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The effect of Brønsted acids on the stability of oxo-alkoxide and imido-alkoxide complexes of molybdenum

Vernon C. Gibson,* Andrew J. Graham, Daniel L. Ormsby, Brian P. Ward, Andrew J. P. White and David J. Williams

Department of Chemistry, Imperial College, South Kensington, London, UK SW7 2AY

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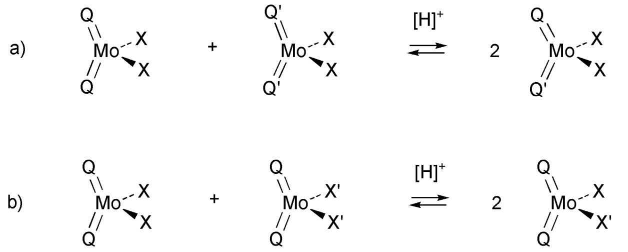
Proton acids are found to catalyse the decomposition of the oxo-alkoxide and imido-alkoxide complexes Mo(O)$_2$(O-t-Bu)$_2$ and Mo(N-2,6-i-Pr$_2$C$_6$H$_3$)$_2$(O-t-Bu)$_2$, respectively; the molecular structure of the tetranuclear molybdenum decomposition product [Mo$_4$(N-2,6-i-Pr$_2$C$_6$H$_3$)$_6$(O-t-Bu)$_2$(μ-O)$_4$(μ$_3$-OH)$_2$] is described.

In recent studies we have shown that proton acids play a catalytic role in the non-redox exchange of dianionic ligands such as oxo and imido, and monoanionic ligands such as alkoxo and amido, between metal centres (Scheme 1).[1] The availability of well-defined proton sources such as H(Et$_2$O)$_2$BAr$^F_4$ [Ar^F = 3,5-(CF$_3$)$_2$C$_6$H$_3$][2] allows the effect of acid to be probed without complicating side reactions arising from the action of a strongly coordinating and reactive anion such as those typically associated with mineral acids.



Scheme 1 The inter-metal exchange of: a) dianionic ligands where Q, Q′ = oxo or imido, X = alkoxo; b) monoanionic ligands where X, X′ = alkoxo or amido, Q = imido.

During the course of this work we became intrigued by the apparent ready decomposition of certain molybdenum oxo-alkoxide complexes, especially so it seemed in the presence of a proton acid. A particular example is Mo(O)$_2$(O-t-Bu)$_2$[3] whose decomposition, once commenced, occurs very rapidly and apparently auto-catalytically to give a blue solid characteristic of molybdenum(V) oxy-hydroxide species, often referred to as 'molybdenum blue oxides'.[4] We therefore decided to undertake a more detailed investigation of the role of Brønsted acids in decomposition reactions of oxo-alkoxide and imido-alkoxide metal complexes.

In a modified procedure to that described previously,[3] Mo(O)$_2$(O-t-Bu)$_2$ was isolated as a colourless oil by treatment of Mo(O)$_2$Cl$_2$(dme) (dme = 1,2-dimethoxyethane) with two equivalents of LiO-t-Bu in diethyl ether. Upon treatment of Mo(O)$_2$(O-t-Bu)$_2$ with 10% H(Et$_2$O)$_2$BAr$^F_4$ [Ar^F = 3,5-(CF$_3$)$_2$-C$_6$H$_3$] in CD$_2$Cl$_2$, decomposition proceeds rapidly and reproducibly to afford 2-methylpropene (isobutylene) and the characteristic blue solid, suggesting that the acid is indeed enhancing the rate of the decomposition process. The intractability of the solid product from this reaction, however, and the difficulty of following its formation by a convenient spectroscopic technique, severely limits the information that can be obtained on this system.

We therefore decided to examine the analogous imido metal system, Mo(N-2,6-Pr$^i_2$C$_6$H$_3$)$_2$(O-t-Bu)$_2$, where it was envisaged that the more solubilising organoimido units might afford tractable products. In the absence of acid, this imido complex shows no evidence for decomposition in solution at room temperature.† By contrast, its treatment with 10% H(Et$_2$O)$_2$BAr$^F_4$ in CD$_2$Cl$_2$ at room temperature gives rise to an immediate colour change from yellow to red. The ^{1}H NMR spectrum revealed the presence of isobutylene and free ArNH$_2$; the reaction goes to completion within 72 hours.‡ A similar transformation was found to occur when HBF$_4$·Et$_2$O was used in place of HBAr$^F_4$. Upon scale-up of this reaction, a batch of red crystals suitable for an X-ray structure determination could be isolated.

The X-ray analysis§ revealed the structure to be the centrosymmetric tetranuclear molybdenum cluster shown in Fig. 1. The structure consists of two edge sharing Mo(VI) octahedra linked by hydroxide bridges joined to tetrahedral Mo(VI) centres *via* oxo bridges. The two Mo(1)–O–Mo(2) bridges are noticeably asymmetric, with the distances to Mo(2) being shorter [at 1.818(4) to O(1) and 1.798(4) Å to O(3′)] than those to Mo(1) [at 2.042(4) to O(1) and 2.020(4) Å to O(3)] suggesting the presence of some Mo(2)=O double bond character.

The geometry at the Mo(2) centres is distorted tetrahedral with angles subtended at the metal in the range 101.7(2)–122.2(3)°. The Mo(2)–N(3) distance, at 1.716(5) Å, combined with an imido bend angle of 176.7(6)°, are consistent with a quasi-linear imido ligand containing a pseudo triple bond. The bonds to the three oxygen atoms are fairly similar [1.818(4) to O(1), 1.798(4) to O(3′) and 1.772(6) Å to O(4)] and all suggest a degree of multiple bond character. By contrast, the geometry at the Mo(1) centres is very distorted octahedral with *cis* angles subtended at the metal in the range 66.2(2)–105.8(3)°; the most acute being associated with the two hydroxy bridges. The two Mo–N bond lengths of 1.722(6) [N(1)] and 1.740(6) Å [N(2)] again reflect their pseudo triple bond character [angles at nitrogen are near linear, 171.3(6)° at N(1) and 163.5(5)° at N(2)], and in each case the molybdenum centre is displaced towards the imido ligand out of the plane of the four atoms perpendicular to this direction [by 0.32 Å towards N(1), and 0.31 Å towards N(2)]. The hydroxy bridges between the two Mo(1) centres are both long and symmetric [Mo(1)–O(2) 2.270(4), O(2)–Mo(1′) 2.282(3) Å] reinforcing our conclusion that these are indeed hydroxy rather than oxo linkages. This bridging hydroxy group also makes a close approach to the flattened O$_3$ base of the Mo(2) tetrahedron, suggesting a degree of triply bridging character for this group [O(2)–Mo(2) 2.361(3) Å]. Although this tetranuclear cluster represents only one of many possible products from the reaction, its isolation provides support for the formation of oxo-hydroxide species, since conceptually it may be viewed as arising from condensation of fragments such as [Mo(O)(OH)(NAr)(O-t-Bu)] and [Mo(NAr)$_2$(O)].

With a view to obtaining insight into the mechanism by which acid might assist the decomposition reaction, a series of DFT calculations were carried out on non-protonated, and protonated, Mo(O)$_2$(O-t-Bu)$_2$. It has previously been postulated that metal *tert*-butoxide species decompose *via* an intramolecular γ-hydrogen transfer from one of the *tert*-butoxide methyl groups to an adjacent functional group[5,6] (*cf.* Scheme 2a). The calculations¶ on Mo(O)$_2$(O-t-Bu)$_2$ afforded an

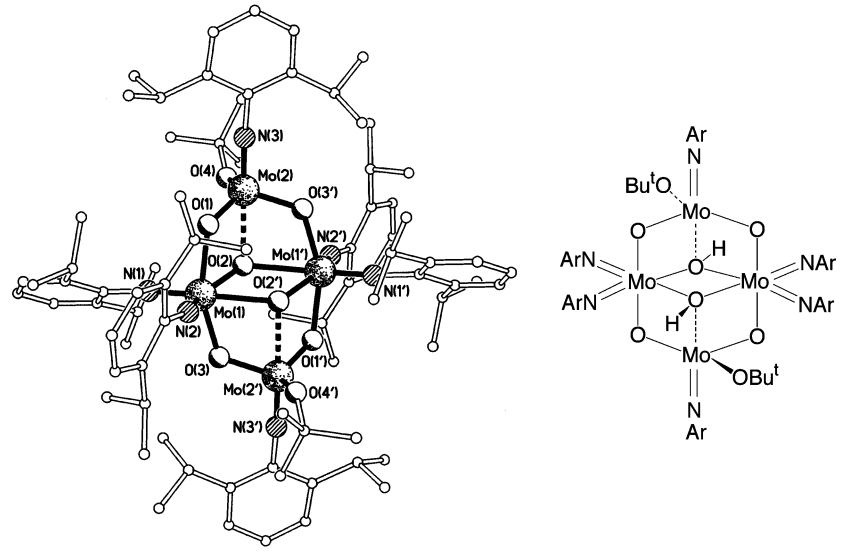
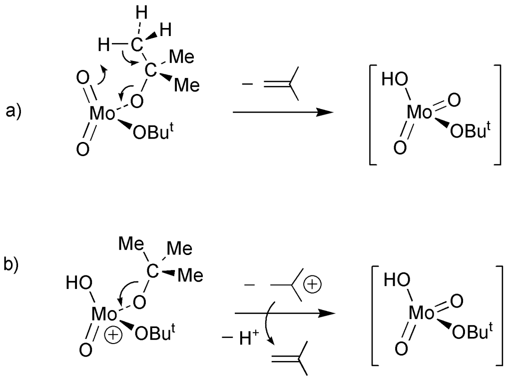


Fig. 1 The molecular structure of the tetranuclear molybdenum complex $[Mo_4(N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_6(O\text{-}t\text{-}Bu)_2(\mu\text{-}O)_4(\mu_3\text{-}OH)_2]$ showing the extended chair conformation of the Mo_4O_4 ring.



Scheme 2 Decomposition pathways: a) for $Mo(O)_2(O\text{-}t\text{-}Bu)_2$ *via* an intramolecular γ-hydrogen migration, and b) for protonated $Mo(O)_2(O\text{-}t\text{-}Bu)_2$ *via* heterolytic cleavage.

enthalpy barrier ($\Delta H^{\ddagger}$) of 34 kcal mol^{-1} for concerted γ-hydrogen abstraction *via* the neighbouring oxo unit. For the protonated species $[Mo(O)(OH)(O\text{-}t\text{-}Bu)_2]^+$, a concerted intramolecular hydrogen transfer process proved energetically inaccessible. Rather an enthalpy barrier of 15 kcal mol^{-1} is found for a heterolytic cleavage of the C–O bond to give *tert*-butyl cation (Scheme 2b). Thus it seems that an important outcome of protonation is to make accessible a low energy heterolytic cleavage pathway.

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Notes and references

† In their studies on the mechanism of imine metathesis reactions mediated by molybdenum imido complexes, Jordan and Meyer[5] have noted that $W(N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)(OBu^t)_2Cl_2(thf)$ decomposes to give isobutylene and free aniline (along with *t*-BuCl as a secondary by-product) and speculated that HCl may play a role in this decomposition reaction.

‡ It should be noted that the decomposition reactions are slower than the ligand exchange processes described in ref. 1.

§ Crystal data for **1**: $C_{80}H_{122}N_6O_8Mo_4\cdot 0.5C_7H_{16}$, M = 1729.7, triclinic, $P\bar{1}$ (no. 2), a = 12.276(2), b = 15.073(2), c = 15.184(2) Å, α = 97.76(1), β = 108.43(1), γ = 113.90(1)°, V = 2322.0(5) Å^3, Z = 1 (C_i symmetry), D_c = 1.237 g cm^{-3}, μ(Cu-Kα) = 4.71 mm^{-1}, T = 293 K, ruby red prisms; 6652 independent measured reflections, F^2 refinement, R_1 = 0.058, wR_2 = 0.137, 4687 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \le 120°$], 471 parameters. CCDC reference number 181356. See http://www.rsc.org/suppdata/dt/b2/b202281h/ for crystallographic data in CIF or other electronic format.

¶ Computational methods. All minima and transition states were initially calculated using the mixed basis set of 3-21G* on O, C and H centres, and LANL2DZ with pseudopotential on Mo within the RHF methodology. Minima were located with standard optimization routines and transition states were located using the QST2/3 routine. Final optimization and frequency analysis on all points was performed using the mixed basis set of 6-31G** on O, C and H centres and LANL2DZ with pseudopotential on Mo within the B3LYP methodology. All calculations were performed using the GAUSSIAN98[7] package on an Athlon based RedHat Linux system.

1 I. J. Blackmore, V. C. Gibson, A. J. Graham, M. Jolly, E. L. Marshall and B. P. Ward, *J. Chem. Soc., Dalton Trans.*, 2001, 3242.

2 M. Brookhart, B. Grant and A. F. Volpe, *Organometallics*, 1992, **11**, 3920.

3 M. H. Chisholm, K. Folting, J. C. Huffman and C. C. Kirkpatrick, *Inorg. Chem.*, 1982, **21**, 978.

4 *Advanced Inorganic Chemistry*, 6th edn., F. A. Cotton, G. Wilkinson, C. A. Murillo and M. Bochmann, Wiley-Interscience, New York, ch. 18, pp. 923–924.

5 A. Y. Jordan and T. Y. Meyer, *J. Organomet. Chem.*, 1999, **591**, 104.

6 (*a*) T. A. Budzichowski, M. H. Chisholm, K. Folting, J. C. Huffman and W. E. Streib, *J. Am. Chem. Soc.*, 1995, **117**, 7428; (*b*) C. P. Schaller, C. C. Cummins and P. T. Wolczanski, *J. Am. Chem. Soc.*, 1996, **118**, 591; J. Belgacem, J. Kress and J. A. Osborn, *J. Mol. Catal.*, 1994, **86**, 267.

7 GAUSSIAN98, Revision A.1, Gaussian Inc., Pittsburgh, PA, 1998.