Facile Conversion of a Cationic Mo^{IV} Phosphinimato Complex into an Anionic Nitrido-bridged Dimer with a Bis(trimethylphosphine)iminium Counterion

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$[Mo(NPMe_3)Cl_2(PMe_3)_3]Cl$ is formed in 82% yield upon treatment of $[Mo(N)Cl_3]$ with four equivalents of trimethylphosphine in CH_2Cl_2 and rearranges to the nitrido-bridged dimer $[(Me_3P)_2Cl_3MoNMoCl_3(PMe_3)_2][Me_3PNPMe_3]$ upon standing at room temperature in CH_2Cl_2; *X*-ray structural analyses of these compounds are reported.

Transition metal complexes possessing NPR_3 (phosphinimato) ligands have been characterized for a number of transition elements,[1] and *X*-ray structural analyses have been reported for seven of these compounds.[2] The $MNPR_3$ fragment may be regarded as a species in which a 'naked' metal-bound nitrogen atom is protected by a tertiary phosphine group, and thus there exists much scope for exploiting the reactivity of the nitrogen atom in this environment. However, very few reactivity studies have been reported.[3] Here, we describe the formation of a cationic Mo^{IV} phosphinimato complex and its facile conversion to an anionic d^2 nitrido-bridged dimer with a bis(trimethylphosphine)iminium counterion. The bonding in such nitrogen-bridged metal complexes has attracted recent attention due to its analogy with the π-bonding in polyenes.[4]

Treatment of a dichloromethane suspension of $Mo(N)Cl_3$ with four equivalents of trimethylphosphine affords the pale green, paramagnetic d^2 complex $[Mo(NPMe_3)Cl_2(PMe_3)_3]Cl$† in 82% yield (equation 1).

$$[Mo(N)Cl_3] + 4PMe_3 \xrightarrow{CH_2Cl_2,\ \text{room temp.}} \underset{(\mathbf{1})}{[Mo(NPMe_3)Cl_2(PMe_3)_3]Cl} \qquad (1)$$

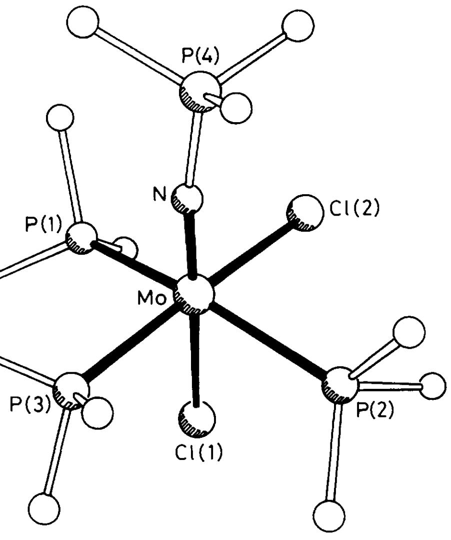

Figure 1. Structure of the cation of (**1**), with non-carbon atoms labelled. Key dimensions: Mo–Cl(1) 2.482(2), Mo–Cl(2) 2.522(2), Mo–P(1) 2.530(2), Mo–P(2) 2.516(1), Mo–P(3) 2.489(2), Mo–N 1.775(4), N–P(4) 1.636(4) Å; Mo–N–P(4) 167.6(3)°.

$$\underset{(\mathbf{1})}{[Mo(NPMe_3)Cl_2(PMe_3)_3]Cl} \xrightarrow{CH_2Cl_2,\ \text{room temp.}} \underset{(\mathbf{2})}{[(PMe_3)_2Cl_3MoNMoCl_3(PMe_3)_2][Me_3PNPMe_3]} \qquad (2)$$

An excellent crop of green needles may be obtained by allowing a CH_2Cl_2 solution of (**1**), layered with an equal volume of toluene, to stand at room temperature for 24 h. A single crystal *X*-ray structure analysis‡ reveals an octahedral co-ordination geometry with meridional PMe_3 groups and a *cis*-dichloro ligand arrangement (Figure 1). The Mo–N–P angle of 167.6(3)° and Mo–N distance of 1.775(4) Å are consistent with lone pair donation from nitrogen to molyb-

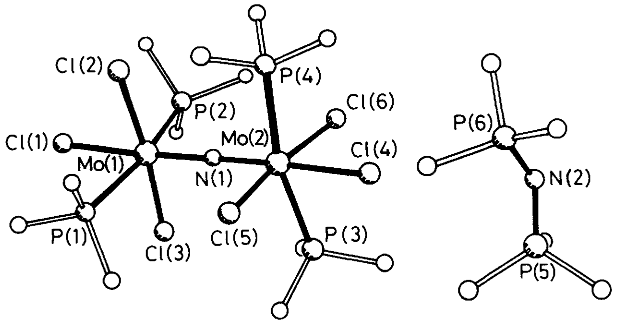

Figure 2. Structure of the cation and anion of (**2**), with non-carbon atoms labelled. Key dimensions for the anion: Mo(1)–N(1) 1.873(8), Mo(2)–N(1) 1.851(8) Å; Mo(1)–N(1)–Mo(2) 175.3(4)°. For the cation: N(2)–P(5) 1.564(6), N(2)–P(6) 1.560(6) Å; P(5)–N–P(6) 141.7(5)°.

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† Satisfactory elemental analyses have been obtained.

‡ *Crystal data* for (**1**): $C_{12}H_{36}NP_4Cl_3Mo{\cdot}CH_2Cl_2$, $M = 605.6$, orthorhombic, $P2_12_12_1$, $a = 11.183(2)$, $b = 14.262(3)$, $c = 17.752(4)$ Å, $U = 2831.3$ Å^3, $Z = 4$, $D_c = 1.420$ g cm^{-3}, $\lambda(\text{Mo-}K_\alpha) = 0.71073$ Å, $\mu = 1.15$ mm^{-1}, $F(000) = 1240$, $T = 295$ K. The structure was determined by direct methods and refined[5] to a minimum of $\Sigma w\Delta^2[\Delta = |F_0|-|F_c|$, $w^{-1} = \sigma^2(F) = \sigma_c^2(F) + 58 + 63G + 47G^2 - 150H + 103H^2 - 138GH$, $G = F_0/F_{max}$, $H = \sin\theta/\sin\theta_{max}]$[6] from 4020 reflections with $2\theta < 50°$ and $F > 4\sigma_c(F)$ (σ_c from counting statistics only), measured with a Stoe–Siemens diffractometer and on-line profile fitting.[7] Anisotropic thermal parameters were refined for all non-H atoms, H atoms were constrained. Final $R = 0.050$, $R_w = (\Sigma w\Delta^2/\Sigma wF_0^2)^{1/2} = 0.037$, for 217 parameters. For (**2**): $C_{18}H_{54}N_2P_6Cl_6Mo_2{\cdot}CH_2Cl_2$, $M = 974.0$, triclinic, $P\bar{1}$, $a = 10.880(2)$, $b = 14.620(3)$, $c = 15.493(3)$ Å, $\alpha = 64.03(1)$, $\beta = 80.48(1)$, $\gamma = 81.36(1)°$, $U = 2176.6$ Å^3, $Z = 2$, $D_c = 1.486$ g cm^{-3}, $\mu = 1.29$ mm^{-1}, $F(000) = 988$. The structure was determined and refined as above $[w^{-1} = \sigma^2(F) = \sigma_c^2(F) + 10 - 30G + 99G^2 - 15H + 16H^2 - 39GH]$ from 3819 reflections with $2\theta < 45°$ and $F > 4\sigma_c(F)$. Final $R = 0.052$, $R_w = (\Sigma w\Delta^2/\Sigma wF_0^2)^{1/2} = 0.039$, for 334 parameters. 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.

denum, while the N–P distance of 1.636(4) Å lies within the range expected for a nitrogen–phosphorus double bond.

Upon standing at room temperature for several days, the pale green dichloromethane solution of (**1**) gradually adopts an orange colouration attributable to the paramagnetic anionic d^2 nitrido-bridged dimer $[(PMe_3)_2Cl_3MoNMoCl_3(PMe_3)_2][Me_3PNPMe_3]$† (**2**) (equation 2). The rate of conversion of (**1**) to (**2**) may be increased with warming such that a solution of (**1**) heated at 50 °C for 1 h yields (**2**) in 90% yield upon removal of the CH_2Cl_2 solvent. Large orange prisms readily form at the interface of a layered CH_2Cl_2/toluene (50 : 50) solution.

The *X*-ray structure‡ of (**2**) reveals eclipsed ligand axes for the dimolybdenum anion with staggered, *trans*-orientated PMe_3 groups and a meridional arrangement of the chloro ligands resulting in overall D_{2d} symmetry (Figure 2). The M–N distances, averaging 1.86 Å, are equivalent within experimental error and correspond to double bonds. The bonds to the chloro ligands lying *trans* to the nitrido group are considerably elongated [2.535(3) and 2.571(3) Å respectively] compared with the *cis*-Mo–Cl distances [av. 2.411(2) Å]; similar lengthening of the halide ligands *trans* to a bridging nitride have been noted in the related anions $[W_2NCl_{10}]^{-}$[8] and $[Ta_2NBr_{10}]^{3-}$.[9] The bis(trimethylphosphine)iminium counterion is bent, with a P–N–P angle of 141.7(5)° and equivalent phosphorus–nitrogen distances of 1.56 Å. Hoffmann and co-workers[4] have analysed the bonding in μ_2-nitrido dimers of this type: the frontier orbitals may be considered to arise by combination of four metal d and two nitrogen p orbitals giving two orthogonal sets of π-bonding, non-bonding and π-antibonding orbitals. For the d^2 molybdenum centres of (**2**), the degenerate non-bonding orbitals on each metal will be singly occupied, consistent with the paramagnetism observed for (**2**). Their non-bonding character also suggests that they will not have a significant influence on the metal–nitrogen interactions, and no substantial deviations are found in the metal–nitrogen bond lengths and angles of (**2**) compared with the d^0 analogue $[W_2NCl_{10}]^-$. Studies are presently focussed on assessing the mechanism of this remarkable transformation and extending the investigation to the analogous tungsten system. It is worth noting that the tungsten analogue of (**1**) can be prepared by treatment of $W(N)Cl_3$ with trimethylphosphine by an essentially analogous procedure.

The authors are grateful to the S.E.R.C. for financial support.

Received, 30th August 1989; Com. 9/03673C

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