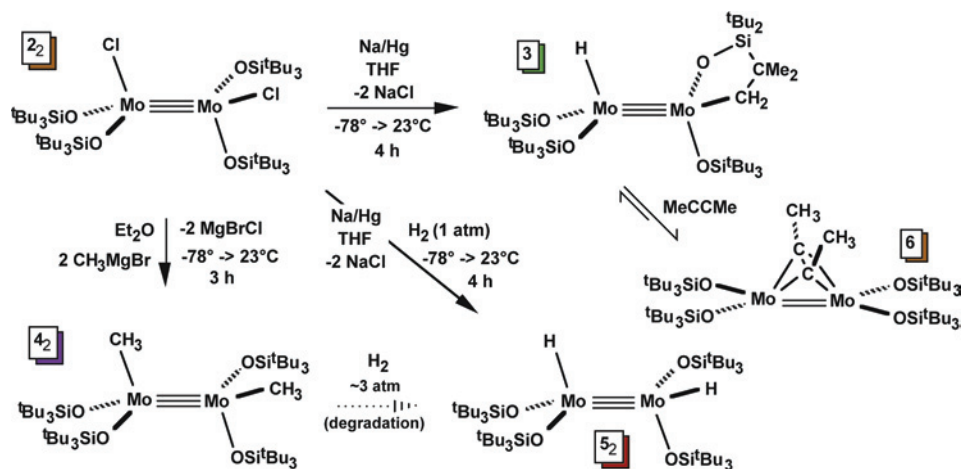
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Scheme 1



of numerous low-coordinate, low-valent compounds, “(silox)₂M” (M = Mo, W) is unlikely to be a stable entity, and even the quadruple-bonded “[(silox)₂M]₂” dimers are probably too reactive to isolate on the basis of previous W₂ chemistry. Efforts at generating [(silox)₂W]₂ resulted in cyclometalation to afford (silox)₂HWW(κ-O,C-OSi^tBu₂-CMe₂CH₂)(silox),¹⁰ and the transient dimer is also the likely reactive species that degrades ethylene to [(silox)₂W]₂(μ-CH)₂ and dihydrogen via [(silox)₂W]₂(μ-CH)(μ-CH₂)(μ-H).¹¹ The first-row group 6 analogue, “(silox)₂Cr”, exists as the siloxide-bridged dimer, [(t-Bu₃SiO)Cr]₂(μ-OSi^tBu₃)₂;¹² hence, there is modest precedent for stabilizing group 6 M(II) centers in dimeric form.

During these studies, the use of PMe₃ has been extremely advantageous in trapping low-valent silox-containing intermediates prior to degradation or metal–metal bond formation.^{1,4,13,14} Herein, efforts to generate low-coordinate, low-valent group 6 M(II) compounds are described, including efficient syntheses of critical starting materials, the successful generation of (silox)₂Mo(PMe₃)₂, and an analysis of its electronics via computation.

Results

Approaches to [(silox)₂Mo]₂. 1. Reduction and Methylation of [(silox)₂MoCl]₂. Although the putative *D*_{2d} [(silox)₂W]₂ transient dimer proved too reactive to isolate,¹⁰ the lowered proclivity of Mo(II) to oxidize via CH oxidative addition was enough incentive to consider the synthesis of [(silox)₂Mo] (1₂). The synthesis of *gauche* C₂ [(t-Bu₃SiO)₂MoCl]₂ (2₂) from MoCl₃ and Na(silox) has been previously described,³ and this was deemed an attractive starting material. As Scheme 1 illustrates, the reduction of 2₂

unfortunately resulted in the cyclometalated derivative, (silox)₂HMoMo(κ-O,C-OSi^tBu₂CMe₂CH₂)(silox) (3), which was isolated as a green-brown solid in 90% yield. ¹H NMR spectra of 3 revealed three silox groups, two singlets for the remaining *tert*-butyl groups, singlets for two Me groups, diastereotopic methylene hydrogens, and a hydride at δ 14.30, as Table 1 indicates.

Crystallization of crude 3 proved unsuccessful; hence, other methods of preparation were attempted. The addition of 2.0 equiv of MeMgBr in Et₂O to [(t-Bu₃SiO)₂MoCl]₂ (2₂), with subsequent filtration and recrystallization from pentane, afforded the purple dimethyl compound, [(t-Bu₃SiO)₂MoCH₃]₂ (4₂), in 85% yield. Its *gauche* C₂ symmetric structure^{3,10} was substantiated by the presence of two inequivalent silox resonances in the ¹H NMR spectrum (δ 1.19, δ 1.28), equivalent methyl resonances (δ 3.48), and related ¹³C{¹H} NMR spectral signals. The stoichiometric hydrogenation of 4₂ to (silox)₂HMoMo(κ-O,C-OSi^tBu₂CMe₂CH₂)(silox) (3) and 2 equiv of MeH could not be affected, and 4₂ proved to be unreactive to 1 atm of H₂ at 23 °C. Upon extended thermolysis under excess H₂ at 70 °C, evidence of a dihydride was present, but continued heating or higher temperatures resulted in degradation.

2. Trapping of [(silox)₂Mo]₂. The reduction of [(t-Bu₃SiO)₂MoCl]₂ (2₂) with 2.0 equiv of Na/Hg in the presence of 1 atm of H₂ in THF resulted in the formation of reddish-brown [(t-Bu₃SiO)₂MoH]₂ (5₂). Two silox singlets in the ¹H NMR spectrum again revealed *gauche* C₂ symmetry of the dihydride,¹⁰ and an additional resonance at δ 16.85 characterized the MoH units (Table 1). A strong ν(MoH) was observed at 1965 cm⁻¹ in the infrared spectrum of 5₂. In contrast to the tungsten analog,¹⁰ 5₂ could not be isolated by recrystallization from various hydrocarbon and ethereal solvents, and the presence of ~5% t-Bu₃SiONa, ~3% t-Bu₃SiOH, and residual THF were typically evident in its ¹H NMR spectrum. Unfortunately, the percentages of these impurities did not change when the reaction times were varied (3–48 h).

In an NMR tube experiment, (silox)₂HMoMo(κ-O,C-OSi^tBu₂CMe₂CH₂)(silox) (3) was explored as an alternative means to generating the putative [(silox)₂Mo]₂ (1₂). With 1 equiv of 2-butyne as a trapping reagent, thermolysis at 100

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Table 1. ^1H , $^{13}\text{C}\{^1\text{H}\}$, and ^{31}P NMR Spectral Assignments^a for Diamagnetic Group 6 Siloxide Complexes

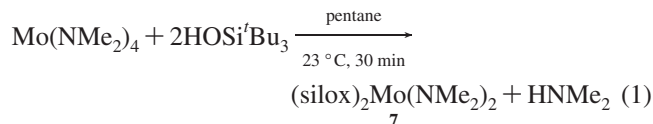
compound	^1H NMR (δ (J(Hz)), assmt)		$^{13}\text{C}\{^1\text{H}\}$ NMR (δ , (J(Hz) assmt))		
	^t Bu	R/H etc.	SiC	SiC(CH ₃) ₃	R/H etc.
[(silox) ₂ MoCl] ₂ (2) ^b	1.25		23.98	30.98	
	1.27		24.53	31.67	
(silox) ₂ HMoMo(silox)(κ -O,C-Si ^t BuCM ₂ CH ₂) (3)	1.13	1.27, 1.37 (^t Bu)	24.42	30.74	23.94, 23.40 (SiC)
	1.24	1.54, 1.56 (Me)	24.06	31.23	23.85 (CMe ₂)
	1.34	3.78 (d, 11, CHH)	23.21	31.24	29.89 (MoCH ₂)
		3.86 (d, 11, CHH)			31.66, 31.93 (C(CH ₃) ₃)
		14.30 (MoH)			34.24, 34.43 (C(CH ₃) ₂)
[(silox) ₂ MoCH ₃] ₂ (4) ₂	1.19	3.48 (Me)	24.18	31.38	48.27 (Me)
	1.28		24.66	31.41	
[(silox) ₂ MoH] ₂ (5) ^c	1.22	16.85 (H)	23.20	30.79	
	1.31		23.97	31.40	
[(silox) ₂ Mo] ₂ (μ : η^2 , η^2 -C ₂ Me ₂) (6)	1.05	3.17 (Me)			
	1.35				
(silox) ₂ Mo(NMe ₂) ₂ (7)	1.21	3.27 (NMe ₂)	22.85	30.15	60.56 (N(CH ₃) ₂)
(silox) ₂ MoCl ₄ (8)	1.28		26.11	30.69	
(silox) ₂ MoCl ₂ (PMe ₃) (12) ^d	1.25	1.06 (d, 11, ^e PMe ₃)	24.99	30.95	18.31 (32, ^f PMe ₃)
(silox) ₂ HW(η^2 -CH ₂ PMe ₂)PMe ₃ (14) ^g	1.31	1.25 (d, 10, ^e PMe)	24.00	31.46	19.63 (br, PMe)
	1.35	1.26 (d, 8, ^e PMe ₃)	24.24	31.57	25.35 (21, ^f PMe)
		1.34 (d, 10, ^e PMe)			26.14 (32, ^f PMe ₃)
		2.35 (ddd, 7, 7, ^e 5, ^e CHH)			
		4.83 (dd, 87, ^e 27, ^e 53, ^h WH)			
		5.05 (ddd, 14, ^e 7, ^e 7, CHH)			
(silox) ₂ WCl ₄ (15) ^b	1.38		27.23	32.55	
(silox) ₂ WCl ₂ (PMe ₃) (16) ⁱ	1.29	1.18 (d, 12, ^e PMe ₃)	24.96	30.95	31.06 (36, ^f PMe ₃)

^a Benzene-*d*₆ unless otherwise noted; J_{HH} unless otherwise noted. ^b Taken from ref 3. ^c IR (nujol), $n(\text{MoH}) = 1965 \text{ cm}^{-1}$. ^d ^{31}P NMR $\delta -6.35$. ^e J_{PH} , ^f J_{PC} . ^g $^{31}\text{P}\{^1\text{H}\}$ NMR $\delta -3.01$ (d with satellites, $J_{\text{PP}} = 8$, $J_{\text{WP}} = 204$), -33.16 (d with satellites, $J_{\text{PP}} = 7$, $J_{\text{WP}} = 178$). ^h From tungsten satellites, this is J_{WH} . ⁱ ^{31}P NMR $\delta -68.13$ ($J_{\text{PW}} = 610$).

$^{\circ}\text{C}$ for 48 h produced only 80% [(silox)₂Mo]₂(μ : η^2 , η^2 -C₂Me₂) (**6**), according to ^1H NMR analysis ($K \sim 460 \text{ M}^{-1}$; $\Delta G^{\circ} \sim -4.5 \text{ kcal/mol}$). 2-Butyne-bridged **6** possesses a C₂ twist that is observed via two silox resonances in its ^1H NMR spectrum, just like its tungsten analogue.¹¹ Along with the formation of [(^tBu₃SiO)₂MoH]₂ (**5**) from a reduction of [(^tBu₃SiO)₂-MoCl]₂ (**2**), these results strongly suggest that [(silox)₂Mo]₂ (**1**) is a viable species, but unstable with respect to its cyclometalation product, **3**. Further trapping reactions with alkynes and olefins were not attempted with **3**, nor were any attempts made to isolate pure **6**. Unlike the alkyne scission that occurs in the thermolysis of [(silox)₂W]₂(μ : η^2 , η^2 -C₂Me₂) at 80 $^{\circ}\text{C}$,¹¹ **6** remained thermally stable to 120 $^{\circ}\text{C}$.

Precursors to the (silox)₂Mo Core. 1. (silox)₂Mo-(NMe₂)₂. The aforementioned experiments suggested that [(silox)₂Mo]₂ (**1**) was not stable, and that cleavage of multiply bonded dimolybdenum complexes was unlikely to be a successful approach toward Mo(II) species. As a consequence, routes derived from mononuclear starting materials were sought. Despite its potential, the Mo(IV) tetraamide, Mo(NMe₂)₄, has not been routinely used as a starting material because its original synthesis—from MoCl₅ and LiMe₂—results in $\sim 10\%$ yield and requires separation from [(Me₂N)₃Mo]₂.^{15,16} The use of Mo(IV) starting materials MoCl₄(THF)₂ and MoCl₄(DME) gave modestly better yields (~ 10 – 15%), and the use of Zr(NMe₂)₄ and Sn(NMe₂)₄ as nonreductive amide sources led to mostly diamagnetic product mixtures. The best procedure was determined to be the direct treatment of MoCl₄(OEt₂)₂ with a stoichiometric amount of LiNMe₂ in Et₂O, which afforded 25% purple

Mo(NMe₂)₄ upon sublimation. The treatment of Mo(NMe₂)₄ with 2 equiv of (silox)H in pentane provided (silox)₂Mo-(NMe₂)₂ (**7**) as a maroon diamagnetic solid in 70% yield (eq 1).



Somewhat surprisingly, (silox)₂Mo(NMe₂)₂ (**7**) was remarkably unreactive toward NH₃, H₂PPh, 2,6-Ph₂-C₆H₃NH₂, and RNH₂ (R = adamantyl, Si^tBu₃) at 150 $^{\circ}\text{C}$ in C₆D₆. The diamide did react with MeI and TMSCl in C₆D₆, but only TMS-NMe₂ could be identified among many paramagnetic products in each reaction. As a consequence, molybdenum halides were revisited as potential starting materials.

2. bis-Silox Derivatives from MoCl₅. As in Weidenbruch's original report of silox-containing transition metal complexes,¹⁷ the silanolysis of MoCl₅ was explored. Treatment of MoCl₅ with (silox)H in refluxing CCl₄ led to (silox)₂MoCl₄ (**8**) and (silox)₂MoCl₃ (**9**) in proportions that were highly dependent on the purity of the initial halide and the length of the reaction. During a 2 h procedure with an Ar purge, the ratio of **8**/**9** was roughly 1:4 on the basis of ^1H NMR integration of a singlet corresponding to a diamagnetic product at δ 1.28 in relation to a broad ($\nu_{1/2} \sim 35 \text{ Hz}$) singlet at δ 1.36. Extended periods ($> 6 \text{ h}$) provided almost exclusively the Mo(VI) tetrachloride **8** in preference to the Mo(V) trichloride **9**, as shown in Scheme 2. Presumably, extended reaction times permitted a slower oxidation of **9** by CCl₄ to occur. Unfortunately, the greater reflux times

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Scheme 2

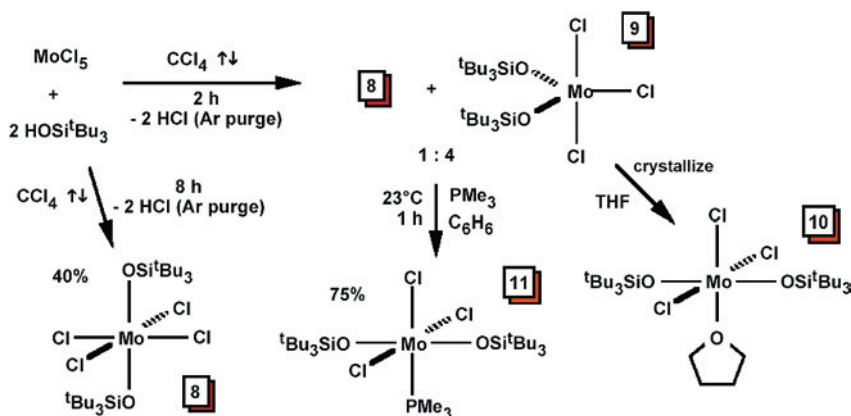


Table 2. Crystallographic Data for (silox)₂MoCl₃(THF) (**10**), (silox)₂MoCl₂(PMe₃) (**12**), (silox)₂HW(η²-CH₂PMe₂)PMe₃ (**14**), and (silox)₂Mo(PMe₃)₂ (**17**)

	10^a	12	14	17
formula	C ₂₈ H ₆₂ O ₃ Si ₂ Cl ₃ Mo	C ₂₇ H ₆₃ O ₂ Si ₂ Cl ₂ PMo	C ₃₀ H ₇₂ O ₂ Si ₂ P ₂ W	C ₃₀ H ₇₂ O ₂ Si ₂ P ₂ Mo
fw	705.27	673.79	766.88	678.94
space group	C2/c	P2 ₁ /n	P $\bar{1}$	P2 ₁ /n
Z	4	4	2	4
a, Å	8.7262(8)	8.5082(6)	8.6908(9)	9.2725(4)
b, Å	15.4639(17)	15.5481(10)	13.0276(16)	28.0138(13)
c, Å	27.145(2)	26.5089(17)	17.333(2)	15.0447(7)
α, deg	90	90	99.970(6)	90
β, deg	96.374(3)	97.070(3)	94.754(6)	90.252(3)
γ, deg	90	90	101.066(6)	90
V, Å ³	3640.3(6)	3480.1(4)	1883.2(4)	3907.9(3)
r _{calcd} , g cm ⁻³	1.287	1.286	1.352	1.152
μ, mm ⁻¹	0.672	0.667	3.239	0.501
temp, K	173(2)	173(2)	173(2)	173(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073
R indices [I > 2σ(I)] ^{b,c}	R ₁ = 0.0340 wR ₂ = 0.0841	R ₁ = 0.0246 wR ₂ = 0.0647	R ₁ = 0.0438 wR ₂ = 0.0957	R ₁ = 0.0572 wR ₂ = 0.1191
R indices (all data) ^{b,c}	R ₁ = 0.0516 wR ₂ = 0.0876	R ₁ = 0.0320 wR ₂ = 0.0662	R ₁ = 0.0660 wR ₂ = 0.1017	R ₁ = 0.0684 wR ₂ = 0.1251
GOF ^d	1.102	1.124	1.006	1.008

^a Half of a molecule of **10** constitutes an asymmetric unit. ^b $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$. ^c $wR_2 = [\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2]^{1/2}$. ^d GOF (all data) = $[\sum w(|F_o| - |F_c|)^2 / (n - p)]^{1/2}$, n = number of independent reflections, p = number of parameters.

also increased the amount of an impurity, which was spectroscopically identified as (silox)₂Mo(O)₂.¹⁸ It is not certain whether the dioxo species is derived from impure starting material or whether the copious HCl produced as a byproduct helps dehydrate the glass reaction vessel, but it does limit the isolated yield of **8** to ~40%. The tungsten analogue, (silox)₂WCl₄, was produced in similar fashion from WCl₆, and (silox)₂WCl₃ can be generated from it via reduction.³

Attempts to separate (silox)₃MoCl₃ (**9**) from (silox)₂MoCl₄ (**8**) via fractional crystallization failed in most solvents, but in THF, orange-red crystals of a THF adduct, *mer*-(silox)₂MoCl₃(THF) (**10**), were produced in 40% yield. A more efficient means of producing a Mo(V) starting material involved treatment of the **8/9** mixture with PMe₃ to precipitate the nearly insoluble phosphine adduct, (silox)₂MoCl₃(PMe₃) (**11**), from benzene in ~75% yield on the basis of MoCl₅.

3. Structure of *mer*-(silox)₂MoCl₃(THF) (10**).** Table 2 provides the X-ray crystallographic data pertaining to *mer*-(silox)₂MoCl₃(THF) (**10**), while pertinent bond distances and

angles are given in Table 3. Figure 1 shows that **10** is a nearly perfect octahedron with one chloride ligand and the THF opposite one another (180° by symmetry) and a set of *trans*-silox groups (179.42(8)°). The remaining *trans*-chlorides (172.86(2)°) are tipped slightly toward the THF (86.43(2)°), and the corresponding Cl1–Mo–Cl2 angles are 93.57(2)°. All remaining angles are within 1.2° of 90°, and the bond distances are normal for Mo(V), with a $d(\text{MoO})$ of 1.8348(12) Å and 2.3429(7) Å that describe the silox and THF interactions, respectively. The chloride opposite THF is slightly closer to Mo (2.3429(7) Å) than the others (2.369(2) Å), as expected from *trans*-influence arguments.

4. Synthesis of (silox)₂MoCl₂(PMe₃) (12**).** The phosphine adduct, (silox)₂MoCl₃(PMe₃) (**11**), proved to be a convenient starting material. The reduction of **11** with Na/Hg in diethyl ether with PMe₃ present (~3 equiv gave optimum yields) afforded the diamagnetic blue Mo(IV) complex, (silox)₂MoCl₂(PMe₃) (**12**), in 90% yield according to eq 2. In the ¹H NMR spectrum of **12**, the singlet corresponding to the silox was at δ 1.25, and a doublet attributed to the PMe₃ was observed at δ 1.06 ($J_{\text{PH}} = 11$ Hz). The ¹³C{¹H} NMR

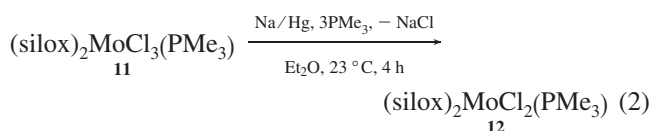
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Table 3. Selected Bond Distances (Å) and Angles (deg) for *mer*-(silox)₂MoCl₃(THF) (**10**), (silox)₂MoCl₂(PMe₃) (**12**), (silox)₂HW(η²-CH₂PMe₂)PMe₃ (**14**), and (silox)₂Mo(PMe₃)₂ (**17**)

	10^a	12^b	14^c	17^d
M–O1	1.8348(12)	1.8317(7)	1.918(3)	1.975(3)
M–O2		1.8358(7)	1.914(3)	1.943(3)
Mo–O(THF)	2.1676(17)			
Mo–Cl1	2.3689(5)	2.4277(3)		
Mo–Cl2	2.3429(7)	2.4424(3)		
M–P1		2.3933(3)	2.3537(13)	2.3374(13)
M–P2			2.3713(13)	2.3330(13)
W–C1			2.235(6)	
(P–C) _{av}		1.802(7)	1.801(38)	1.806(7)
(O–Si) _{ave}	1.7066(13)	1.691(3)	1.638(6)	1.616(5)
O1–M–O1'/2	179.42(8)	157.91(3)	104.87(13)	136.67(13)
O1–M–O(THF)	90.29(4)			
O1–Mo–Cl1		90.43(3)		
O–Mo–Cl1'	88.85(4)			
O1–Mo–Cl2	89.71(4)	89.28(3)		
Cl1–Mo–O(THF)	86.43(2)			
Cl2–Mo–O(THF) 180				
O2–Mo–Cl1		90.48(3)		
O2–Mo–Cl2		88.71(3)		
Cl1–Mo–Cl1'	172.86(2)			
Cl1–Mo–Cl2	93.57(2)	177.11(2)		
P1–M–O1		100.57(3)	96.84(9)	96.85(10)
P1–M–O2		101.49(2)	132.79(9)	111.74(10)
P2–M–O1			134.62(9)	99.62(10)
P2–M–O2			96.83(10)	110.14(10)
P1–M–P2			96.74(5)	93.10(5)
P1–Mo–Cl1		89.81(2)		
P1–Mo–Cl2		93.08(2)		
O1–W–C1			132.33(19)	
O2–W–C1			91.04(19)	
P1–W–C1			45.47(17)	
P2–W–C1			85.56(18)	
W–P1–C1			63.7(2)	
W–P1–C2			136.4(3)	
W–P1–C3			118.23(18)	
W–C1–P1			70.8(2)	
M–O1–Si1	171.86(8)	163.57(5)	157.2(2)	152.2(2)
M–O2–Si2		158.85(5)	167.2(2)	175.1(2)

^a The apical chloride is Cl2. ^b The Mo–P1–C's are 111.85(5)°, 112.08(5)°, and 117.93(5)°. ^c The W–P2–C angles are 114.1(2)°, 122.1(3)°, and 120.8(4)°; the C–P2–C angles are 90.1(4)°, 97.1(4)°, and 105.7(5)°; the C–P1–C angles are 109.7(4)°, 111.4(3)°, and 104.5(4)°. ^d The Mo–P1–C angles are 114.0(2)°, 114.9(2)°, and 123.8(2)°, and the Mo–P2–C angles are 114.8(2)°, 118.8(2)°, and 120.6(2)°.

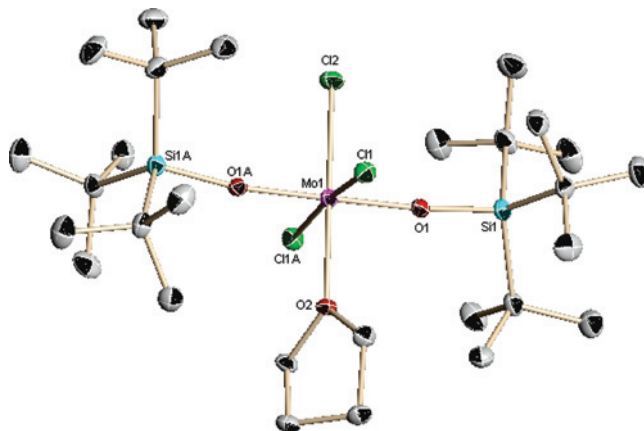
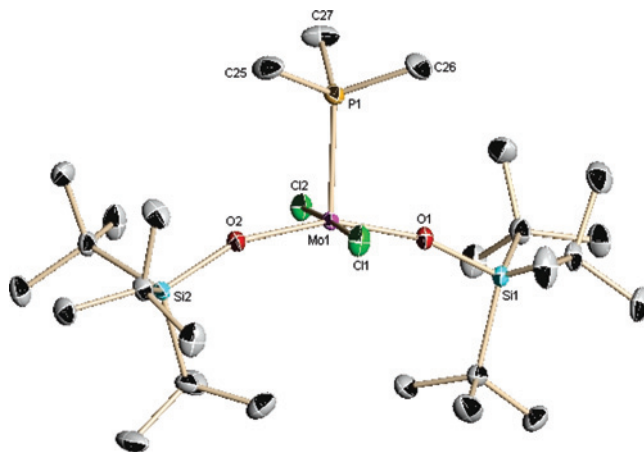
spectrum was consistent with this formulation, and the ³¹P NMR spectrum showed a single resonance at δ –6.35.



5. Structure of (silox)₂MoCl₂(PMe₃) (12**).** Structural details of (silox)₂MoCl₂(PMe₃) (**12**) can be found in Table 2, and core bond distances and angles are provided in Table 3. As Figure 2 illustrates, **12** is a square-pyramidal molecule with PMe₃ in the apical position, and *trans*-silox and *trans*-chlorides occupying the basal positions. There is a modest distortion—presumably steric—from a perfect square pyramid as the O–Mo–P angles average 101.0(7)°, while the Cl–Mo–P angles are 89.81(2)° and 93.08(2)°. All of the O–Mo–Cl angles within the base average 89.7(9)°, and the O–Mo–O and Cl–Mo–Cl angles are 157.91(3)° and 177.11(2)°, respectively. The *d*(MoCl) averages 2.435(10) Å, which is >0.06 Å longer than the *d*(MoCl) average in

mer-(silox)₂MoCl₃(THF) (**10**). Taking the chlorides along the *x* axis, this lengthening may manifest 2e[–] occupation of the Cl → Mo dπ* bonding d_{xz} orbital, rather than the π* component of the stronger π-donor siloxides (d_{yz}). The phosphine has a slight lean away from Cl2 (P1–Mo–Cl2 = 93.08(2)°, P1–Mo–Cl1 = 89.81(2)°), and the corresponding asymmetry in the C–P1–Mo angles (110.85(5)°, 112.08(5)°, and 117.93(5)°) is consistent with slight σ/π mixing to maximize Mo–P bonding.^{4,13} The *d*(MoO) average is 1.834(3) Å, essentially the same as in **10**, and the *d*(MoP) is normal at 2.3933(3).

Approaches to the (silox)₂W Core. 1. Via (silox)₃WCl (13**).** The W(III) PMe₃ complex (silox)₃WPMe₃ was prepared via Na/Hg (~1 equiv) reduction of (silox)₃WCl (**13**) in moderate yield (~40%),⁴ but **13** was discovered to be prone to overreduction. The product of a controlled reduction using 2 equiv of Na/Hg in the presence of 10 equiv of PMe₃ was the red hydride (silox)₂HW(η²-CH₂PMe₂)PMe₃ (**14**; eq 3), which was isolated in only 15% yield via fractional crystallization despite being present in ~90% yield according to ¹H NMR analysis. Its origin is likely to be the transient (silox)₂W(PMe₃)₂ (**15**) complex, which is expected to be susceptible to CH bond oxidative addition to its W(II) center.

**Figure 1.** Molecular view of *mer*-(silox)₂MoCl₃(THF) (**10**).**Figure 2.** Molecular structure of (silox)₂MoCl₂(PMe₃) (**12**).

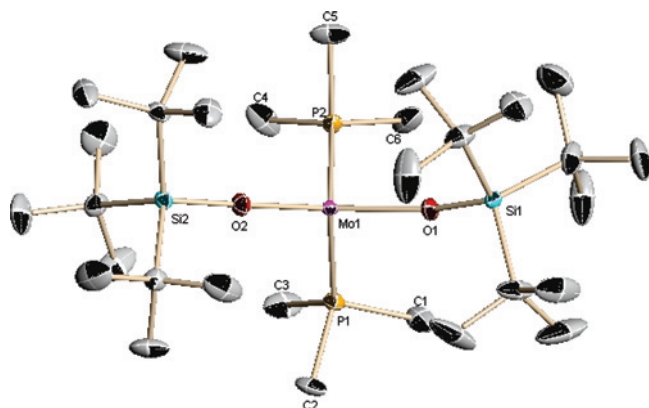
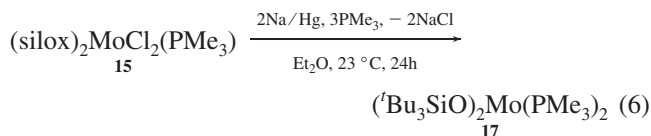


Figure 4. Molecular view of $(t\text{Bu}_3\text{SiO})_2\text{Mo}(\text{PMe}_3)_2$ (**17**).

attempt would be successful for Mo(II).^{19–22,24} The reduction of $(\text{silox})_2\text{MoCl}_2(\text{PMe}_3)$ (**12**) with Na/Hg in Et_2O with 3 equiv of PMe_3 present afforded red $(t\text{Bu}_3\text{SiO})_2\text{Mo}(\text{PMe}_3)_2$ (**17**) in 68% yield upon crystallization from pentane. Compound **17** is paramagnetic, with a solution μ_{eff} of 2.6 at 23 °C, but NMR spectra were revealing. Two resonances were observed in the ^1H NMR spectrum at δ 2.33 ($\nu_{1/2} = 75$ Hz) and δ 11.44 ($\nu_{1/2} = 120$ Hz), while only one signal was apparent in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum at δ 91.40 ($\text{C}(\text{CH}_3)_3$). The data appeared promising for an $S = 1$ Mo(II) species, but an X-ray crystal structure was necessary to confirm the composition.



2. Structure of $(\text{silox})_2\text{Mo}(\text{PMe}_3)_2$ (17**).** Information on data collection regarding $(t\text{Bu}_3\text{SiO})_2\text{Mo}(\text{PMe}_3)_2$ (**17**) is available in Table 2, metric features are given in Table 3, and its pseudo- T_d geometry is evident in Figure 4. Elongated $d(\text{MoO})$'s of 1.943(3) and 1.975(3) Å provide testament to the low oxidation state of the complex, whereas the shorter $d(\text{MoP})$'s of 2.3330(13) and 2.3374(13) Å give evidence of the backbonding that occurs when PMe_3 binds to Mo(II). On the basis of a pure tetrahedral geometry, a diamagnetic complex would not be surprising for a second row element,²⁵ but instead, **17** manifests certain distortions that do not appear to be steric in origin. The O–Mo–O angle is opened up to $136.67(13)^\circ$, whereas the P–Mo–P angle is closed down to $93.10(5)^\circ$, despite the cone angle of PMe_3 (118°)^{26,27} being roughly the same as that of silox ($\sim 120^\circ$ (est)).²⁸ What is more curious is the asymmetry of the P–Mo–P plane to the O–Mo–O plane. The O1–Mo–P1 and O1–Mo–P2 angles are $96.85(10)^\circ$ and $99.62(10)^\circ$, respectively, but the related O2–Mo–P1 and O2–Mo–P2 angles are signifi-

cantly greater ($111.74(10)^\circ$ and $110.14(10)^\circ$, respectively). O1, P1, and P2 occupy fac positions of an octahedron, and O2 is leaning away from the phosphines in a manner that does not make sense on pure steric grounds.

Discussion

Synthetic Studies. It is not surprising that the stability of the dimolybdenum triple bond hampered the elaboration of Mo(III),^{7,8} but the inability to manipulate $(\text{silox})_2\text{Mo}(\text{NMe}_2)_2$ (**7**) was disappointing given the investment in improving the yield of $\text{Mo}(\text{NMe}_2)_4$.^{15,16} Fortunately, a return to Weidenbruch's silanolysis routes¹⁷ has enabled the ready preparation of silox halides of molybdenum and tungsten. Aside from some modest separation problems, the syntheses of $(\text{silox})_2\text{MCl}_4$ ($\text{M} = \text{Mo}$, **8**; W , **15**),³ $(\text{silox})_2\text{MoCl}_3$ (**9**), and its derivatives have solved the problem of gaining an entryway into the chemistry of the second and third row transition metals of group 6.

$(\text{silox})_2\text{Mo}(\text{PMe}_3)_2$ (17**) versus $(\text{silox})_2\text{HW}(\eta^2\text{-CH}_2\text{PMe}_2)\text{-PMe}_3$ (**14**).** Similar to the case of $(\text{silox})_3\text{M}$ ($\text{M} = \text{Mo}$, W), where the molybdenum complex is isolable but the tungsten is not,⁴ Mo(II) can be stabilized by the combination of silox and PMe_3 ,^{1,4,13,14} whereas “ $(\text{silox})_2\text{W}(\text{PMe}_3)_2$ ” is prone to the oxidative addition of an internal CH bond.^{19–22,24} These observations follow the periodic trend that third row transition elements are more easily oxidized than their second row congeners.²⁰ However, it is surprising that Mo(II) is stabilized in a four-coordinate environment. Now that Cotton and Schmid have debunked the claims of “ $\text{Cl}_2\text{Mo}(\text{PMe}_3)_2$ ” (i.e., $\text{Cl}_2\text{Zn}(\text{PMe}_3)_2$),^{29,30} $(\text{silox})_2\text{Mo}(\text{PMe}_3)_2$ (**17**) is likely the only four-coordinate Mo(II) species known. Related use of 2,6- $\text{Ph}_2\text{-C}_6\text{H}_3\text{O}$ by the groups of Parkin and Rothwell led to discovery of the $\eta^6\text{-Ph}, \eta^1\text{-O}$ coordination mode, yielding the seven-coordinate $[\eta^1\text{-}(\eta^6\text{-2-Ph})(6\text{-Ph})\text{C}_6\text{H}_3\text{O}]\text{Mo}(\text{PR}^1\text{R}^2)_2\text{H}$ ($\text{R}^1 = \text{R}^2 = \text{Me}$;³¹ $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{Ph}$)³² derivatives. These studies were preceded by the synthesis of octahedral *tert*-butoxide complexes by Chisholm et al. as $(t\text{BuO})_2\text{Mo}(\text{py})_2(\text{CO})_2$ ³³ and $(t\text{BuO})_2\text{Mo}(\text{bipy})_2$.³⁴ Thiolates have also seen activity as ligands compatible with Mo(II) centers, but these $t\text{BuS}^-$,^{35,36} 2,6- $\text{Ph}_6\text{-C}_6\text{H}_3\text{S}^-$, and 2,4,6- $\text{PrC}_6\text{H}_2\text{S}^-$ ³⁷ compounds all possess higher coordination numbers than four.

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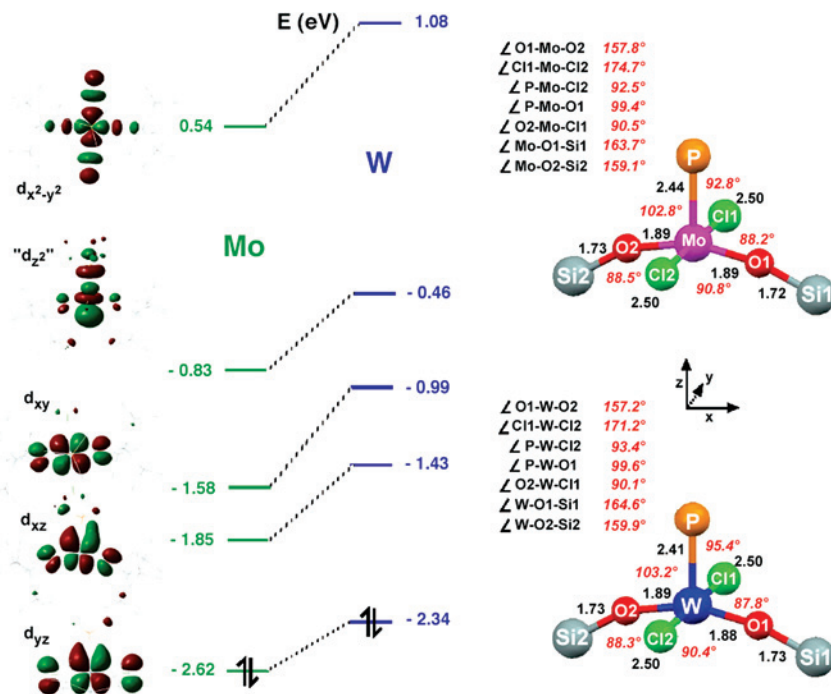


Figure 5. Calculated geometries and d-orbital splitting diagrams of (silox)₂MoCl₂PMe₃ (**12'**) and (silox)₂WCl₂PMe₃ (**16'**). Distances (black) are in angstroms; angles are in *italicized red*.

As for the cyclometalation of PMe₃ to afford (silox)₂HW(η^2 -CH₂PMe₂)PMe₃ (**14**), this CH bond activation was first observed for tungsten by Green et al. in their attempt to prepare “W(PMe₃)₆”.^{19,21} The cyclometalation product (Me₃P)₄HW(η^2 -CH₂PMe₂) was isolated instead. Later efforts by Parkin demonstrated that the Mo⁰ center of (Me₃P)₆Mo is less prone to activating the CH bond of a PMe₃ ligand than its tungsten counterpart.²⁴

Electronic Structures. 1. (silox)₂MCl₂PMe₃ (M = Mo, **12; W, **16**).** The X-ray crystal structure determination of (silox)₂MoCl₂PMe₃ (**12**) confirmed its expected square-pyramidal arrangement, but the diamagnetism observed for **12** and its third row congener (silox)₂WCl₂PMe₃ (**16**) was not an obvious consequence. Figure 5 illustrates the d-orbital splitting diagrams for the full models (**12'** and **16'**) as determined from high-level quantum mechanics/molecular mechanics calculations (QM/MM).^{38–43} The calculated

structure (**12'**) essentially reproduces the geometry determined by the crystal structure, except that the bond lengths are ~0.04–0.06 Å longer. The tungsten analogue (**16'**) has a virtually identical arrangement, with the exception of a significantly shorter *d*(WP) of 2.41 Å (*d*(MoP) = 2.44 Å), which is in concert with its anomalously large *J*_{WP} of 610 Hz.

The ordering of the orbitals portrayed in Figure 5 is standard, and the spread of energies is greater for W (3.42 eV) relative to the second row element (3.16 eV), as predicted on the basis of the slightly larger radial extent of the 5d orbitals. The slightly better σ and π overlaps for the third row metal are reflected in the generally greater gaps between each orbital pair. The lowest orbital, *d*_{yz}, is π^* with respect to the MCl bonds and π^b to phosphorus. There is a considerable gap (Mo, 0.77 eV; W, 0.91 eV) between *d*_{yz} and the next orbital, *d*_{xz}, that explains the diamagnetism. This is in part due to a modest amount of metal–oxygen σ^* character to the orbital, which is primarily metal–oxygen π^* and MP π -bonding. The cant of the siloxides relative to PMe₃ (e.g., P–Mo–O ~ P–W–O ~ 101°) turns on the σ antibonding character and elevates the orbital considerably, since it approaches the *d*_{xy} π^* orbital in energy (Mo, 0.30 eV; W, 0.44 eV). It is interesting to note that *d*_{xy} has virtually no MCl π^* character but possesses a considerable metal–oxygen π^* interaction. The *d*_{z²} orbital for W is slightly

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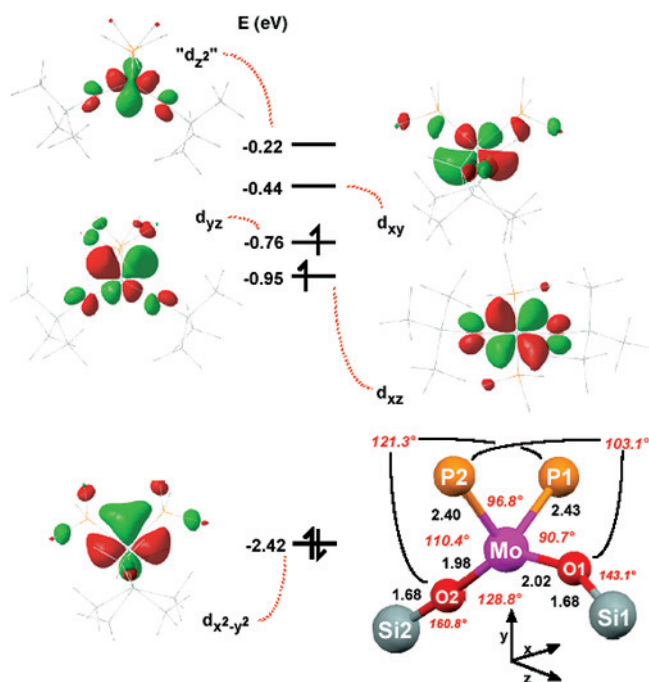


Figure 6. Calculated geometry and d-orbital splitting diagram of $(\text{silox})_2\text{Mo}(\text{PMe}_3)_2$ (**17'**). Distances (black) are in angstroms; angles are in italicized red.

higher—relative to d_{yz} —than in Mo, perhaps indicative of the greater 6s involvement in WP bonding.³ Note that the $d_{x^2-y^2}$ orbital has more MCl than metal–oxygen σ^* character, as expected on the basis of ΔE_{MX} arguments.

2. $(\text{silox})_2\text{Mo}(\text{PMe}_3)_2$ (17**).** In a pseudo- T_d geometry, a “3 over 2” orbital arrangement would be expected to generate a low-spin ($S = 0$) d^4 configuration for a second or third row transition element.²⁵ In an attempt to better understand the observed $S = 1$ electronic state of $(\text{silox})_2\text{Mo}(\text{PMe}_3)_2$ (**17**), high-level QM/MM calculations were conducted on the full model (**17'**).^{38–43} While most of the major geometric features of the structure were effectively modeled by **17'**, the tilt of the P–Mo–P plane with respect to the O–Mo–O plane was not. Instead of tilting toward one silox ligand, the P–Mo–P plane has a much greater twist with respect to the O–Mo–O plane ($\text{O–Mo–P} = 90.7^\circ$ and 103.1° vs 110.4° and 121.3°), as Figure 6 reveals, and the calculated $d(\text{MoO})$ and $d(\text{MoP})$ are 0.03–0.04 Å and 0.07–0.10 Å greater, respectively. The geometric distortions occurred whether or not the crystal structure coordinates or a geometry generated from a molecular-mechanics-based conformational search was used to initiate the QM/MM-based geometry optimization. There is no obvious rationale for the angular discrepancies, and such subtleties are unlikely to alter the electronics to a great extent. The calculated P–Mo–P angle of 96.8° and O–Mo–O of 128.8° are also off by $\sim 3.7^\circ$ and $\sim 7.8^\circ$, respectively, but the general features of the core are similar to the X-ray crystal structure and may simply indicate that **17** lies in a shallow minimum, whereby its angular changes are sensitive to the chemical environment.

The calculations reproduce the $S = 1$ ground state implicated by the solution magnetism of $(\text{silox})_2\text{Mo}(\text{PMe}_3)_2$ (**17**), and corresponding singlet and quintet excited states are 2.3 and 13.8 kcal/mol above the triplet, respectively. A

perusal of the orbitals in Figure 6 reveals nothing obvious that would cause the “twist” described above, so the contention that subtle bonding interactions are at play appears reasonable. The lowest orbital in the ligand field is best construed as $d_{x^2-y^2}$, and it is at -2.42 eV relative to the two singly occupied d_{xz} (-0.95 eV) and d_{yz} (-0.76 eV) orbitals. It is clear that $d_{x^2-y^2}$ has a significant $\text{Mo}(d\pi) \rightarrow \text{P}(d/\sigma^*)$ backbonding component, while d_{xz} and d_{yz} carry the brunt of the $\text{O}(p\pi) \rightarrow \text{Mo}(d\pi)^*$ antibonding interaction of the silox ligands, and d_{yz} has some σ^* character. At -0.44 eV and -0.22 eV are d_{xy} and “ d_{z^2} ”, and these are σ^* towards the phosphines and the silox oxygens, respectively, although the low symmetry renders the latter orbital rather difficult to identify. The orbital energies must be treated with caution, as density functional theory (DFT) is prone to error in comparing filled versus half-filled versus empty orbitals,⁴⁴ but the expected “3 over 2” configuration is not apparent. By opening the O–Mo–O angle, d_{yz} becomes significantly less σ^* in character and is lower in energy, but the penalty is greater π^* character in d_{xz} , which is higher in energy; the proximity of the two leads to the $S = 1$ ground state, and their ~ 0.19 eV separation is not enough to overcome a pairing energy. Thus “3 over 2” becomes “2 over 2 over 1”, with $d_{x^2-y^2}$ greatly stabilized by the backbonding interaction, and through mixing with “ d_{z^2} ”, which takes any σ^* character away.

Conclusions

The combination of tBu_3SiO (silox) and PMe_3 again proves to make a potent duo in the synthesis of low-coordinate, low-oxidation-state species via the stabilization of Mo(II) as $(\text{silox})_2\text{Mo}(\text{PMe}_3)_2$ (**17**). This combination is unable to overcome the propensity of W(II) to oxidation; hence, the related “ $(\text{silox})_2\text{W}(\text{PMe}_3)_2$ ” formula is found as the PMe_3 cyclometalation product, $(\text{silox})_2\text{HW}(\eta^2\text{-CH}_2\text{PMe}_2)\text{PMe}_3$ (**14**).

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 sodium benzophenone ketyl and vacuum-transferred from the same prior to use. Benzene- d_6 was dried over activated 4 Å molecular sieves, vacuum-transferred, and stored under N_2 . All glassware was oven-dried, and NMR tubes for sealed tube experiments were additionally flame-dried under a dynamic vacuum. MoCl_5 was obtained from Strem Chemical, and $\text{MoCl}_4(\text{THF})_2$, $\text{MoCl}_3(\text{THF})_3$,⁴⁵ and $\text{MoCl}_4(\text{OEt}_2)_2$,⁴⁶ were prepared according to literature procedures, as were $[(\text{Bu}_3\text{SiO})_2\text{MoCl}]_2$ (**2**), $(\text{silox})_3\text{WCl}$ (**2-Cl**), and $(\text{silox})_2\text{WCl}_4$ (**15**).³

NMR spectra were obtained using Varian XL-400, INOVA-400, and Unity-500 spectrometers, and chemical shifts are reported relative to benzene- d_6 (^1H , δ 7.15; $^{13}\text{C}\{^1\text{H}\}$, δ 128.39). Infrared spectra were recorded on a Nicolet Impact 410 spectrophotometer

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interfaced to a Gateway PC, or a Nicolet Avatar 370 DTGS spectrophotometer interfaced with an IBM ThinkPad. Solution magnetic measurements were conducted via Evans' method in C₆D₆ unless otherwise noted.⁴⁷ Elemental analyses were performed by Oneida Research Services, Whitesboro, New York, or Robertson Microлит Laboratories, Madison, New Jersey.

Procedures. 1. (silox)₂HMoMo(κ-O,C-OSi^tBu₂CMe₂CH₂)-(silox) (3). To a 100 mL flask containing 1.00 g (1.78 mmol) of [(^tBu₃SiO)₂MoCl]₂ (**2**) and 4.52 g of Na/Hg (0.95%, 1.87 mmol) was distilled 50 mL of THF at -78 °C. The solution was allowed to warm slowly from -78 to 23 °C. After the green-brown solution was stirred for 4 h at 23 °C, all volatiles were removed *in vacuo*. The reaction mixture was triturated three times with 10 mL of hexanes and filtered in hexanes. The removal of all volatiles yielded 0.843 g (0.80 mmol, 90%) of **3** as a green-brown solid. IR (nujol mull, Na/Cl, cm⁻¹): 1945 (ν, MoH). Anal. calcd for C₅₀H₁₀₈Cl₂Mo₂O₄Si₄: C, 54.61; H, 10.50. Found: C, 54.24; H, 10.65.

2. [(^tBu₃SiO)₂MoCH₃]₂ (4₂). To a 100 mL flask containing 1.00 g (0.889 mmol) of **2** was distilled 20 mL of Et₂O at -78 °C. CH₃MgBr (0.6 mL, 3.0 M in Et₂O) was added via syringe. The solution was allowed to warm to 23 °C and was stirred for 3 h. The flask was evacuated and the reaction mixture stripped of all volatiles. The resulting dusty-purple solid was dissolved in 50 mL of pentane and filtered, and the salt cake was repeatedly washed until no traces of product remained. The filtrates were concentrated to ~5 mL, cooled to -78 °C, and filtered to give 0.818 g (0.755 mmol, 85%) of **4** as dusty-purple microcrystals. Anal. calcd for C₅₀H₁₀₈Cl₂Mo₂O₄Si₄: C, 55.42; H, 10.60. Found: C, 54.89; H, 10.76.

3. [(^tBu₃SiO)₂MoH]₂ (5₂). To a 100 mL round-bottom flask containing 2.00 g (1.78 mmol) of **2** and 9.04 g of Na/Hg (0.95%, 3.73 mmol) was distilled 50 mL of THF at -78 °C. The solution was exposed to 1 atm of H₂ and allowed to warm slowly from -78 to 23 °C. After the red-brown solution was stirred for 4 h at 23 °C, all volatiles were removed *in vacuo*, and the reaction mixture was filtered in hexanes. The removal of all volatiles yielded 1.78 g (1.69 mmol, 95%) of **5** as a red-brown solid. IR (nujol mull, Na/Cl, cm⁻¹): 1965 (ν(MoH)). Anal. calcd for C₅₀H₁₀₈Cl₂Mo₂O₄Si₄: C, 54.61; H, 10.50. Found: C, 54.24; H, 10.65.

4. [(silox)₂Mo]₂(μ:η²η²-C₂Me₂) (6). A NMR tube attached to a needle valve adaptor was charged with a solution of **3** (30 mg, 0.028 mmol) in 0.65 mL of C₆D₆. The tube was fitted with a 180° needle valve and freeze-pump-thaw degassed three times. 2-Butyne (176 Torr, 0.28 mmol) was transferred via a calibrated 30.1 mL gas bulb. The tube was sealed and heated for 48 h at 100 °C. Partial conversion (80%) was seen by ¹H NMR spectroscopy, but 20% of the starting material remained even after continued thermolysis (8 h, 120 °C).

5. Mo(NMe₂)₄. To a 1 L three-neck round-bottom flask containing 30 g (0.59 mol) of LiNMe₂ was vacuum-transferred 300 mL of Et₂O. The LiNMe₂ solution was cooled to 0 °C, and a suspension of MoCl₄(OEt)₂⁴⁶ (55 g, 0.142 mol) in 150 mL of Et₂O was cannulated into the ice-cold LiNMe₂ solution. The reaction mixture was stirred at 0 °C for 4 h and then stirred at 23 °C for 48 h. The Et₂O was removed from the brown reaction mixture *in vacuo*, and the flask was fitted with a condenser. The surface of the condenser was cooled with a dry ice/acetone mixture, and the residue was heated to 80 °C for 2 h at 10⁻³ Torr. The resulting purple solid

(7.80 g) deposited on the condenser was collected, and the process was repeated to give an additional 1.88 g for a combined yield of 25%. ¹H NMR (C₆D₆, 400 MHz): δ 3.27.

6. (silox)₂Mo(NMe₂)₂ (7). To a 100 mL flask containing 2.00 g (7.34 mmol) of Mo(NMe₂)₄ and 3.17 g (14.7 mmol) of ^tBu₃SiOH was distilled 30 mL of pentane at -78 °C. The solution developed a deep maroon color upon warming. After stirring for 30 min, the solution was filtered and stripped of all volatiles. The solid was redissolved in minimal pentane (~5 mL), cooled to -78 °C, and filtered to give 2.73 g (5.13 mmol, 70%) of **7** as maroon microcrystals. ¹H NMR (C₆D₆, 400 MHz): δ 1.21 (s, ^tBu, 27H), 3.27 (s, N(CH₃)₂, 6H). ¹³C{¹H} NMR (C₆D₆, 400 MHz): δ 23.84 (C(CH₃)), 23.99 (C(CH₃)), 30.88 (C(CH₃)), 31.42 (C(CH₃)). Anal. calcd for C₂₉H₆₆N₂MoO₂Si₂: C, 65.59; H, 12.53; N, 5.28. Found: C, 65.43; H, 12.63; N, 5.11.

7. (silox)₂MoCl₄ (8) and (silox)₃MoCl₃ (9) in 1:4 Ratio. To a 500 mL flask containing 10.0 g of ^tBu₃SiOH (46.2 mmol) and 6.94 g of MoCl₅ (25.4 mmol) was vacuum-transferred 250 mL of CCl₄ at -78 °C. The dark purple suspension evolved copious amounts of HCl gas as the reaction mixture warmed to 23 °C and changed to a deep red color. The removal of HCl was further affected by the periodic exposure of the reaction mixture to a liquid-nitrogen-cooled trap under static vacuum for 1 h (~15 cycles of HCl removal). The reaction mixture was then heated in a 45 °C water bath under a static vacuum with occasional evacuation of the vacuum manifold (~15 min intervals). The reaction mixture was then stripped of all volatiles and assayed by ¹H NMR to reveal a 1:4 mixture of (^tBu₃SiO)₂MoCl₄ (**8**) and (^tBu₃SiO)₃MoCl₃ (**9**), respectively.

8. (silox)₂MoCl₄ (8). To a 250 mL flask containing 5.00 g of ^tBu₃SiOH (23.1 mmol) and 6.31 g of MoCl₅ (23.1 mmol) was vacuum-transferred 100 mL of CCl₄ at -78 °C. The purple suspension was warmed to 23 °C under a heavy argon purge and allowed to stir for an hour. The deep red solution containing a dark precipitate was then heated to 65 °C under a gentle argon purge for 8 h. The red reaction mixture was stripped of all volatiles, and the soluble portion was redissolved in 150 mL of CCl₄. The reaction mixture was filtered, and the filtrates were concentrated to ~15 mL. The red solution was cooled to 0 °C for 30 min and filtered to give 3.09 g of **8** (40%). Anal. calcd for C₂₄H₅₄Cl₄MoO₂Si₂: C, 43.11; H, 8.14. Found: C, 42.77; H, 8.39.

9. mer-(silox)₂MoCl₃(THF) (10). Procedure 6 was followed to obtain **8/9** in a ~1:4 ratio. A small portion of the mixture (0.250 g) was taken up in 25 mL of THF, and the resulting solution was filtered, leaving behind a dark red solid (presumably **8**). The red solution was allowed to evaporate at room temperature until crystals were seen to form. Small orange-red crystals of **10** were isolated by decanting the remaining mother liquor (0.088 g, 40%). The reaction was not optimized. ¹H NMR (C₆D₆, 300 MHz): δ 0.95 (27 H, ν_{1/2} ≈ 117 Hz), 1.92 (4 H, ν_{1/2} ≈ 102 Hz). ¹³C{¹H} NMR (C₆D₆, 500 MHz): δ 37.35 (C(CH₃)₃ ν_{1/2} ≈ 625 Hz). Anal. calcd for C₂₈H₆₂Cl₃MoO₃Si₂: C, 47.68; H, 8.86. Found: C, 47.31; H, 8.43.

10. (silox)₂MoCl₃(PMe₃) (11). Procedure 6 was followed to obtain **8/9** in a ~1:4 ratio. The product mixture was redissolved in 300 mL of CCl₄ and filtered, leaving behind a small amount of dark solid. The CCl₄ was removed *in vacuo*, and the reaction mixture was suspended in 100 mL of Et₂O. The transfer of 2 equiv of PMe₃ (stoichiometry based on ^tBu₃SiOH consumed) via calibrated gas bulb into the red suspension at -78 °C resulted in a bright orange solid and a green solution upon warming to 23 °C. The reaction mixture was stirred for 1 h and filtered, and the filter cake was washed to give bright orange (^tBu₃SiO)₂MoCl₃(PMe₃)

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(**11**; 12.29 g, 75%). The formulation is tentative and based on EA and reactivity studies. Anal. calcd for $C_{36}H_{82}MoO_3Si_3$: C, 45.72; H, 8.95. Found: C, 44.70; H, 8.02.

11. (silox)₂MoCl₂(PMe₃) (12). To a 100 mL round-bottom flask containing 2.43 g of **11** (3.43 mmol) and 9.12 g of Na/Hg amalgam (1.1 equiv, 3.77 mmol) was vacuum-transferred ~40 mL of Et₂O at -78 °C. PMe₃ (3 equiv, 10.29 mmol) was transferred to the reaction mixture via calibrated gas bulb. The reaction mixture was warmed to 23 °C and stirred vigorously for 4 h. The orange suspension slowly turned green and then blue during the course of reaction. The blue suspension was stripped of all volatiles, and the Hg⁰ was decanted. To the reaction mixture was transferred 50 mL of toluene. The blue solution was filtered, and the filter cake was washed with toluene until no trace of color remained. The blue filtrates were stripped of all volatiles; 20 mL of Et₂O was transferred into the flask, and the suspension was filtered to give microcrystalline **12** (2.08 g, 90%). Anal. calcd for $C_{27}H_{63}MoO_2PSi_2$: C, 48.13; H, 9.42. Found: C, 47.81; H, 9.13.

12. (silox)₂WCl₂(PMe₃) (16). To a 100 mL flask containing 1.00 g of (silox)₂WCl₄ (**15**; 1.32 mmol) and 6.72 g of Na/Hg amalgam (2.1 equiv, 2.78 mmol Na) was vacuum-transferred ~40 mL of Et₂O at -78 °C. PMe₃ (3 equiv, 3.96 mmol) was transferred to the reaction mixture via calibrated gas bulb. The reaction mixture was warmed to 23 °C and stirred vigorously for 4 h. The red suspension slowly turned purple throughout the course of the reaction. The purple suspension in purple solution was stripped of all volatiles, and the Hg⁰ was decanted. To the reaction mixture was transferred 50 mL of toluene. The purple solution was filtered, and the filter cake was washed with toluene until no trace of color remained. The purple filtrates were stripped of all volatiles; 20 mL of Et₂O was transferred into the flask, and the suspension was filtered to give microcrystalline **26** (0.724 g, 72%). Anal. calcd for $C_{27}H_{63}O_2PSi_2W$: C, 42.58; H, 8.34. Found: C, 42.19; H, 8.02.

13. (silox)₂HW(η²-CH₂PMe₂)PMe₃ (14). a. From (silox)₂WCl₂(PMe₃) (16). To a 100 mL round-bottom flask containing 1.00 g of **16** (1.16 mmol) and 5.73 g of Na/Hg (2.37 mmol) was vacuum-transferred 50 mL of Et₂O at -78 °C. PMe₃ (10 equiv, 11.6 mmol) was vacuum-transferred into the reaction mixture via calibrated gas bulb. The reaction mixture was allowed to warm to 23 °C and stir for 24 h. The red solution with white precipitate was stripped of all volatiles; the mercury was decanted, and the reaction mixture was dissolved and filtered in 50 mL of pentane. The removal of solvent in vacuo resulted in a mixture of red solid **14** and NaOSi^tBu₃. Pure red **14** (0.133 g, 0.173 mmol) was isolated by fractional crystallization from a slowly evaporating Et₂O solution at -30 °C.

b. From (silox)₂WCl₄(15). To a 100 mL round-bottom flask containing 2.00 g of **15** (2.64 mmol) and 26.2 g of Na/Hg (10.8 mmol) was vacuum-transferred 50 mL of Et₂O at -78 °C. PMe₃ (3 equiv of 7.92 mmol) was vacuum-transferred into the -78 °C reaction mixture via calibrated gas bulb. The dark red suspension was allowed to warm to 23 °C and stirred for 12 h. Within the first hour of the reduction, a dramatic color change to a green-brown solution with orange precipitate and then to a purple solution with a purple precipitate occurred. The reaction mixture gradually turned to red over the remaining reaction time. The reaction mixture was stripped of all volatiles; the Hg⁰ was decanted, and the red solid was dissolved in 50 mL of pentane. The reaction mixture was filtered and the pentane removed in vacuo. The red solid was

dissolved in minimal Et₂O and recrystallized at -30 °C over 12 h to give 1.72 g of **14** (2.24 mmol, 85%). Anal. calcd for $C_{30}H_{72}O_2P_2Si_2W$: C, 46.99; H, 9.46. Found: C, 46.55; H, 9.66.

14. (tBu₃SiO)₂Mo(PMe₃)₂ (17). To a 100 mL round-bottom flask containing 1.83 g of **12** (2.72 mmol) and 13.83 g of Na/Hg amalgam (2.1 equiv, 5.71 mmol Na) was vacuum-transferred ~50 mL of Et₂O at -78 °C. PMe₃ (3 equiv, 8.16 mmol) was transferred to the reaction mixture via calibrated gas bulb. The reaction mixture was warmed to 23 °C and stirred for 24 h. The blue reaction mixture slowly turned red throughout the course of the reaction. All volatiles were removed in vacuo, and the Hg⁰ was decanted. Pentane (30 mL) was transferred to the reaction mixture, and the deep red solution was filtered. The red filtrates were concentrated to ~2 mL, and the red product was crystallized by slow evaporation of the saturated solution at -30 °C for 18 h. The small amount of solution remaining was removed, yielding 1.26 g (68%) of **17**. ¹H NMR (C₆D₆, 300 MHz): δ 2.33 (ν_{1/2} = 75 Hz), 11.44 (ν_{1/2} = 120 Hz). ¹³C{¹H} NMR (C₆D₆, 500 MHz): δ 91.40 (C(CH₃)₃). Anal. calcd for $C_{27}H_{63}O_2PSi_2W$: C, 42.58; H, 8.34. Found: C, 42.19; H, 8.02. μ_{eff} (293 K) = 2.6 μ_B(C₆D₆).

15. Single-Crystal X-Ray Diffraction Studies. Upon isolation, the crystals were covered in polyisobutylene and placed under a 173 °C N₂ stream on the goniometer head of a Siemens P4 SMART CCD area detector system (graphite-monochromated Mo Kα radiation, λ = 0.71073 Å). The structures were solved by direct methods (SHELXS). All non-hydrogen atoms were refined anisotropically unless stated, and hydrogen atoms were treated as idealized contributions (Riding model).

16. mer-(silox)₂MoCl₃(THF) (10). A yellow block (0.6 × 0.35 × 0.15) was obtained from tetrahydrofuran. A total of 14 811 reflections were collected with 4409 being symmetry-independent ($R_{int} = 0.0406$), and 3302 were greater than 2σ(*I*). The data were corrected for absorption by SADABS, and the refinement utilized $w^{-1} = \sigma^2(F_o^2) + (0.0399p)^2 + 0.2684p$, where $p = (F_o^2 + 2F_c^2)/3$.

17. (silox)₂MoCl₂(PMe₃) (12). A blue rod (0.5 × 0.4 × 0.3) was obtained from diethyl ether. A total of 29 927 reflections were collected, with 8586 being symmetry-independent ($R_{int} = 0.0252$), and 7143 were greater than 2σ(*I*). The data were corrected for absorption by SADABS, and the refinement utilized $w^{-1} = \sigma^2(F_o^2) + (0.0316p)^2 + 0.6198p$, where $p = (F_o^2 + 2F_c^2)/3$.

18. (silox)₂HW(η²-CH₂PMe₂)PMe₃ (14). A red rod (0.2 × 0.05 × 0.03) was obtained from diethyl ether. A total of 32 273 reflections were collected, with 6351 being symmetry-independent ($R_{int} = 0.0914$), and 4775 were greater than 2σ(*I*). The data were corrected for absorption by SADABS, and the refinement utilized $w^{-1} = \sigma^2(F_o^2) + (0.0470p)^2 + 0.0000p$, where $p = (F_o^2 + 2F_c^2)/3$. The PMe₃ group was partially disordered by rotation along the W-P bond. The hydride H atom was not visible on a difference Fourier map. It was placed using a "sterically most feasible" model.

19. (tBu₃SiO)₂Mo(PMe₃)₂ (17). A red plate (0.2 × 0.15 × 0.03) was obtained from pentane. A total of 25 756 reflections were collected, with 4052 being symmetry-independent ($R_{int} = 0.0728$), and 3529 were greater than 2σ(*I*). The data were corrected for absorption by SADABS, and the refinement utilized $w^{-1} = \sigma^2(F_o^2) + (0.0403p)^2 + 16.2911p$, where $p = (F_o^2 + 2F_c^2)/3$.

Computational Methods. Calculations were performed on full silox-decorated models using the Gaussian 03 package.³⁸ DFT, specifically the BLYP functional, was utilized for all simulations.³⁹ The transition metals and heavy main group atoms (Si and P) were described with the Stevens effective core potentials and attendant valence basis sets (VBSs).⁴⁰ This scheme, dubbed CEP-31G, entails a valence triple-ζ description for the transition metals, and a

double- ζ VBS for the main group elements. The 6-31G(d) all-electron basis set was used for C, H, and O atoms. All main group VBSs are augmented with a d polarization function ($C(\xi_d) = O(\xi_d) = 0.8$; $Si(\xi_d) = 0.3247$; $P(\xi_d) = 0.37$). This level of theory was selected on the basis of a series of test calculations on the singlet and triplet states of $Nb(OH)_3$, $Ta(OH)_3$,¹ and their olefin adducts.⁴¹

Full silox models were studied using hybrid QM/MM techniques within the ONIOM framework.⁴² The QM region of $M(\text{silox})_3(X)$ complexes contained the transition metal, the O and Si atoms of the silox group, and the entire X group (if present). The QM level of theory employed is that described above. The remainder of the molecule, that is, the *tert*-butyl groups of silox, was modeled with the universal force field.⁴³

Full geometry optimizations without any metric or symmetry restrictions were employed to obtain the minima in this research. All of the resultant stationary points were characterized as true minima (i.e., no imaginary frequencies) by calculation of the energy Hessian. Enthalpic and entropic corrections to the total electronic

energy were calculated using harmonic vibrational frequencies determined at the same level of theory employed for geometry optimization and are calculated at 1 atm and 298.15 K.

Closed- and open-shell species were described with the restricted and unrestricted Kohn–Sham formalisms, respectively, with no evidence of spin contamination for the latter.

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Supporting Information Available: CIF files of **10**, **12**, **14**, and **17**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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