In a continuing investigation into the reactivity of low-coordinate transition metal complexes,1–4 d2 group 6 (silox)2M=NBu (M = Cr, Mo (1), W (2))5 species were sought as lower-symmetry analogues to (silox)3M (M = V, Nb-L (L = 4-picoline, PMe3), Ta; silox = Bu4SiO). The large singlet–triplet gap accorded (silox)3Ta renders it stable, whereas the niobium congeners have not been isolated. Likewise, while 2 has been crystallographically characterized,3 the second row analogue, (silox)2Mo=NBu (1), proved to be elusive, and [([silox])2Mo=NBu](μ-Hg) (1-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 Mo2 π-bond energy.7–9

Treatment of (dme)Cl2 Mo(1) with 2 equiv of Bu4SiOH and 1 equiv of HCl in benzene afforded [H3N tBu](Cl2 Mo(1) and [(HO)2 Mo(1) reduced with Na/Hg to yield olive-green, paramagnetic [(silox)2 Mo]2-Hg, 95%, whose magnetic susceptibility (δ = 3.95 emu) resulting from mixing with the 3 Bg orbital, and Na/Hg reduction of 3 yielded green, paramagnetic ([silox])2Mo=NBu(1-Hg) (1-Hg, 56%),11 whose C2s structure is composed of distorted trigonal MoO2N 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=NH2]Hg (1-Hg)12,13 reveal a 3c4e MoHg interaction (Figure 2),6 consistent with the modest electronegativity difference between Hg (γHg = 2.00) and Mo (γMo = 2.16). The 3c4e situation is unusual because the symmetric combination of d1 orbitals derived from (HO)2 Mo=NH (1)14 interacts with the Hg 6s orbital to generate the bonding MO (1a u at −8.22 eV; MoN π*-contributions are also evident), while the antisymmetric combination (1b u at −5.74 eV) is essentially “non-bonding” because the Hg 6p orbital is too energetically high to interact.

The frontier orbitals of 1-Hg are the π (1a u, −2.70 eV) and π* (1b u, −2.51 eV) combinations of the dπ orbital isomers from 1; the former manifests essentially no contribution from Hg 6pπ, and the Mo–Hg rotational barrier is negligible. Note that dπ is the HOMO of 1′, and dπ is an 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-Hg lowers the Mo π* character of dπ at the expense of dπ.13,14 Magnetic studies (SQUID) corroborate the proximity of the 1a u and 1b u orbitals. At 4 K the ground-state approaches 1Ag, but at 300 K, 1-Hg exhibits a μu of 1.7 μB due to TIP (1270 × 10−6 emu) resulting from mixing with the 1B1g excited state (i.e., ΔE(1Ag → 1B1g) ≈ 550 cm−1 (estimated)).

Calculations on the scission of [(HO)2 Mo=NH2]Hg (1-Hg) to (HO)2 Mo=NH (1) and [(HO)2 Mo=NH2]Hg (1-Hg) place the dissociation enthalpy at 22.4 kcal/mol,12,13 yet 1-Hg is indefinitely stable in benzene solution at 23 °C; at 140 °C, its degradation rate

Figure 1. Molecular view of [(silox)2Mo=NBu]2-Hg (1-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=NBu]2-Hg (1-Hg); four states derived from its frontier orbitals.

is roughly 1 × 10−4 s−1 (ΔG‡ ≈ 32 kcal/mol). Dissociation of 1-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-Hg (α2β2γ2) is different...
from the products of the quintet surface ($\alpha^2\pi^e$ for $1$, $\alpha^2\pi^o\tau^e$ for $1'$). As a consequence, the calculated relative $\Delta\gamma$ of the crossing point ($1'F_2g - 1F_2g$) is quite high ($\sim 28$ kcal/mol) and within reason of the observed $\Delta\gamma$ of degradation.

The empty, low-lying ($\sim 2.19$ eV) symmetric antibonding component ($2\alpha_v$) of the 3$e$e manifold renders $1H_2$ susceptible to nucleophilic attack and Mo-Hg bond cleavage. Treatment of [(silox)$_2$Mo=NBu($\mu$-Hg)]($1H_2$) with excess PMe$_3$ or py afforded maroon (silox)$_2$(BuN)MoPMe$_3$ (1-PMe$_3$, S = 0) and dark blue-purple (silox)$_2$(BuN)Mo(C$_2$H$_4$) (1-Py, S = 0) within 5 min. Poorer nucleophiles were ineffective at cleavage. With 4.8 equiv of 2-butyne, only 59% of (silox)$_2$(TuBuN)Mo(C$_2$H$_4$)(1 = I-Me) was obtained. Isothermal $\Delta T$-Hg cleavage do not reflect the thermodynamics.

As Figure 2 illustrates, the $1a_o$ and $1b_o$ orbitals of $1H_2$ have no Hg component and can be considered dimolybdenum $\pi$- and $\pi^o$-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$_2$X$_2$Mo) systems to diminish $\Delta\gamma_1$-$\gamma_2$-Hg cleavage do not reflect the thermodynamics.

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Supporting Information Available: Spectral, magnetic and analytical data, CIF file for $1$-$H_2$, experimental procedures, and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(7) Cotton, F. A.; Nocera, D. G. Acc. Chem. Res. 2000, 33, 483–490. $E(1A_g) = 0$, $E(B_1g) = |\Delta W + K|^\dagger + K$, $E(B_2g) = |2\Delta W + K|^\dagger$.
(12) Geometry optimizations: B3PW91 hybrid density functional; Stevens effective core potential scheme. Stevens valence basis sets (CPEP-31G) included a d-polarization function (main group). DFT calculations used a Gaussian 03 open shell and spherical basis set with an unrestricted Kohn–Sham formalism.
(13) $1$-$H_2$: $d$(MoHg) = 2.75 Å; $d$(MoO) = 1.92, 1.93 Å; $d$(Mo) = 1.73 Å; $O$–Mo–O = 115°; $O$–Mo–N = 118°; $O$–Hg–Mo = 96°; $O$–Hg–N = 90°. $E(1A_g) = 1.93$ Å; $d$(Mo) = 1.74 Å; $d$(MoHg) = 3.08 Å; $d$(Mo) = 1.93 Å; $d$(MoHg) = 1.74 Å; $O$–Mo–O = 117°; $O$–Mo–N = 119°, 122°; $Hg$–Mo = 92°, 93°; $Hg$–N = 97°.
(14) $1'$- orbitals energies: nb, $(d_y^o)^2$, $-2.85$ eV; MoO $\pi^o$ and $(d_z^o)^2$, $-2.54$ eV; MoO $\pi^o$, $\tau^o$, $-1.71$; MoO $\sigma^o$ and MoO $\sigma^o$, $d_z^o$, $-0.64$; MoO $\sigma^o$ and MoO $\sigma^o$, $d_z^o$, 0.19.
(15) $E(1'Y_1g)$ = $E(1'H_2g)$; $h$ + $2$ $|^1$-$H_2g$, $\Delta H = -25.6$ kcal/mol; $Hg$ + $|^1$-$H_2g$, $\Delta H = -3.1$ kcal/mol; $|^1$-$H_2g$, $\Delta H = -22.4$ kcal/mol.