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Communication

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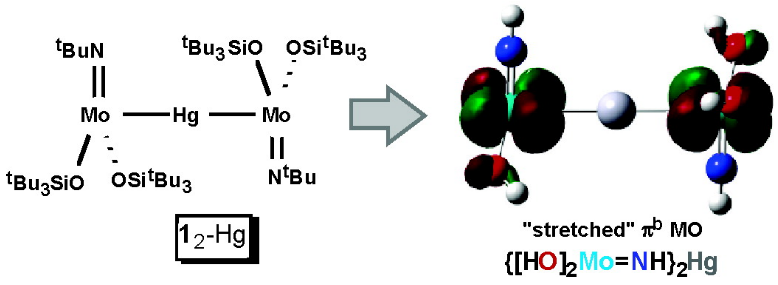

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COMMUNICATIONS

3-Center-4-Electron Bonding in $[(silox)_2Mo{=}N^tBu]_2(\mu\text{-}Hg)$ Controls Reactivity while Frontier Orbitals Permit a Dimolybdenum π-Bond Energy Estimate

Devon C. Rosenfeld,† Peter T. Wolczanski,*,† Khaldoon A. Barakat,‡ Corneliu Buda,‡ and Thomas R. Cundari*,‡

Department of Chemistry & Chemical Biology, Baker Laboratory, Cornell University, Ithaca, New York 14853, and Department of Chemistry, University of North Texas, Box 305070, Denton, Texas 76203

Received February 18, 2005; E-mail: ptw2@cornell.edu; tomc@unt.edu

In a continuing investigation into the reactivity of low-coordinate transition metal complexes,[1−4] d^2 group 6 $(silox)_2M{=}N^tBu$ (M = Cr, Mo (**1**), W (**2**))[5] species were sought as lower-symmetry analogues to $(silox)_3M$ (M = V, Nb-L (L = 4-picoline, PMe_3), Ta; silox = $^tBu_3SiO$). The large singlet−triplet gap accorded $(silox)_3Ta$ renders it stable, whereas the niobium congener has not been isolated. Likewise, while **2** has been crystallographically characterized,[5] the second row analogue, $(silox)_2Mo{=}N^tBu$ (**1**), proved to be elusive, and $[(silox)_2Mo{=}N^tBu]_2(\mu\text{-}Hg)$ ($\mathbf{1}_2$-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 $(dme)Cl_2Mo({=}N^tBu)_2$[10] with 2 equiv of $^tBu_3SiOH$ and 1 equiv of HCl in benzene afforded $[H_3N^tBu]Cl$ and $(silox)_2Cl_2Mo{=}N^tBu$ (**3**, 82%). Whereas $(silox)_2W{=}N^tBu$ (**2**) was isolated from reduction of the analogous tungsten complex,[5] various reducing agents failed to elicit "$(silox)_2Mo{=}N^tBu$ (**1**)". Instead, Na/Hg reduction of **3** yielded olive-green, paramagnetic $[(silox)_2Mo{=}N^tBu]_2(\mu\text{-}Hg)$ ($\mathbf{1}_2$-Hg, 56%),[11] whose C_{2h} structure is composed of distorted trigonal MoO_2N cores that lean slightly toward the linear μ-Hg bridge from the imido position (Figure 1).

High level quantum calculations conducted on the model $[(HO)_2Mo{=}NH]_2Hg$ ($\mathbf{1'}_2$-Hg)[12,13] reveal a 3c4e Mo_2Hg interaction (Figure 2),[6] consistent with the modest electronegativity difference between Hg ($\chi_{Hg} = 2.00$) and Mo ($\chi_{Mo} = 2.16$). The 3c4e situation is unusual because the *symmetric* combination of d_{z^2} orbitals derived from $(HO)_2Mo{=}NH$ ($\mathbf{1'}$))[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 $\mathbf{1'}_2$-Hg are the π ($1a_u$, −2.70 eV) and π^* ($1b_g$, −2.51 eV) combinations of the d_{yz} orbitals from $\mathbf{1'}$; 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 $\mathbf{1'}$, 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 $\mathbf{1'}$, $\mathbf{1'}$-Hg, and $\mathbf{1}_2$-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 ^1A_g, but at 300 K, $\mathbf{1}_2$-Hg exhibits a μ_{eff} of 1.7 μ_B due to TIP (1270 × 10^{-6} emu) resulting from mixing with the ^3B_u excited state (i.e., $\Delta E(^1A_g \rightarrow {}^3B_u) \approx 550\ cm^{-1}$ (estimated)).

Calculations on the scission of $[(HO)_2Mo{=}NH]_2Hg$ ($\mathbf{1'}_2$-Hg) to $(HO)_2Mo{=}NH$ ($\mathbf{1'}$) and $[(HO)_2Mo{=}NH]Hg$ ($\mathbf{1'}$-Hg) place the dissociation enthalpy at 22.4 kcal/mol,[12,15] yet $\mathbf{1}_2$-Hg is indefinitely stable in benzene solution at 23 °C; at 140 °C, its degradation rate is roughly 1 × 10^{-4} s^{-1} ($\Delta G^\ddagger \approx 32$ kcal/mol). Dissociation of $\mathbf{1}_2$-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 $\mathbf{1}_2$-Hg ($\sigma^2\sigma^2\pi^2$) is different

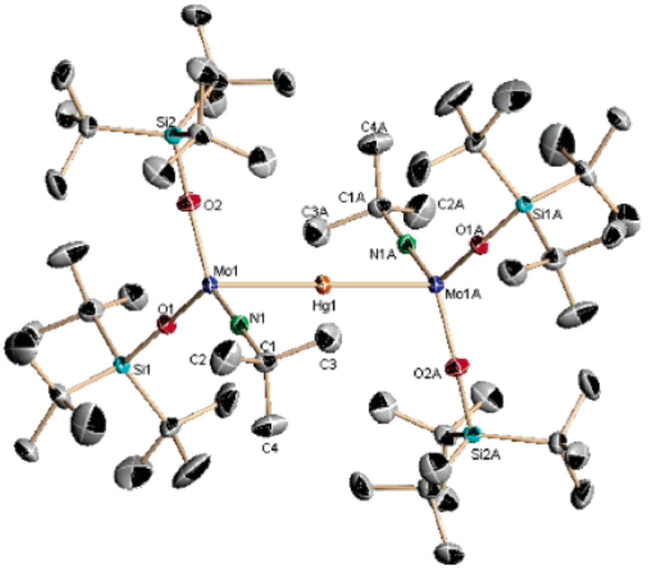

Figure 1. Molecular view of $[(silox)_2Mo{=}N^tBu]_2Hg$ ($\mathbf{1}_2$-Hg). Selected bond distances (Å) and angles (deg): Mo−Hg, 2.6810(5); Mo−N, 1.718(3); Mo−O, 1.894(2), 1.905(2); O−Mo−O, 113.60(9); O−Mo−N, 119.91(11), 121.33(11); N−Mo−Hg, 84.51(8); O−Mo−Hg, 103.37(7), 105.42(7).

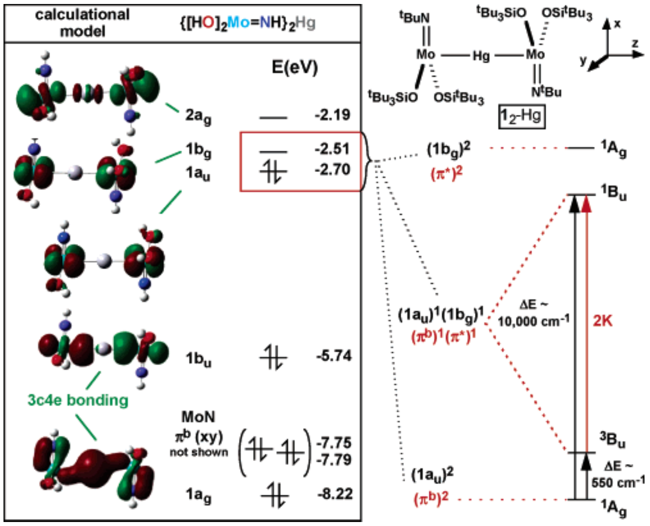

Figure 2. 3c4e bonding in $[(silox)_2Mo{=}N^tBu]_2Hg$ ($\mathbf{1}_2$-Hg); four states derived from its frontier orbitals.

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† Cornell University.
‡ University of North Texas.

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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 ΔG° of the crossing point ($\mathbf{1'}_2$-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 $\mathbf{1}_2$-Hg susceptible to nucleophilic attack and Mo−Hg bond cleavage. Treatment of $[(\mathrm{silox})_2\mathrm{Mo{=}N^tBu}]_2(\mu\text{-Hg})$ ($\mathbf{1}_2$-Hg) with excess PMe$_3$ or py afforded maroon $(\mathrm{silox})_2(^t\mathrm{BuN})\mathrm{MoPMe_3}$ (**1**-PMe$_3$, $S = 0$) and dark blue-purple $(\mathrm{silox})_2(^t\mathrm{BuN})\mathrm{Mopy_2}$ (**1**-py$_2$, $S = 0$) within 5 min. Poorer nucleophiles were ineffective at cleavage. With 4.8 equiv of 2-butyne, only 59% of $(\mathrm{silox})_2(^t\mathrm{BuN})\mathrm{Mo(MeC{\equiv}CMe)}$ (**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% $(\mathrm{silox})_2(^t\mathrm{BuN})\mathrm{Mo(C_2H_4)}$ (**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% $(\mathrm{silox})_2(^t\mathrm{BuN})\mathrm{MoO}$ (**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 $\mathbf{1}_2$-Hg cleavage do *not* reflect the thermodynamics.

As Figure 2 illustrates, the $1a_u$ and $1b_g$ orbitals of $\mathbf{1}_2$-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 $\mathbf{1}_2$-Hg can be considered similarly. The energy difference between the ^1B_u and ^3B_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 $\mathbf{1}_2$-Hg is a weak absorption ($\epsilon \approx 160\ \mathrm{M^{-1}\ cm^{-1}}$) at 1000 nm that is assigned to the x,y-allowed $^1A_g \rightarrow {}^1B_u$ transition ($K = 4700\ \mathrm{cm^{-1}}$, $\Delta W = 2450\ \mathrm{cm^{-1}}$); intensity stealing from an O(pπ) → Mo(d_{yz}-π) LMCT band may aid its observation.[21] An assignment of the related $\pi^2 \rightarrow \pi^1\pi^{*1}$ band (528 nm, $e \approx 1200\ \mathrm{M^{-1}\ cm^{-1}}$) in Schrock's $[\mathrm{Mo(NAr)(CH_2{}^tBu)(OC_6F_5)}]_2$ (**4**)[22] permits a crude assessment of its dimolybdenum π-bond energy as $\{E(\pi^2 \rightarrow \pi^1\pi^{*1}$ in **4**$) - E(^1A_g \rightarrow {}^1B_u$ in $\mathbf{1}_2$-Hg$)\} + E(^1A_g \rightarrow {}^3B_u$ in $\mathbf{1}_2$-Hg$) = 9540\ \mathrm{cm^{-1}}$ (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 $\mathbf{1}_2$-Hg is negligible, and configuration interaction contributes minimally to the ^1B_u ($\mathbf{1}_2$-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 $\mathbf{1'}_2$-Hg model, the $\Delta E(^1A_g \rightarrow {}^1B_u)$ transition is calculated to be at ~890 nm with $K = 4740\ \mathrm{cm^{-1}}$, $\Delta W = 4425\ \mathrm{cm^{-1}}$, and $D(\pi(\mathrm{Mo_2})) = 27$ kcal/mol. Given the difficulty of calculating excited states, the values are within reason, but more importantly, the calculations implicate substantial mixing in ^1B_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 ^1A_g and ^3B_u states are ~90% "pure". Complementary structural, reactivity, and electronic studies on $\mathbf{1}_2$-Hg and various derivatives are continuing.

Acknowledgment. We dedicate this article to the memory of Vincent M. Miskowski, an aficionado of the multiple bond. We thank the National Science Foundation (CHE-0415506 (P.T.W.) and CHE-0309811 (T.R.C.)), Prof. Francis J. DiSalvo, Prof. Karsten Meyer (UCSD, magnetic data), and Prof. Richard R. Schrock (MIT, UV−vis spectrum of **4**).

Supporting Information Available: Spectral, magnetic and analytical data, CIF file for $\mathbf{1}_2$-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) $\mathbf{1'}_2$-Hg: $d(\mathrm{MoHg}) = 2.75$ Å; $d(\mathrm{MoO}) = 1.92, 1.93$ Å; $d(\mathrm{MoN}) = 1.73$ Å; ∠O−Mo−O = 115°; ∠O−Mo−N = 118°, 121°; ∠Hg−Mo−O = 96°, 107°; ∠Hg−Mo−N = 90°. **1′**: $d(\mathrm{MoO}) = 1.93$ Å; $d(\mathrm{MoN}) = 1.74$ Å; ∠O−Mo−O = 117°; ∠O−Mo−N = 120°, 123°. **1′**-Hg: $d(\mathrm{MoHg}) = 3.08$ Å; $d(\mathrm{MoO}) = 1.93$ Å; $d(\mathrm{MoN}) = 1.74$ 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) $E(^3[\mathbf{1'}_2\text{-Hg}]) \approx E(^1[\mathbf{1}_2\text{-Hg}])$: $^1\mathrm{Hg} + 2\ {}^3[\mathbf{1'}] \rightarrow {}^3[\mathbf{1'}_2\text{-Hg}]$, $\Delta H = -25.6$ kcal/mol; $^1\mathrm{Hg} + {}^3[\mathbf{1'}] \rightarrow {}^3[\mathbf{1'}\text{-Hg}]$, $\Delta H = -3.1$ kcal/mol; $^3[\mathbf{1'}\text{-Hg}] + {}^3[\mathbf{1'}] \rightarrow {}^3[\mathbf{1'}_2\text{-Hg}]$, $\Delta H = -22.4$ kcal/mol.

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