Controlled Hydrolysis of Molybdenum(VI) Alkyls and Alkylidenes: *X*-Ray Structure of the Molybdate-bridged Trimetallic Complex $[\{Mo(NBu^t)(CH_2Bu^t)_3\}_2(MoO_4)]$

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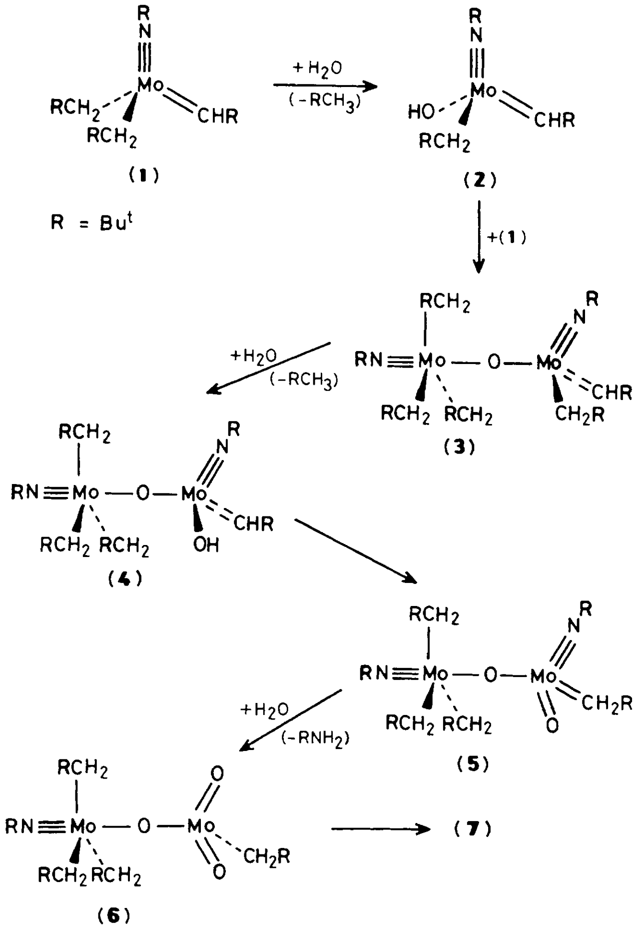
Hydrolysis of $[Mo(NBu^t)(CH_2Bu^t)_2(CHBu^t)]$, which leads to the trimetallic title compound, is shown to occur stepwise *via* four identifiable oxo-bridged dimetallic intermediates.

Reaction pathways involved in the hydrolysis of high oxidation state organometallic compounds are of interest both in catalysis (for interpreting the behaviour of transition metal complexes in aqueous media or on moist supports) and in new syntheses of metal oxides. In our recent report[1] concerning the synthesis of several Mo^{VI} alkyl and alkylidene complexes, we observed the formation in variable yield of an unexpected carbene compound, which we formulated as $[Mo_2O(NBu^t)_2(CHBu^t)(CH_2Bu^t)_4]$ (**3**). We have now found that compound (**3**) was formed from $[Mo(NBu^t)(CH_2Bu^t)_2(CHBu^t)]$ (**1**) by reaction with adventitious water, and we present here details of this and related hydrolysis reactions. The few earlier studies of hydrolysis of d^0 transition metal complexes have led mainly to complexes containing only oxo and alkyl ligands.[2—5]

The complex (**3**) is formed in high yield in 2—3 h by treatment of (**1**) with H_2O in benzene; its formula was confirmed by elemental analysis and mass spectral data (M^+ 696 for ^{92}Mo). The proposed molecular structure (Scheme 1) is based on our earlier n.m.r. and i.r. data.[1] Following this reaction in C_6D_6 by ^1H n.m.r. indicates the formation of an intermediate carbene complex [$\delta(H_\alpha)$ 11.44] with liberation of Bu^tCH_3 and, by analogy with the reaction of (**1**) with Ph_3SiOH,[1] structure (**2**) (Scheme 1) can be reasonably proposed for this intermediate. Addition of the acidic OH function in (**2**) across the Mo=CHBu^t double bond in (**1**) would then yield the complex (**3**) in a reaction which is similar to that of C_6F_5OH with (**1**).[1]

When the complex (**3**) was left to react with H_2O for 48 h, a further compound was produced which was recrystallised from hexane to yield colourless crystals. An *X*-ray diffraction study† showed this to be the trimetallic complex $[\{Mo(NBu^t)(CH_2Bu^t)_3\}_2(MoO_4)]$ (**7**), in which two quasi trigonal pyramidal molybdenum-imido-trineopentyl fragments are bridged by an almost tetrahedral molybdate group (Figure 1).



Scheme 1

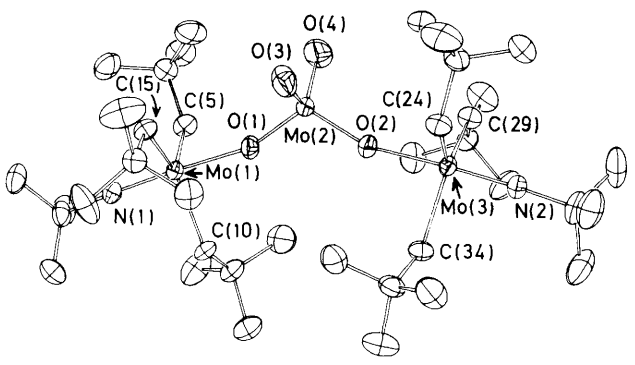


Figure 1. ORTEP view of the molecule $[\{Mo(NBu^t)(CH_2Bu^t)_3\}_2(MoO_4)]$ (**7**). Selected bond lengths (Å) and angles (°): Mo(1)–O(1) 2.017(3), Mo(2)–O(1) 1.825(3), Mo(2)–O(2) 1.806(3), Mo(2)–O(3) 1.704(4), Mo(2)–O(4) 1.690(4), Mo(3)–O(2) 2.031(3), Mo(1)–N(1) 1.729(3), Mo(3)–N(2) 1.728(3), Mo(1 or 3)–C 2.153(4)—2.141(5); N(1)–Mo(1)–O(1) 177.1(1), Mo(1)–O(1)–Mo(2) 158.0(2), O(1)–Mo(2)–O(2) 112.1(1), Mo(2)–O(2)–Mo(3) 159.7(2), O(2)–Mo(3)–N(2) 177.2(2), O(3)–Mo(2)–O(4) 108.1(3).

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† *Crystal data for* (**7**): $C_{38}H_{72}N_2O_4Mo_3$, orthorhombic, space group *Pbca*, $a = 18.996(6)$, $b = 17.836(6)$, $c = 28.351(9)$ Å, $\alpha = \beta = \gamma = 90°$; $U = 9605.7$ Å^3, $D_c = 1.251\ g\ cm^{-3}$; $Z = 8$; $\mu(Mo\text{-}K_{\bar{\alpha}}) = 9.8\ cm^{-1}$. A total of 9214 independent reflections was recorded (θ—2θ flying step-scan) at −100 °C in the range $3 < \theta < 25°$ (graphite-monochromated Mo-$K_{\bar{\alpha}}$ radiation, $\lambda = 0.71063$ Å) with a Philips PW 1100 diffractometer; 5971 reflections with $I > 3\sigma(I)$ were used for determining the structure by conventional Patterson methods and refinement by full-matrix least-squares methods to an unweighted *R* value of 0.030. Hydrogen atoms were placed at their computed co-ordinates (C–H 0.95 Å) with isotropic temperature factors, but not refined. Atomic co-ordinates, bond lengths and angles, and temperature factors have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue 1.

The metal–oxygen distances of $[MoO_4]^{2-}$ differ as expected from those of the free ion in K_2MoO_4 (*ca* 1.76 Å),[6] being shorter for the terminal Mo–O bonds (*ca.* 1.70 Å) but longer for the bridging ones (*ca.* 1.81 Å). The third type of molybdenum–oxygen distance is long (2.02 Å); this is presumably a result *inter alia* of the *trans* effect of the strongly π-donating imido groups. Furthermore, the Mo(1)–O(1)–Mo(2) and Mo(2)–O(2)–Mo(3) angles are large but not linear[4] (*ca.* 159°), and the two ends of the molecule are almost perfectly eclipsed, with one Mo–C bond of each also eclipsing one of the two terminal Mo–O double bonds of the central molybdate unit.

The formation of the complex (**7**) from (**3**) can be followed by ^1H n.m.r. (C_6D_6; 25 °C). The intermediates (**4**) and (**6**) (Scheme 1) may be observed directly;[‡] only the hydroxy ligand signal of (**4**) is not found. Compound (**5**) was not detected *in situ* but could be synthesised from (**3**) by a Wittig reaction[7] with 1 equiv. of PhCHO, with liberation of $PhHC{=}CHBu^t$. Thus prepared, compound (**5**) reacts rapidly with H_2O to yield (**6**). Benzaldehyde also converts (**5**) into (**6**), with formation of $PhHC{=}NBu^t$.[8] The mode of conversion of (**6**) into (**7**) is still unclear; possible mechanisms will be discussed elsewhere.

The complex (**7**) can also be obtained by hydrolysis of $[Mo(NBu^t)(CH_2Bu^t)_3Br]$[1] in the presence of triethylamine; although the mechanism has not been fully investigated, compound (**6**) is again observed as an intermediate.

In summary we note that (a) the hydrolysis of the Mo–C bond occurs readily in tetraco-ordinate but not in pentaco-ordinate Mo units, the $Mo(NBu^t)(CH_2Bu^t)_3$ moiety being stable under these conditions; (b) proton transfer from Mo–OH to a $Mo{=}CHBu^t$ group is relatively slow, and can occur either inter- or intra-molecularly; and (c) the imido ligand is hydrolysed relatively slowly, even in a tetrahedral species, but appears to be activated by the presence of a strong π-donor oxo ligand on the same metal.[8]

Received, 22nd February 1988; Com. 8/00663F

[‡] *Selected spectroscopic data:* ^1H N.m.r. (200 MHz; C_6D_6; δ values; *J* in Hz): (**4**) 12.24 (s, 1H, $C\mathit{H}CMe_3$), 2.63 [d, 3H, $^2J(H_A,H_B)$ 7, $C\mathit{H}_AH_BCMe_3$], 2.44 [d, 3H, $^2J(H_A,H_B)$ 7, $CH_A\mathit{H}_BCMe_3$], 1.61 (s, 9H, $NC\mathit{Me}_3$), 1.47 (s, 9H, $NC\mathit{Me}_3$), 1.45 (s, 9H, $CHC\mathit{Me}_3$), and 1.24 (s, 27H, $CH_2C\mathit{Me}_3$); (**5**) 2.68 [d, 3H, $^2J(H_A,H_B)$ 7, $C\mathit{H}_AH_BCMe_3$], 2.60 (s, 2H, $C\mathit{H}_2CMe_3$), 2.42 [d, 3H, $^2J(H_A,H_B)$ 7, $CH_A\mathit{H}_BCMe_3$], 1.70 (s, 9H, $NC\mathit{Me}_3$), 1.48 (s, 9H, $NC\mathit{Me}_3$), 1.44 (s, 9H, $CH_2C\mathit{Me}_3$), and 1.26 (s, 27H, $CH_2C\mathit{Me}_3$); (**6**) 2.59 (s, 6H, $C\mathit{H}_2CMe_3$), 2.54 (s, 2H, $C\mathit{H}_2CMe_3$), 1.40 (s, 9H, $NC\mathit{Me}_3$), 1.37 (s, 9H, $CH_2C\mathit{Me}_3$), and 1.21 (s, 27H, $CH_2C\mathit{Me}_3$); (**7**) 2.79 (s, 12H, $C\mathit{H}_2CMe_3$), 1.48 (s, 18H, $NC\mathit{Me}_3$), and 1.38 (s, 54H, $CH_2C\mathit{Me}_3$). A useful criterion in the identification of the dimetallic species is the occurrence [as in (**3**)—(**5**) but not in (**6**)] of AB splitting for the methylenic protons of the $Mo(NBu^t)(CH_2Bu^t)_3$ units, which indicates whether the second metal centre is chiral. I.r. data (Nujol; ν in cm^{-1}) for compound (**7**): 920, 850 ($\nu_{Mo=O}$), and 765 ($\nu_{Mo-O-Mo}$).

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