A Diazoalkane Derivative of a Polyoxometalate: Preparation and Structure of $[Mo_6O_{18}(NNC(C_6H_4OCH_3)CH_3)]^{2-}$**

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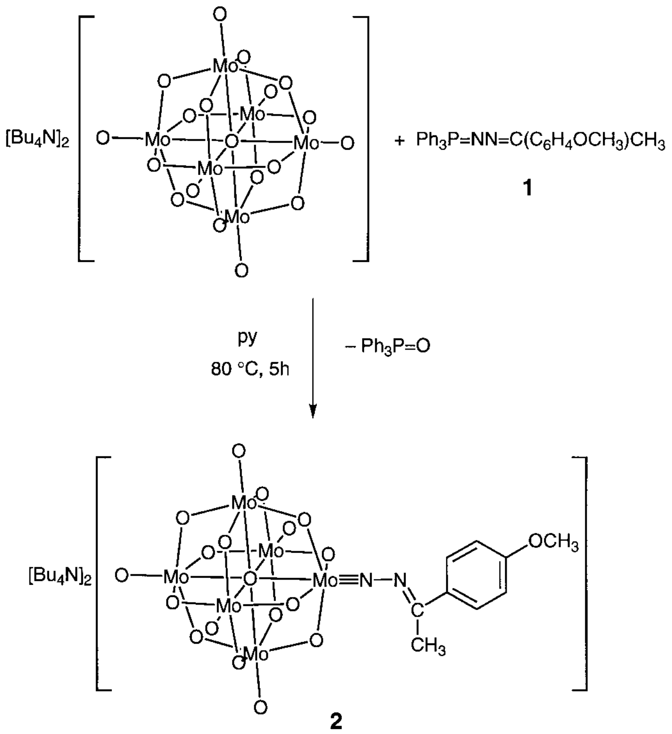
Dedicated to Professor Rupert A. D. Wentworth

Diazoalkane complexes $[L_nM(N_2CR_2)]$[1] are distinguished by their utility in important organic transformations[2] and by the variety of their coordination modes.[3] Such systems are generally prepared by the direct interaction of R_2CN_2 with low-valent ($\leq d^2$) metal complexes; in unusual and noteworthy cases, diazoalkane complexes have been prepared by elaboration of ligated N_2[4] and $[NNH_2]$ groups.[5] When compared with the chemistry of related organoimido complexes $[L_nM(NR)]$,[6] that of diazoalkane complexes is less systematic, in part because of the restrictions imposed by available preparative routes. We illustrate here a high-yield metathetical synthesis, involving the exchange of oxo and diazoalkane ligands, which promises to allow the introduction of diazoalkane ligands into previously inaccessible coordination environments.



Scheme 1. Metathetical synthesis of the diazoalkane–hexamolybdate **2**.

Reaction of $[Bu_4N]_2[Mo_6O_{19}]$ with phosphazine **1** in pyridine at 80 °C for 5 h produces $Ph_3P{=}O$ and the diazoalkane–hexamolybdate complex **2** (Scheme 1). After solvent evaporation and washing the residue with toluene (to remove the phosphane oxide byproduct), **2** is obtained as an analytically pure dark orange powder in 84 % yield. To our knowledge, **2** is the first diazoalkane–polyoxometalate complex.[7] Other singly functionalized derivatives of $[Mo_6O_{19}]^{2-}$ bearing multiply bonded nitrogen ligands include $[Mo_6O_{18}(NO)]^{3-}$,[8] $[Mo_6O_{18}(NNAr)]^{3-}$,[9] $[Mo_6O_{18}(NNMePh)]^{2-}$,[10] and a variety of organoimido complexes $[Mo_6O_{18}(NR)]^{2-}$.[11]

In the IR spectrum of **2**, the C=N stretching vibration occurs at 1610 cm^{-1}. In the Mo≡O stretching region, a sharp and distinct band at 986 cm^{-1} is observed as a shoulder on the main feature at 956 cm^{-1}; this pattern is characteristic of many monosubstituted hexamolybdate species.[11] The lowest energy band in the electronic spectrum of a solution of **2** in CH_3CN occurs at $\lambda_{max} = 397$ nm ($\varepsilon = 7.7 \times 10^4$) which we assign as arising from nitrogen-to-molybdenum charge transfer. A second prominent band at $\lambda_{max} = 311$ nm ($\varepsilon = 7.3 \times 10^4$) is assigned as a $\pi \rightarrow \pi^*$ transition within the $[N_2CMeAr]$ ligand; in the spectrum of the corresponding hydrazone $H_2NNCMeAr$, this feature is observed at $\lambda_{max} = 271$ nm ($\varepsilon = 3.2 \times 10^4$).

Cyclic voltammetry studies of **2** (CH_3CN; 298 K; Pt electrode; $[Bu_4N][PF_6]$ supporting electrolyte; scan rate 100 $mV\,s^{-1}$) in the range from +1.0 V to −1.0 V (vs. Ag/Ag^+) reveal a one-electron reduction wave at −0.894 V ($\Delta E_p = 0.147$ V); under these conditions, the electrochemical couple of deliberately added $[Mo_6O_{19}]^{2-}$ was observed at $E_{1/2} = -0.706$ V ($\Delta E_p = 0.085$ V). The cathodic shift in reduction potential of **2** versus that of $[Mo_6O_{19}]^{2-}$ is comparable to those observed for various $[Mo_6O_{18}(NR)]^{2-}$ complexes,[11] indicating that the donor ability of the $[N_2CMeAr]$ group is superior to that of the oxo ligand and similar to that of an [NR] group.

The structure[12] of the anionic cluster within **2** is shown in Figure 1. The diazoalkane ligand is bound at a terminal position in a monodentate fashion. Its metrical parameters (Mo1–N1 1.738(11), N1–N2 1.337(14), N2–C1 1.31(2) Å; Mo1-N1-N2 172.0(10), N1-N2-C2 117.3(11)°) are consistent

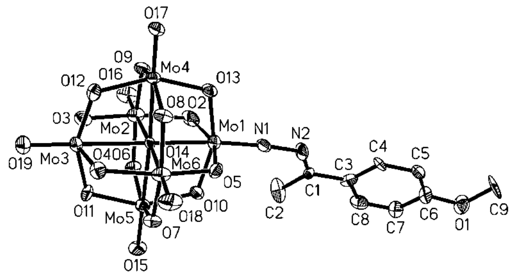


Figure 1. Thermal ellipsoid drawing of the $[Mo_6O_{18}(N_2CMeC_6H_4OMe)]^{2-}$ anion within **2**. Selected bond lengths [Å] and angles [°]: Mo1–N1 1.738(11), N1–N2 1.337(14), N2–C1 1.31(2), Mo1–O5 1.954(8), Mo1–O2 1.963(9), Mo1–O13 1.949(8), Mo1–O10 1.990(8), Mo1–O14 2.164(7), Mo3–O3 1.923(8), Mo3–O4 1.913(9), Mo3-O11 1.892(9), Mo3–O12 1.926(9), Mo3-O14 2.399(7); Mo1-N1-N2 172.0(10), N1-N2-C1 117.3(11).

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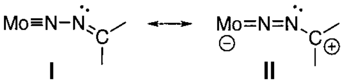
with a description as a dianionic "hydrazone-type" species, involving contributions from the resonance structures **I** and **II**, with form **I** dominating.



I **II**

No discernable variations are observed among the Mo–O$_t$ bond lengths which span the narrow range from 1.679 to 1.698 Å; these values are quite close to those in $[Mo_6O_{19}]^{2-}$.[13] Within the equatorial belt of the cluster, a regular pattern of bond length alternation[14] is evident: each O$_b$ atom forms one long (2.00 Å) and one short (1.88 Å) bond to its pair of Mo atoms. Bond lengths from the equatorial set of Mo atoms to the central O14 atom range from 2.335 to 2.346 Å, again similar to the corresponding distances in $[Mo_6O_{19}]^{2-}$ (2.32 Å). At the diazoalkane binding site, Mo1–O$_b$ distances are distinctly longer than the corresponding Mo3–O$_b$ distances at the *trans* terminal oxo site: Mo1–O$_b$ distances range from 1.949 to 1.990 Å (av 1.964 Å), while Mo3–O$_b$ distances range from 1.892 to 1.926 Å (av 1.914 Å). Since the [N$_2$CMeAr] ligand is superior to an oxo ligand as an electron donor, this longitudinal shift of O$_b$ electron density away from Mo1 provides a mechanism to equalize the valence at Mo1 and Mo3. Along the Mo1–Mo3 axis, the central O14 atom is substantially nearer to Mo1 (2.164 Å) than to Mo3 (2.399 Å). The large discrepancy in these relatively weak interactions is expected given the much larger *trans* influence of terminal oxo ligands as compared to that of multiply bonded nitrogen ligands.[15]

In summary, we have demonstrated a new route to metal complexes of diazoalkane ligands. As illustrated by the preparation of **2**, this metathetical approach promises to provide diazoalkane complexes in previously inaccessible environments. Studies to discern both the range of diazo functionality which may be transferred and the generality of this process with other oxo–metal complexes are underway.

Experimental Section

p-Methoxyacetophenone hydrazone[16] was converted to the corresponding triphenylphosphazine **1** by reaction with Ph_3PBr_2 in benzene in the presence of two equivalents of Et_3N.[17] Compound **1** (0.46 g, 1.1 mmol) and $[Bu_4N]_2[Mo_6O_{19}]$[18] (1.00 g, 0.73 mmol) were combined in pyridine (10 mL) and stirred at 80°C for 5 h under N_2. The reaction mixture was filtered, volatiles were removed under vacuum, and the red residue was washed successively with Et_2O and toluene to yield 0.93 g (84%) of **2** as an analytically pure dark orange solid. Crystals were grown by diffusion of Et_2O vapor into a CH_3CN solution at 25°C. Elemental analysis for $C_{41}H_{82}N_4O_{19}Mo_6$ (%): calcd: C 32.60, H 5.47, N 3.71; found: C 32.84, H 5.54, N 3.82; ^1H NMR (400.1 MHz, CD_3CN, 25°C): $\delta = 7.85$, 7.83, 6.98, 6.96 (AA'BB', 4H, C_6H_4), 3.85 (s, 3H, OCH_3), 2.73 (s, 3H, CH_3), 3.09 (m, 16H, N-CH_2), 1.60 (m, 16H, CH_2), 1.34 (m, 16H, CH_2), 0.96 (t, 24H, CH_3); IR (Nujol, cm^{-1}): $\tilde{\nu} = 1610$ (C=N), 986, 956 (Mo≡O); UV/Vis (CH_3CN): λ_{max} (ε) = 397 (7.7×10^4), 311 nm (7.3×10^4).

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[12] Summary of crystal structure data: $M_r = 1510.75$, orthorhombic, *Pbca*, $a = 15.6577(3)$, $b = 16.9507(3)$, $c = 42.9741(6)$ Å, $V = 11405.7(3)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.760$ g cm^{-3}, $T = 173(2)$ K, crystal size $= 0.13 \times 0.12 \times 0.02$ mm, $\mu = 1.348$ mm^{-1}, $\lambda = 0.71073$ Å; 51189 reflections (10034 independent) were collected on a Siemens SMART system ($2\theta_{max} = 50.06°$). The structure was solved by direct methods and refined by full-matrix least-squares (on F^2) and difference Fourier cycles (SHELXTL V5.0). An absorption correction (SADABS; G. M. Sheldrick, **1996**) was applied ($T_{min}/T_{max} = 0.818$). All non-hydrogen atoms were refined anisotropically. H atoms were treated as idealized isotropic contributions. Final residuals ($I > 2\sigma(I) = 6536$) were $R1 = 0.1114$ and $wR2 = 0.1840$. Largest difference peak and hole = 0.989 and −0.996 e Å^{-3}. GOF (F^2) = 1.186. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-102874. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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