Dealkylation of an Organoimido Ligand Leading to a Binuclear (μ-Nitrido) Complex of Molybdenum(iv): Structure of the [Cl₃(py)₂MoNMo(py)₂Cl₃]⁻ Anion
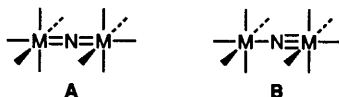
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Pyridine abstracts an allyl group from the Mo^{VI} allylimido complex [CH₂=CH–CH₂–N≡MoCl₄(thf)], leading to the ultimate formation of the N-allylpyridinium salt of an unusual μ-nitrido binuclear Mo^{IV} species, [CH₂=CH–CH₂-py][Cl₃(py)₂MoNMo(py)₂Cl₃].

Within the family of bimetallic μ-nitrido complexes, there exist two common structural motifs. In structure A, the two metal–nitrogen bond lengths are equal and correspond to metal–nitrogen double bonds, while in structure B the M–N distances are decidedly different and conform to metal–nitrogen single and triple bonds. Many examples of both structural types are known[1] and detailed theoretical analyses of the bonding in these systems have been published.[2] Among complexes of Mo and W, typical values for the single, double, and triple M–N bonds described above are 2.10, 1.84, and 1.68 Å, respectively.[1,2] To our knowledge, there exists only a single bimetallic μ-nitrido complex that apparently does not conform to either of the above structural representations, namely [PPh₄][Cl₅WNWCl₅]:[3] although the structural data for this system are somewhat imprecise, the two W–N bond lengths are 1.79(2) and 1.88(2) Å. We now report the unusual preparation and structure of another bimetallic μ-nitrido complex featuring an analogous asymmetry in the disposition of the nitrido bridge.

$$\underset{\textbf{A}}{-\overset{|}{\underset{|}{M}}=N=\overset{|}{\underset{|}{M}}-} \qquad \underset{\textbf{B}}{-\overset{|}{\underset{|}{M}}-N\equiv\overset{|}{\underset{|}{M}}-}$$

CH₂Cl₂ solutions containing the unstable Mo^{VI} allylimido complex, [CH₂=CH–CH₂–N≡MoCl₄(THF)], 1, can be prepared by the oxidation of [MoCl₄(THF)₂] with allyl azide.[4] Treatment of such a solution with dry pyridine affords, after workup and crystallization,† a low yield of dark-red crystals (5% based on Mo). The compound's ¹H NMR spectrum indicated that it was a paramagnetic species, and elemental analysis data could not be interpreted in terms of any expected

products. Accordingly, a single crystal X-ray diffraction study was carried out‡ and revealed the material to be the N-allylpyridinium salt of a μ-nitrido dimolybdenum(iv) anion, namely [CH₂=CH–CH₂-py] [Cl₃(py)₂MoNMo(py)₂Cl₃], 2, see Fig. 1.

The octahedral coordination spheres about the two Mo^{IV} centres are staggered by ca. 30° with respect to one another (Fig. 2), leading to approximate D_2 symmetry for the anion. The two Mo–N distances involving the nitrido ligand differ by 0.1 Å [Mo(1)–N(5) = 1.887(10) Å; Mo(2)–N(5) = 1.793(10) Å] and the Mo–Cl bonds trans to the nitrido ligand [Mo(1)–Cl(2) = 2.524(3) Å; Mo(2)–Cl(5) = 2.550(3) Å] are lengthened by ca. 0.1 Å with respect to the average cis Mo–Cl bond length of 2.424(3) Å. The unequal Mo–N bond lengths and staggered geometry observed in 2 may be contrasted with the structure of its Me₃P analogue [Me₃P=N=PMe₃][Cl₃-(Me₃P)₂MoNMo(PMe₃)₂Cl₃], 3, prepared by Gibson et al.[5] In the structure of 3, the anion displays overall D_{2d} symmetry in which the octahedral coordination spheres about each Mo^{IV} centre are rotated by 90° with respect to each other. Furthermore, 3 contains essentially identical Mo–N bond lengths of 1.873(8) and 1.851(8) Å.

In their analysis of transition metal nitrides, Hoffmann et al.[2] noted the orbital analogy between the allyl cation and μ-nitrido species of structure A: for the nitrido system, the combination of each metal's d_{xz} and d_{yz} orbitals with the p_x and p_y orbitals of the nitrido ligand affords orthogonal pairs of π-bonding, non-bonding, and π-antibonding orbitals. Within the anion of 2, the two π-bonding Mo–N–Mo orbitals will be filled, and the four d-electrons of the two Mo^{IV} centres can be housed in the four available non-bonding orbitals (the above-mentioned pair plus the d_{xy} orbital of each metal). This situation should lead to a quintet spin state for 2. Consistent
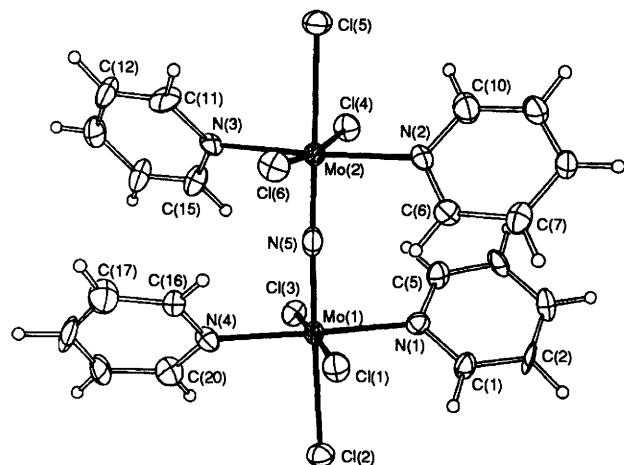
Fig. 1 ORTEP view and labelling scheme for the anion within 2. Ellipsoids are at 35% probability. Selected bond lengths (Å) and angles (°): Mo(1)–N(5) = 1.887(10); Mo(2)–N(5) = 1.793(10); Mo(1)–Cl(1) = 2.422(3); Mo(1)–Cl(2) = 2.524(3); Mo(1)–Cl(3) = 2.431(3); Mo(1)–N(1) = 2.201(9); Mo(1)–N(4) = 2.185(9); Mo(2)–Cl(4) = 2.423(3); Mo(2)–Cl(5) = 2.550(3); Mo(2)–Cl(6) = 2.423(3); Mo(2)–N(2) = 2.206(9); Mo(2)–N(3) = 2.223(10); Mo(1)–N(5)–Mo(2) = 176.4(5).
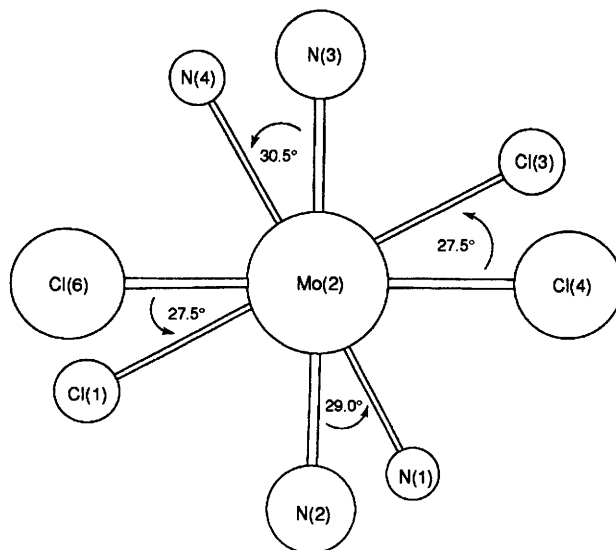
Fig. 2 Coordination sphere within the anion of 2, as viewed along the Mo(2)–Mo(1) axis, illustrating pseudo-torsional angles
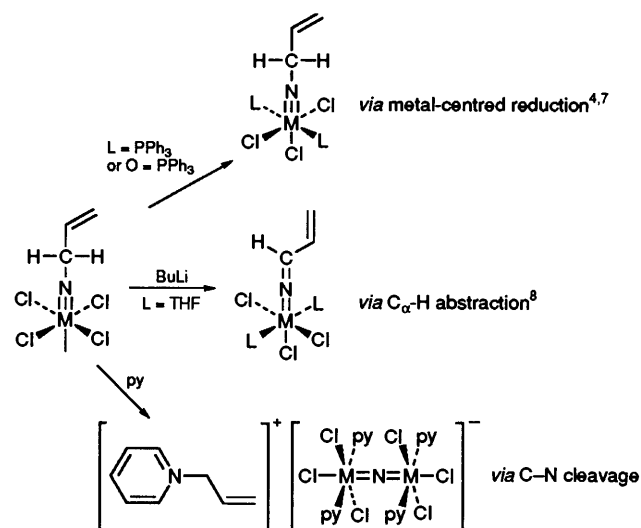
Scheme 1 Reactivity patterns observed for d^0 allylimido complexes of Mo and W

with this picture, we observe $\mu_{eff} = 6.06 \mu_B$ ($\mu_B = 9.274 \times 10^{-24}$ J T^{-1}) (Faraday method; 21.8 °C), a value which may be compared to the expected spin-only value of 4.90 μ_B. While we are reluctant to rationalize the unexpected asymmetry of the Mo–N–Mo core, we note that the calculations presented by Hoffmann et al. reveal a shallow energy surface for motion of the nitrido ligand within a fixed M–M distance.[2]

The mechanism by which **2** is formed is not clear. Cleavage of the C–N bond within an organoimido ligand to produce a nitrido species is a rare occurence for which there is limited precedent,[6] and with one exception,[6c] the fate of the imido substituent in these reactions remains obscure. The presence of the N-allylpyridinium cation in **2** suggests that the allyl group within **1** suffers nucleophilic attack by pyridine (at either C_α or C_γ) eliminating an anionic Mo-nitrido species which may displace chloride from the [MoCl$_4$L$_2$] precursor forming the μ-nitrido backbone; further reductive incorporation of pyridine could lead to **2**. It is likely that cleavage of the allylimido C–N bond within **1** is facilitated by the stability of the nascent allyl cation.

At least two other reaction sequences are likely to be occurring in this system (Scheme 1), and can account in part for the low yield obtained for **2**. Nucleophiles such as Ph$_3$P[4] and Ph$_3$P=O[7] react with **1** to produce allylimido Mo^V species [CH$_2$=CH–CH$_2$–N≡MoCl$_3$L$_2$] and it is reasonable to assume that a similar process is occurring with the pyridine nucleophile. In addition, small amounts (ca. 6% based on Mo) of [C$_5$H$_5$NH]Cl are isolated in the preparation of **2**: this product suggests that **1** also participates in an overall dehydrohalogenation process, forming the allylideneamido Mo^{IV} species [CH$_2$=CH–CH=N=MoCl$_3$(py)$_2$], as has been demonstrated previously for the tungsten(vi) analogue of **1**.[8]

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Footnotes

† *Preparation and characterization*: allyl azide (1 equiv.) was added to a suspension of [MoCl$_4$(THF)$_2$] (5.24 mmol) in CH$_2$Cl$_2$ (75 ml) at room temp. under N$_2$. After 30 min stirring, dry pyridine (15 ml) was added and the solution was stirred overnight. Hexane (20 ml) was added, a precipitate was removed by filtration, and the filtrate was allowed to stand at −10 °C for one week, yielding 0.2 g of 2·CH$_2$Cl$_2$. IR (Nujol), cm^{-1}: 1041 (ν_{asym} Mo–N–Mo).

‡ *Crystal data* for 2·CH$_2$Cl$_2$: C$_{29}$H$_{32}$N$_6$Cl$_8$Mo$_2$, $M = 940.12$, monoclinic, $P2_1/n$, $a = 9.256(2)$, $b = 17.959(4)$, $c = 23.161(5)$ Å, $\beta = 90.974(18)°$, $V = 3849.6(16)$ Å^3, $Z = 4$, $D_c = 1.622$ g cm^{-3}, μ(Mo-Kα) = 12.25 cm^{-1}, $T_{(max)}/T_{(min)} = 1.143$. Three dark-red crystals (all approximately $0.42 \times 0.38 \times 0.16$ mm) were used to collect 5122 reflections (two octants, Nicolet R3m/μ diffractometer, graphite monochromator, $4° \leq 2\theta \leq 45°$, 296 K) of which 4726 were independent and systematically present, and 2642 were considered observed [$5\sigma(F_o)$]. Three crystals were required due to radiation decomposition. No absorption correction was applied to the data. The structure was solved by direct methods which located the Mo atoms. The remaining non-hydrogen atoms were located through subsequent least squares and difference Fourier syntheses. At convergence, with all non-hydrogen atoms anisotropic and calculated isotropic hydrogen atom contributions, $R(F) = 5.67\%$, $R(wF) = 5.42\%$, gof = 1.135, $\Delta/\sigma_{(max)} = 0.076$, $\Delta(\rho) = 0.873$ e Å^3, and $N_o/N_v = 6.5$. All calculations used the SHELXTL program library (5.1) [G. Sheldrick; Nicolet (Siemens), Madison, WI]. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

References

1 K. Dehnicke and J. Strähle, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 955.
2 R. A. Wheeler, R. Hoffmann and J. Strähle, *J. Am. Chem. Soc.*, 1986, **108**, 5381.
3 T. Godemeyer, A. Berg, H.-D. Gross, U. Müller and K. Dehnicke, *Z. Naturforsch.*, 1985, **40b**, 999.
4 E. A. Maatta, Y. Du and A. L. Rheingold, *J. Chem. Soc., Chem. Commun.*, 1990, 756.
5 V. C. Gibson, D. N. Williams and W. Clegg, *J. Chem. Soc., Chem. Commun.*, 1989, 1863.
6 (a) Os(NBu^t)O$_3$ affords [N≡OsCl$_5$]$^-$ and Cl$_2$ upon treatment with concentrated aqueous HCl: A. F. Clifford and C. S. Kobayashi, *Inorg. Synth.*, 1960, **6**, 204; (b) A putative Os^{VI} methyl imido complex affords an Os^{VI} nitrido complex: C. J. Barner, T. J. Collins, B. E. Mapes and B. D. Santarsiero, *Inorg. Chem.*, 1986, **25**, 4323; (c) Complexes of Ru^{VI} and Os^{VI} which are likely to contain a *tert*-butylimido ligand yield 2-methylprop-2-ene and the corresponding nitrido complexes: W.-H. Leung, G. Wilkinson, B. Hussain-Bates and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1991, 2791.
7 Y. Du, A. L. Rheingold and E. A. Maatta, to be published.
8 E. A. Maatta and Y. Du, *J. Am. Chem. Soc.*, 1988, **110**, 8249.