3-Center-4-Electron Bonding in [(silox)$_2$Mo=N^{t}Bu]$_2$(μ-Hg) Controls Reactivity while Frontier Orbitals Permit a Dimolybdenum π-Bond Energy Estimate

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In a continuing investigation into the reactivity of low-coordinate transition metal complexes,[1−4] d^2 group 6 (silox)$_2$M=N^{t}Bu (M = Cr, Mo (**1**), W (**2**))[5] species were sought as lower-symmetry analogues to (silox)$_3$M (M = V, Nb-L (L = 4-picoline, PMe$_3$), Ta; silox = ^{t}Bu$_3$SiO). The large singlet−triplet gap accorded (silox)$_3$Ta renders it stable, whereas the niobium congener has not been isolated. Likewise, while **2** has been crystallographically characterized,[5] the second row analogue, (silox)$_2$Mo=N^{t}Bu (**1**), proved to be elusive, and [(silox)$_2$Mo=N^{t}Bu]$_2$(μ-Hg) (**1**$_2$-Hg) was prepared instead. Its stability, combined with a sensitivity to nucleophilic attack, is rationalized by 3c4e bonding,[6] and its frontier orbitals can be analyzed to estimate a Mo$_2$ π-bond energy.[7−9]

Treatment of (dme)Cl$_2$Mo(=N^{t}Bu)$_2$[10] with 2 equiv of ^{t}Bu$_3$SiOH and 1 equiv of HCl in benzene afforded [H$_3$N^{t}Bu]Cl and (silox)$_2$Cl$_2$-Mo=N^{t}Bu (**3**, 82%). Whereas (silox)$_2$W=N^{t}Bu (**2**) was isolated from reduction of the analogous tungsten complex,[5] various reducing agents failed to elicit "(silox)$_2$Mo=N^{t}Bu (**1**)". Instead, Na/Hg reduction of **3** yielded olive-green, paramagnetic [(silox)$_2$Mo=N^{t}Bu]$_2$(μ-Hg) (**1**$_2$-Hg, 56%),[11] whose C_{2h} structure is composed of distorted trigonal MoO$_2$N cores that lean slightly toward the linear μ-Hg bridge from the imido position (Figure 1).

High level quantum calculations conducted on the model [(HO)$_2$Mo=NH]$_2$Hg (**1′**$_2$-Hg)[12,13] reveal a 3c4e Mo$_2$Hg interaction (Figure 2),[6] consistent with the modest electronegativity difference between Hg (χ_{Hg} = 2.00) and Mo (χ_{Mo} = 2.16). The 3c4e situation is unusual because the *symmetric* combination of d$_{z^2}$ orbitals derived from (HO)$_2$Mo=NH (**1′**))[14] interacts with the Hg 6s orbital to generate the bonding MO (1a$_g$ at −8.22 eV; MoN π^b-contributions are also evident), while the antisymmetric combination (1b$_u$ at −5.74 eV) is essentially "non-bonding" because the Hg 6p$_z$ orbital is too energetically high to interact.

The frontier orbitals of **1′**$_2$-Hg are the π (1a$_u$, −2.70 eV) and π* (1b$_g$, −2.51 eV) combinations of the d$_{yz}$ orbitals from **1′**; the former manifests essentially no contribution from Hg 6p$_y$, and the Mo−Hg rotational barrier is negligible. Note that d$_{yz}$ is the HOMO of **1′**, and d$_{xz}$ is ∼0.8 eV higher as it is a π* orbital of the Mo=N interaction. The small distortion of the O−Mo−O angles (<120°) in **1′**, **1′**-Hg, and **1**$_2$-Hg lowers the MoO π* character of d$_{yz}$ at the expense of d$_{xz}$.[13,14] Magnetic studies (SQUID) corroborate the proximity of the 1a$_u$ and 1b$_g$ orbitals. At 4 K the ground-state approaches ^{1}A$_g$, but at 300 K, **1**$_2$-Hg exhibits a μ_{eff} of 1.7 μ_B due to TIP (1270 × 10^{-6} emu) resulting from mixing with the ^{3}B$_u$ excited state (i.e., ΔE(^{1}A$_g$ → ^{3}B$_u$) ≈ 550 cm^{-1} (estimated)).

Calculations on the scission of [(HO)$_2$Mo=NH]$_2$Hg (**1′**$_2$-Hg) to (HO)$_2$Mo=NH (**1′**) and [(HO)$_2$Mo=NH]Hg (**1′**-Hg) place the dissociation enthalpy at 22.4 kcal/mol,[12,15] yet **1**$_2$-Hg is indefinitely stable in benzene solution at 23 °C; at 140 °C, its degradation rate
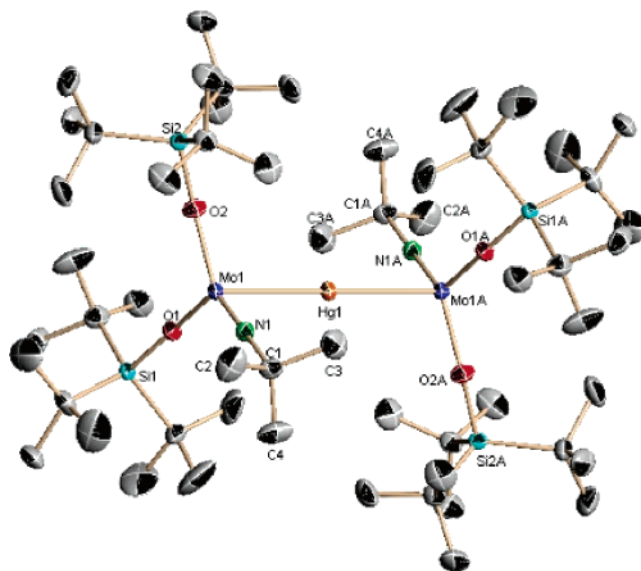
Figure 1. Molecular view of [(silox)$_2$Mo=N^{t}Bu]$_2$Hg (**1**$_2$-Hg). Selected bond distances (Å) and angles (deg): Mo−Hg, 2.6810(5); Mo−N, 1.718(3); Mo−O, 1.894(2), 1.905(2); O−Mo−O, 113.60(9); O−Mo−N, 119.91(11), 121.33(11); N−Mo−Hg, 84.51(8); O−Mo−Hg, 103.37(7), 105.42(7).
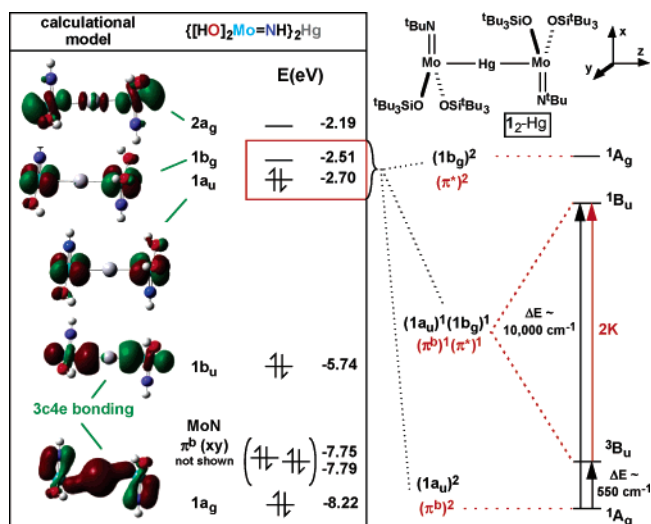
Figure 2. 3c4e bonding in [(silox)$_2$Mo=N^{t}Bu]$_2$Hg (**1**$_2$-Hg); four states derived from its frontier orbitals.

is roughly 1 × 10^{-4} s^{-1} ($\Delta G^{\ddagger}$ ≈ 32 kcal/mol). Dissociation of **1**$_2$-Hg to **1** and **1**-Hg requires a surface crossing, since each product is calculated to be a triplet. While several studies have shown that intersystem crossings are adiabatic when heavy elements are involved,[16−18] the orbital symmetry of **1**$_2$-Hg ($\sigma^2\sigma^2\pi^2$) is different

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from the products of the quintet surface ($\sigma^1\pi^1$ for **1**, $\sigma^2\pi^1\pi^1$ for **1**-Hg).[1] As a consequence, the calculated relative $\Delta G°$ of the crossing point (**1′**$_2$-Hg → **1′** + **1′**-Hg) is quite high (~28 kcal/mol) and within reason of the observed $\Delta G^{\ddagger}$ of degradation.

The empty, low-lying (−2.19 eV) symmetric antibonding component (2a$_g$) of the 3c4e manifold renders **1**$_2$-Hg susceptible to nucleophilic attack and Mo−Hg bond cleavage. Treatment of [(silox)$_2$Mo=N^{t}Bu]$_2$(μ-Hg) (**1**$_2$-Hg) with excess PMe$_3$ or py afforded maroon (silox)$_2$(^{t}BuN)MoPMe$_3$ (**1**-PMe$_3$, $S = 0$) and dark blue-purple (silox)$_2$(^{t}BuN)Mopy$_2$ (**1**-py$_2$, $S = 0$) within 5 min. Poorer nucleophiles were ineffective at cleavage. With 4.8 equiv of 2-butyne, only 59% of (silox)$_2$(^{t}BuN)Mo(MeC≡CMe) (**1**-C$_2$-Me$_2$ $S = 0$) formed after 27 d at 25 °C, and 45 h at 70 °C was required for complete conversion. With ethylene (5 equiv), 23% (silox)$_2$(^{t}BuN)Mo(C$_2$H$_4$) (**1**-C$_2$H$_4$, $S = 0$) formed after 30 h at 23 °C; after 30 h at 63 °C the reaction was complete. Likewise, 2.2 equiv of N$_2$O generated only 10% (silox)$_2$(^{t}BuN)MoO (**1**=O) after 16 h at 25 °C; 20 h at 60 °C effected completion. 2-Butyne and ethylene displace PMe$_3$ from **1**-PMe$_3$ to afford **1**-C$_2$Me$_2$ and **1**-C$_2$H$_4$, and hence the rates of **1**$_2$-Hg cleavage do *not* reflect the thermodynamics.

As Figure 2 illustrates, the 1a$_u$ and 1b$_g$ orbitals of **1**$_2$-Hg have no Hg component and can be considered dimolybdenum π- and π*-orbitals that have been "stretched" beyond a meaningful overlap distance. As others have used the relative rotation of an L$_2$X$_2$Mo fragment in quadruply bonded (L−L)$_2$X$_4$Mo$_2$ systems to diminish or eliminate d-overlap,[19,20] the "stretched" π-interaction in **1**$_2$-Hg can be considered similarly. The energy difference between the ^{1}B$_u$ and ^{3}B$_u$ states derived from the (1a$_u$)^1(1b$_g$)^1 configuration is $2K$, where K is the exchange energy and $\Delta W = E(1b_g) − E(1a_u)$, as in the paradigm provided by Cotton and Nocera for *any two-electron bond*.[6] The lowest energy band in the UV−vis spectrum of **1**$_2$-Hg is a weak absorption ($\epsilon \approx 160$ M^{-1} cm^{-1}) at 1000 nm that is assigned to the x,y-allowed ^{1}A$_g$ → ^{1}B$_u$ transition ($K = 4700$ cm^{-1}, $\Delta W = 2450$ cm^{-1}); intensity stealing from an O(pπ) → Mo(d$_{yz}$-π) LMCT band may aid its observation.[21] An assignment of the related $\pi^2 → \pi^1\pi^{*1}$ band (528 nm, $e \approx 1200$ M^{-1} cm^{-1}) in Schrock's [Mo(NAr)(CH$_2^t$Bu)(OC$_6$F$_5$)]$_2$ (**4**)[22] permits a crude assessment of its dimolybdenum π-bond energy as {$E(\pi^2 → \pi^1\pi^{*1}$ in **4**) − $E(^1$A$_g$ → ^{1}B$_u$ in **1**$_2$-Hg)} + $E(^1$A$_g$ → ^{3}B$_u$ in **1**$_2$-Hg) = 9540 cm^{-1} (27 kcal/mol).[6] This rare spectroscopic estimate of the π-bond strength[23,24] rests on the premise that characteristic energies in these compounds are similar, the contribution from Hg 6p$_z$ to the π^b (1a$_u$) orbital in **1**$_2$-Hg is negligible, and configuration interaction contributes minimally to the ^{1}B$_u$ (**1**$_2$-Hg) and $\pi^1\pi^{*1}$ states (**4**).

Calculations suggest that the model is a fundamental approximation for the dimolybdenum π-bond. Using multireference perturbation theory (MPT)[12,25] on the **1′**$_2$-Hg model, the $\Delta E(^1$A$_g$ → ^{1}B$_u$) transition is calculated to be at ~890 nm with $K = 4740$ cm^{-1}, $\Delta W = 4425$ cm^{-1}, and $D(\pi($Mo$_2$)) = 27 kcal/mol. Given the difficulty of calculating excited states, the values are within reason, but more importantly, the calculations implicate substantial mixing in ^{1}B$_u$ (69% arising from higher energy orbitals outside the two-orbital, two-electron Coulson and Fischer[8] space, i.e., (1a$_u$)^2(1b$_g$)^0). In contrast, the ^{1}A$_g$ and ^{3}B$_u$ states are ~90% "pure". Complementary structural, reactivity, and electronic studies on **1**$_2$-Hg and various derivatives are continuing.

Supporting Information Available: Spectral, magnetic and analytical data, CIF file for **1**$_2$-Hg, experimental procedures, and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) Geometry optimizations: B3PW91 hybrid density functional; Stevens effective core potential scheme. Stevens valence basis sets (CEP-31G) included a d-polarization function (main group). DFT calculations used Gaussian 03 and open shell species were modeled with an unrestricted Kohn−Sham formalism.
(13) **1′**$_2$-Hg: d(MoHg) = 2.75 Å; d(MoO) = 1.92, 1.93 Å; d(MoN) = 1.73 Å; ∠O−Mo−O = 115°; ∠O−Mo−N = 118°, 121°; ∠Hg−Mo−O = 96°, 107°; ∠Hg−Mo−N = 90°. **1′**: d(MoO) = 1.93 Å; d(MoN) = 1.74 Å; ∠O−Mo−O = 117°; ∠O−Mo−N = 120°, 123°. **1′**-Hg: d(MoHg) = 3.08 Å; d(MoO) = 1.93 Å; d(MoN) = 1.74 Å; ∠O−Mo−O = 117°; ∠O−Mo−N = 119°, 122°; ∠Hg−Mo−O = 92°, 93°; ∠Hg−Mo−N = 97°.
(14) **1′** d-orbital energies: nb, (d$_{z^2}$)^1, −2.85 eV; MoO π*, (d$_{yz}$)^1, −2.54 eV; MoN π*, d$_{xz}$, −1.71; MoN σ* and MoO π*, d$_{x^2-y^2}$, −0.64; MoO σ* and MoN π*, d$_{xy}$, 0.19.
(15) $E(^3$[**1′**$_2$-Hg]) $\approx$ $E(^1$[**1**$_2$-Hg]): ^{1}Hg + 2 ^{3}[**1′**] → ^{3}[**1′**$_2$-Hg], ΔH = −25.6 kcal/mol; ^{1}Hg + ^{3}[**1′**] → ^{3}[**1′**-Hg], ΔH = −3.1 kcal/mol; ^{3}[**1′**-Hg] + ^{3}[**1′**] → ^{3}[**1′**$_2$-Hg], ΔH = −22.4 kcal/mol.
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