Molybdenum Hexadimethylamide

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The reaction between $Mo(NMe_2)_4$ and dry O_2 (*ca.* 0.5 equiv.) leads to $Mo(NMe_2)_6$ as an isolable amido compound (*ca.* 30% based on Mo); the $Mo(NC_2)_6$ unit has T_h symmetry with Mo–N 2.034(1) Å, N–C 1.462(2) Å, and Mo–N–C 126.0(1)°.

As one moves across the transition series the effect of the oxidation state of the metal becomes more notable within a group. For example in the Group 6 transition elements the relative oxidizing power of the M^{6+} state is quite pronounced: Cr > Mo > W.[1] In the 6+ oxidation state CrF_6 is unstable below −100 °C and $MoCl_6$ is similarly unstable with respect to formation of $MoCl_5$ and Cl_2. For tungsten, the WX_6 compounds are stable (with respect to elimination of X) for only X = F and X = Cl.[1] For organometallic compounds the oxidation state assignment becomes more of a formality, though it is clear that WMe_6,[2] $W(NMe_2)_6$,[3] and $W(OMe)_6$[4]/$W(OPh)_6$[5] are of historical significance as the first homoleptic members of organometallic/metallo-organic compounds of hexavalent tungsten. To this list we now add our discovery of $Mo(NMe_2)_6$, nearly 20 years after the initial report of $W(NMe_2)_6$. Clearly the possibility of synthesizing $MoMe_6$, $Mo(OR)_6$, and even related CrL_6 compounds should not be dismissed lightly.

In continuing our studies[6] of the chemistry of $Mo(NMe_2)_4$,[7] we examined its reactivity toward dry molecular oxygen [$Mo(NMe_2)_4$ is *extremely* air-sensitive].[7] Addition of dry O_2 (4 equiv.) to $Mo(NMe_2)_4$ (500 mg) in hydrocarbon solutions causes an exothermic reaction with an immediate colour change of the solution: purple to deep red. The solid residue obtained by removal of the solvent under dynamic vacuum and extraction with pentane has a broad i.r. stretching band at 800 cm^{-1} with a shoulder at 840 cm^{-1} in the region consistent with ν(Mo–O) [ν(MoO) 810 cm^{-1} (broad) for $Na_2(MoO_4)$].

The crude solid (186 mg) recovered from the pentane extraction crystallizes from toluene as shiny blue translucent crystals, $Mo(NMe_2)_6$. The ^1H and ^{13}C n.m.r. spectra show one resonance each, at δ 3.22 and 51.78, respectively, in [$^2H_6$]benzene. The electron ionization mass spectrum is similar to that of $W(NMe_2)_6$ with a weak parent ion $Mo(NMe_2)_6^+$, a strong ion for the $Mo(NMe_2)_5^+$ fragment, and a base peak for $Mo(NMe_2)_4^+$.[3b]

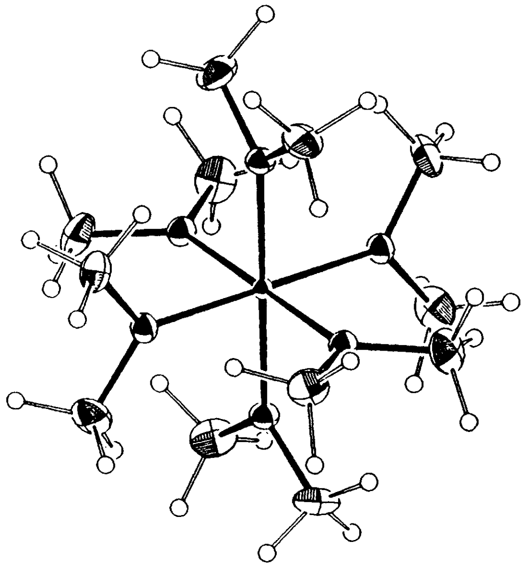

Figure 1. An ORTEP view of the $Mo(NMe)_6$ molecule; pertinent structural parameters are quoted in the text.

$Mo(NMe_2)_6$ crystallizes from toluene in the cubic space group $I23$ with two molecules in the unit cells.[†] The $Mo(NC_2)_6$ moiety has T_h symmetry and there are only the following unique molecular parameters: Mo–N 2.0338(14) Å, N–C 1.4622(18) Å, Mo–N–C 126.0(1)°, and C–N–C 108.0(2)°. The central MoN_6 moiety has rigorous octahedral symmetry.

Isolated $Mo(NMe_2)_6$ reacts further with O_2 in solution to give hydrocarbon-insoluble products. It is also less thermally stable than $W(NMe_2)_6$ and decomposes upon melting at 125 °C. Quite striking is the difference in the behaviour of $Mo(OR)_4$ or $Mo_2(OR)_8$ (R = Bu^t, Pr^i, or CH_2Bu^t) with O_2, giving $MoO(OR)_4$.[8]

Further studies are in progress. We thank the National Science Foundation for support.

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[†] *Crystal data* (−155 °C): $C_{12}H_{36}MoN_6$, $M = 360.40$, space group $I23$, $a = b = c = 9.701(1)$ Å, $Z = 2$, $D_c = 1.414$ g cm^{-3}. Using Mo-K_α radiation, $6° < 2\theta < 75°$, 2273 reflections were collected. Of these the number of unique intensities was 393 and these were used in the final least-squares refinement leading to residuals $R(F) = 0.0165$ and $R_w(F) = 0.0161$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.