Conversion of a Molybdenum Nitride to the Amide and thence to an Oxide and Ammonia, Reactions involving Formal 1,3-Prototropic Shifts. X-Ray Structures of *trans*-[$Mo(NH_2)(OH)(dppe)_2$][$OTf]_2$ and *trans*-[$MoO(OMe)(dppe)_2$][BPh_4] (dppe = $Ph_2PCH_2CH_2PPh_2$; OTf = CF_3SO_3)

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Protonation of *trans*-[$MoN(N_3)(dppe)_2$] by HOTf provides the first example of the conversion of a nitride group to an amide, *trans*-[$Mo(NH_2)(OH)(dppe)_2]^{2+}$ **1**; this amide is slowly converted to *trans*-[$MoO(OMe)(dppe)_2]^+$ **2** on stirring in toluene–methanol and ammonia is released; the formation of **1** and **2**, whose structures have been authenticated by X-ray crystallography, are explained in terms of formal prototropic shifts:

$$\{(H_2O)\ Mo{=}NH\} \rightarrow \{HO{-}Mo{-}NH_2\} \rightarrow \{O{=}Mo\ (NH_3)\}$$

We report the first example of the direct protonation of a nitride to give an amide and the X-ray crystallographic structure of the product, *trans*-[$Mo(NH_2)(OH)(dppe)_2$][$CF_3SO_3]_2$ (**1**·[$OTf]_2$). Methanolysis of **1** releases ammonia and gives *trans*-[$MoO(OMe)(dppe)_2$][CF_3SO_3] (**2**·[OTf]); the structure of this cation has also been determined by X-ray analysis ([BPh_4] salt). The formation of **1** and **2** can be explained by a series of prototropic shifts: $\{(H_2O)Mo{=}NH\} \rightarrow \{HO{-}Mo{-}NH_2\} \rightarrow \{O{=}Mo(NH_3)\}$.

Treatment of *trans*-[$MoN(N_3)(dppe)_2$] with 4 equiv. of CF_3SO_3H (triflic acid, HOTf) in THF at room temperature afforded air-stable purple crystals of *trans*-[$Mo(NH_2)(OH)(dppe)_2$][$OTf]_2$, isolated in 53% yield after work-up and re-crystallisation from acetone–toluene. Compound **1** is also produced by protonation of *trans*-[$Mo(NH)(OMe)(dppe)_2$][OTf] with HOTf under similar conditions.

When **1** is stirred in toluene–methanol (4 : 1 *v/v*) for 120 h at room temperature the dark purple solution slowly fades, yellow crystals of *trans*-[$MoO(OMe)(dppe)_2$][OTf] (**2**·[OTf]) are precipitated in 45% yield and ammonia is formed in 70% yield.

The formulations of **1** and **2** were confirmed by microanalysis, FAB-MS, IR and NMR spectroscopy,† and by single crystal X-ray analysis:‡ views of the structures of the amide and oxo-complexes are shown in Figs. 1 and 2, respectively. Difference Fourier maps for **1**·[$OTf]_2$ revealed the H-atoms of both the NH_2 and OH ligands. One of the H atoms of the amide group is hydrogen-bonded to O of a triflate counter-ion, as is the hydroxy H. The Mo–N bond distance in **1** is 2.053(11) Å; molybdenum–primary amide bond distances of 1.954(23) and 1.964(13) Å have been measured for [Mo(NHEt)(NO)I{HB(3,5-$Me_2C_3HN_2)_3$}] (two crystallographically independent structures[1]) and the average Mo–NR_2 bond length {R = C (sp^3); 44 secondary amides} is 1.955(20) Å.[2] That the Mo–NH_2 bond in **1** is significantly longer than is generally observed for organoamides is probably a consequence of *trans* HO(pπ) → Mo(dπ) donation diminishing H_2N(pπ) → Mo(dπ) interactions.[3]

The Mo=O bond length in **2** is 1.723(4) Å and lies well within the range typical of molybdenum oxo-complexes,[2] whereas in closely related *trans*-[$MoO(OH)(dppe)_2$][BF_4] (**3**·[BF_4]), this bond length is considerably longer, 1.833(5) Å;[4] Again, this appears to attest to a considerable *trans* influence of the hydroxide group at the Mo^{IV} centre. The Mo–OH bond lengths in **1** and **3** and the Mo—OMe bond length of **2** are not statistically different. The Mo–O–Me arrangement in **2**·[BPh_4] is essentially linear {176.0(4)°} and adoption of this somewhat unusual geometry suggests a need to maximise MeO(pπ) → Mo(dπ) interactions. If this were the case, the question arises as to why the Mo=O bond in **2** is not also atypically long. EHMO calculations on cations *trans*-[MoO(OH or OMe)$(dppe)_2$] were carried out and it was found that the linearity of the Mo–O–Me group is predominately a consequence of the need to minimise destabilising steric interactions between OMe and the Ph groups of the dppe ligands rather than an electronic requirement to maximise orbital overlap.

Earlier studies of the reactions of *trans*-[$MoN(N_3)(dppe)_2$][5] with anhydrous HX (X = F, Cl, Br or I) indicate that the formation of *trans*-[$Mo(NH)(N_3)(dppe)_2]^+$ is followed by protonation at the azide ligand and release of HN_3 to expose a site at which X^- then irreversibly binds: a parallel chemistry involving the release of MeOH occurs with *trans*-[$Mo(NH)(OMe)(dppe)_2]^+$.[6,7] The complexes formed by anation, *trans*-[$Mo(NH)(X)(dppe)_2]^+$, are quite inert to further protonation by HX or HOTf, as indeed is *trans*-[Mo(NH)(OTf)(*syn*-Me_8[16]aneS_4)]$^+$.[8]

Protonation with triflic acid presumably follows a similar pathway except now the weakly coordinating anion $CF_3SO_3^-$

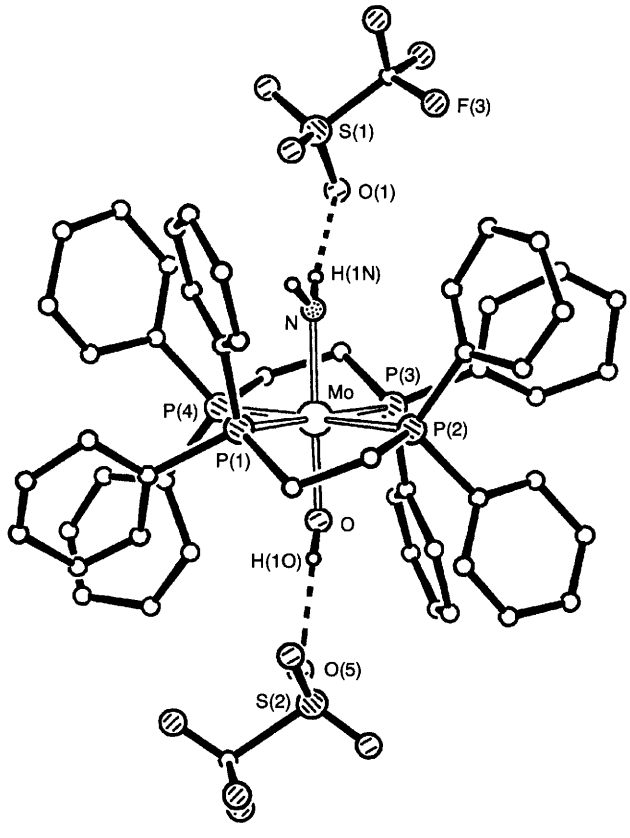


Fig. 1 View of the cation **1** and hydrogen-bonded anions of *trans*-[$Mo(NH_2)(OH)(dppe)_2$]($OTf)_2$·toluene

ineffectively competes with traces of water for the dicationic site. A subsequent 1,3-prototropic shift, which probably occurs *via* proton release from the aquo-ligand and proton attack at the imide group, then leads to the observed amide product **1**. The formation of **2** from **1** can be rationalised in terms of a slow second prototropic shift and replacement of ammonia by methanol (Scheme 1).

Similar reaction pathways to those discussed above explain the release of ammonia and the formation of a mixture of *trans*-$[WO(Cl)(dppe)_2]^+$ and *trans*-$[W(NH)Cl(dppe)_2]^+$ when *trans*-$[W(NH)(OMe)(dppe)_2]^+$ is treated with aqueous HCl.[9] The anion Cl^- and H_2O compete for the dicationic site formed by methanol loss: coordination of the former leads to the substitution product whereas coordination of the latter results in formation of an aquo-complex and thence, *via* successive prototropic shifts, to the oxide and ammonia (Scheme 1).

Transition metal complexes possessing the prototypical metallo-amide group M–NH_2 are uncommon, most are prepared by deprotonation of ammines.[10] As far as we are aware, only two structures containing this group have hitherto been characterised by X-ray crystallography: $[Pd_2Cl_2(NH_2)_2]$[2–11] and $[Cr(NH_2)(O_3SCF_3)\{(H_2N)_2C_6H_2Me_2\}]$.[12] Complexes possessing M–NH_2 groups (M = Mo or W) are of particular interest because they are plausible intermediates in certain chemical, electrochemical or biological reactions which produce ammonia from dinitrogen. Whereas NN, NNH, NNH_2, N, NH or NH_3 groups have been characterised in stable compounds at a single type of mononuclear site, *trans*-$\{MX(dppe)_2\}$ (X = anionic ligand), evidence for the existence of an M–NH_2 species in this sequence has hitherto been confined to the electrochemical detection of unstable *trans*-$[Mo(NH_2)(X)(dppe)_2]$.[13]

This work was supported in part by a Grant-in-Aid for Scientific Research (No. 04241102) in the Priority Area: 'Activation of Inactive Small Molecules' by the Ministry of Education, Sciences and Culture, Japan.

Received, 7th December 1994; Com. 4/07494G

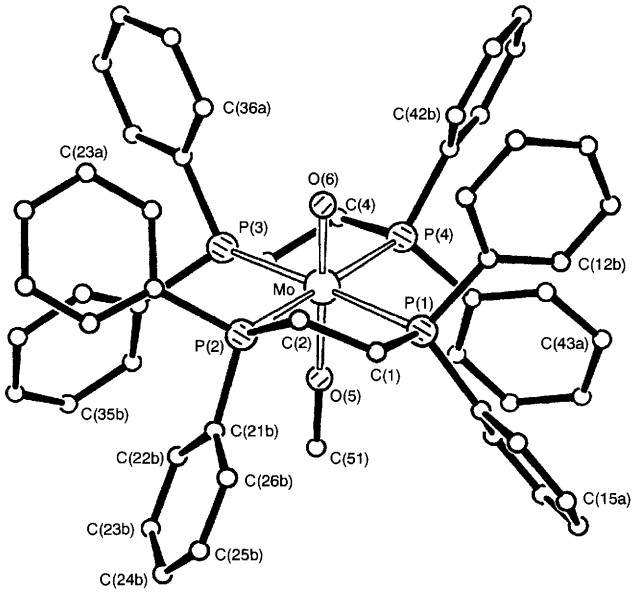
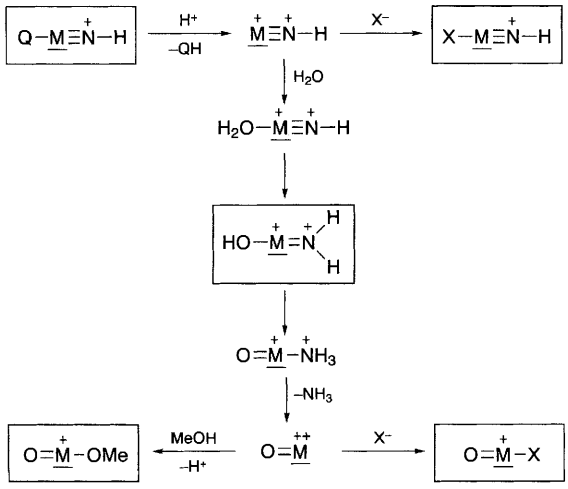


Fig. 2 View of the cation **2** of *trans*-$[MoO(OMe)(dppe)_2][BPh_4]$



Scheme 1 M = Mo or W(dppe)$_2$; Q = N_3 or OMe; boxed species represent stable, fully characterised Mo and/or W compounds

Footnotes

† *Spectroscopic data.* Satisfactory microanalyses (C, H and N) were obtained for the new compounds. For **1**·[OTf]$_2$: ^{1}H NMR (δ, 500 MHz, $CDCl_3$): 2.66 (br mult, 2H, PCH_2), 2.76 (br mult, 2H, CH_2), 3.07 (broad multiplet, 4H, CH_2), 3.92 (s, 1H, OH), 6.58 (br s, 0.5H, NH_2), 7.01 (br s, 0.5H, NH_2), 7.82 (br s, 0.5H, NH_2), 6.7–7.5 (mult, 40H, C_6H_5). The three broad multiplets for the CH_2 protons of the diphosphine ligand and the three half integer signals for the NH_2 protons are indicative of two rotational conformers in solution, the fourth half integer signal is probably buried under the aromatic resonances. Restricted rotation about the M–NR_2 bond is well-established.[19] ν/cm^{-1} (Nujol): 1650 (m, NH bend), 3489 (m, NH stretch), 3300 and 3150 (w, H-bonded NH, OH). FAB MS (*m/z*): 1075 (M^{2+}·TfO^-), 1058 (M^{2+}·TfO^-–OH), 926 (M^+); 908 (M^+–H_2O).

For **2**·[OTf]: ^{1}H NMR (δ, 500 MHz, $CDCl_3$): 1.95 (s, 3H, OCH_3), 2.60 (mult, 4H, CH_2), 2.87 (mult, 4H, CH_2), 6.9–7.5 (mult, 40H, C_6H_5). FAB MS (*m/z*): 941 (M^+). ν/cm^{-1} (Nujol): 892 (Mo=O stretch).

‡ *Crystal data* for **1**·[OTf]$_2$-toluene: $C_{52}H_{51}MoNOP_4$, $2(CF_3O_3S)$, C_7H_8, M = 1316.1, monoclinic, space group *Cc*, a = 23.632(5), b = 13.538(6), c = 19.301(5) Å, β = 91.26(2)°, U = 6174(3) Å^3, Z = 4, D_c = 1.411 g cm^{-3}, μ(Mo-Kα) = 4.39 cm^{-1}, F(000) = 2704. Final $R(R_w)$ = 0.036(0.031) for 5291 reflections [$I > 3.0\sigma(I)$] and 737 variables. The space group *Cc* was confirmed most likely by the refinement process. There is strong pseudosymmetry in the cation, but opposing phenyl groups have significantly different orientations. The O and N atoms on the *trans*-H_2N–Mo–OH axis are distinct and well-resolved from their pseudo-opposites, as are the two anions to which they are hydrogen-bonded; the hydrogen atoms of these OH and H_2N ligands were located in a difference map.

Refinement in the centrosymmetric space group *C2/c* was attempted with less success; currently R = 0.080 and R_w = 0.094 for 3987 reflections. Each of the phosphine phenyl groups is disordered and these have been refined as rigid bodies with isotropic thermal parameters. The O/N ligands, the anion and the solvent molecule are each disordered over two distinct sites.

In each symmetry system, an anion 1···H_2N–Mo–OH···anion 2 hydrogen-bonded arrangement has been identified; in *Cc* it is ordered, in *C2/c* it is disordered. Molecular structure of **1**. Selected bond distances (Å) and angles (°): Mo–P(1) 2.524(4), Mo–P(2) 2.553(4), Mo–P(3) 2.517(4), Mo–P(4) 2.532(4), Mo–N 2.053(11), Mo–O 1.922(9), N–H 0.79 and 0.69, O–H 0.80; P(1)–Mo–P(2) 78.6(1), P(1)–Mo–P(3) 178.8(2), P(2)–Mo–P(4) 179.7(2), P(3)–Mo–P(4) 79.1(1), N–Mo–O 178.5(6), Mo–N–H 127 and 147, Mo–O–H 152.

Crystal data for **2**·[BPh_4]: $C_{53}H_{51}MoO_2P_4$, $C_{24}H_{20}B$, M = 1259.1, monoclinic, space group $P2_1/n$ (equiv. to no. 14), a = 19.028(2), b = 19.024(2), c = 19.645(2) Å, β = 114.533(10)°, U = 6469.2 Å^3, Z = 4, D_c = 1.293 g cm^{-3}, F(000) = 2624, μ(Mo-Kα) = 3.4 cm^{-1}, λ(Mo-Kα) = 0.71069 Å. Final $R(R_w)$ = 0.069(0.077) for 6142 reflections ($I > \sigma_I$), weighted w = $(\sigma^2_F + 0.00146F^2)^{-1}$, and 838 variables. Molecular structure of **2**, Selected bond distances (Å) and angles (°): Mo–P(1) 2.558(2), Mo–P(2) 2.538(2), Mo–P(3) 2.530(3), Mo–P(4) 2.560(2), Mo–O(5) 1.920(4), Mo–O(6) 1.723(4), O(5)–C(51) 1.417(8), P(1)–Mo–P(2) 79.4(1), P(1)–Mo–P(3) 177.7(1), P(2)–Mo–P(4) 179.5(1), P(3)–Mo–P(4) 78.9(1), O(5)–Mo–O(6) 178.8(2), Mo–O(5)–C(51) 176.0(4).

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.

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