A Tris-dinitrogen Complex. Preparation and Crystal Structure of *mer*-[Mo(N_2)$_3$(PPr$^n_2$Ph)$_3$]

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The complex *trans*-[Mo(N_2)$_2$(PPr$^n_2$Ph)$_4$] reacts with N_2 to give *mer*-[Mo(N_2)$_3$(PPr$^n_2$Ph)$_3$] which has been structurally characterised by *X*-ray crystallography.

Metal complexes of dinitrogen generally carry one, or more rarely two, terminal dinitrogen ligands, in contrast to the prevalence of polycarbonyl complexes.[1] Such behaviour for dinitrogen would be expected on the basis of its relatively weak ($\sigma + \pi$)-bonding capacity compared to carbon monoxide[1] and polydinitrogen complexes might therefore be thought to have low stability. We now report that during the course of our studies of dinitrogen complexes with bulky phosphine co-ligands[2] we have isolated the first tris-dinitrogen complex and that it has good thermal stability.

We have synthesised *trans*-[Mo(N_2)$_2$(PPr$^n_2$Ph)$_4$] by reduction of [MoCl$_3$(thf)$_3$] in tetrahydrofuran (thf) by Mg, in the presence of N_2 and PPr$^n_2$Ph (4 mol. equiv.). This red compound [i.r. $\nu(N_2)$ 1920 cm^{-1}, Nujol], although stable under dinitrogen in the solid state, is unstable in solution (thf or benzene) under dinitrogen in the absence of an excess of PPr$^n_2$Ph, giving a clear yellow solution after *ca.* 20 min. Addition of methanol then gives a high yield of yellow crystals.

The ^{31}P n.m.r. spectrum of the yellow solution shows a pattern typical of a complex having a *mer* arrangement of three phosphines[2] [δ −118.3 (t, intensity 1) and −120.3 (d, intensity 2) p.p.m. relative to P(OMe)$_3$] and free PPr$^n_2$Ph (1 mol. equiv.). The yellow product [$\nu(N_2)$ 2080w, 1985s, and 1965s cm^{-1}, Nujol] analyses as [Mo(N_2)$_3$(PPr$^n_2$Ph)$_3$] and thus the observed reaction is that shown in equation (1). Confirmation of the formulation of *mer*-[Mo(N_2)$_3$(PPr$^n_2$Ph)$_3$] comes from the *X*-ray structure shown in Figure 1, which includes important distances and angles.

$$\textit{trans}\text{-}[\mathrm{Mo(N_2)_2(PPr^n_2Ph)_4}] + \mathrm{N_2} \rightleftharpoons \textit{mer}\text{-}[\mathrm{Mo(N_2)_3(PPr^n_2Ph)_3}] + \mathrm{PPr^n_2Ph} \qquad (1)$$

Crystal Data: $C_{36}H_{57}MoN_6P_3$, M = 762.75. Monoclinic, space group $P2_1/n$ (variation of $P2_1/c$, no. 14), a = 14.531(4), b = 16.594(5), c = 17.270(5) Å, β = 101.06(2)°, U = 4086.9 Å^3, D_c = 1.239 g cm^{-3}, Z = 4, μ(Mo-K_α) = 4.6 cm^{-1}, λ(Mo-$K_{\bar\alpha}$) = 0.71069 Å.†

Crystals are translucent, dull yellow, thin diamond-shaped plates. Diffraction intensities were measured on an automated diffractometer with monochromated Mo-radiation. There was considerable crystal deterioration (*ca.* 30%) over the period of measurement, and corrections for this, for Lorenz-polarisation effects, and by Bayesian methods[3] (to ensure no negative intensities) were made. For $\theta < 20°$, 3802 unique reflections were measured; of these, 2366 had $I > 2\sigma(I)$. No absorption corrections were applied.

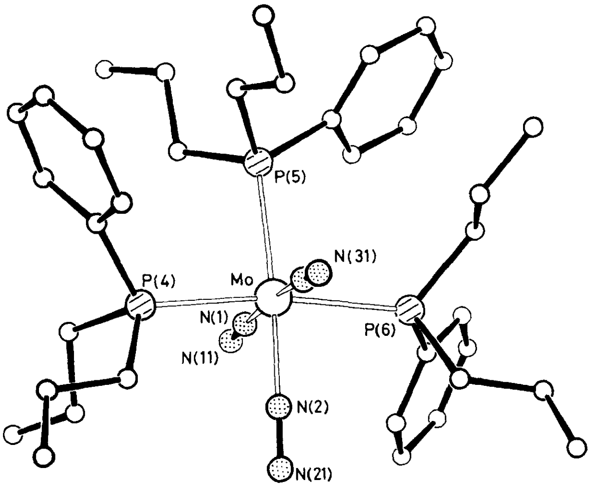

Figure 1. Molecular geometry of *mer*-[Mo(N_2)$_3$(PPr$^n_2$Ph)$_3$] [the unlabelled nitrogen atom is N(3)]. Selected molecular dimensions (Å and °): Mo–N(1) 2.050(9), Mo–N(2) 1.984(9), Mo–N(3) 2.015(8), Mo–P(4) 2.483(2), Mo–P(5) 2.512(2), Mo–P(6) 2.497(2), N(1)–N(11) 1.092(10), N(2)–N(21) 1.124(9), N(3)–N(31) 1.103(9), N(1)–Mo–N(2) 88.7(3), N(1)–Mo–N(3) 175.7(3), N(2)–Mo–N(3) 87.1(3).

The structure was derived from Patterson and electron density maps, and the positions of hydrogen atoms were calculated with idealised geometries (the end methyl groups in staggered conformations). The n-propyl groups have, principally, the extended, *trans* arrangement, but there are indications of slight site disorder of some end methyl groups. This disorder, involving sites of low (<25%) occupation, has not yet been fully resolved. Current refinement is to conventional R = 0.091 and R_W = 0.083 for all 3802 reflections with weights $w = [\sigma(F)^2 + 0.00149\,F^2]^{-1}$.

The complex molecule (Figure 1) has octahedral co-ordination about the Mo-atom, and the three dinitrogen ligands are in the meridional arrangement (as are the three phosphine ligands). There are significant deviations from octahedral geometry at the Mo atom; the rather bulky phosphine groups push the dinitrogen ligands together so that not only are the N–Mo–N angles rather less than 90 and 180°, but also the *trans* Mo–N(1) and –N(3) distances appear rather longer than Mo–N(2), since the overlap of orbitals of Mo with N(1) and N(3) is reduced by the deviation from orthogonality. Correspondingly, the N(1)–N(11) and N(3)–N(31) distances appear to be shorter than N(2)–N(21). Competition for available Mo orbitals between the *trans*-dinitrogen ligands is also expected to cause slightly longer (Mo–N) and shorter (N–N) bond distances compared with those of the unique dinitrogen.

Clearly *mer*-[Mo(N_2)$_3$(PPr$^n_2$Ph)$_3$] is a complex which contains a potentially reactive, unsaturated metal centre as well as

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

activated dinitrogen and its reactions will be reported at a later date.

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References

1 J. Chatt, J. R. Dilworth, and R. L. Richards, *Chem. Rev.*, 1978, 589 and references therein.
2 S. N. Anderson, D. L. Hughes, and R. L. Richards, *J. Chem. Soc., Chem. Commun.*, 1982, 1291.
3 S. French and K. Wilson, *Acta Crystallogr., Sect. A*, 1978, **34**, 517.