A μ-Dinitrogen Complex with a Long N–N Bond. *X*-Ray Crystal Structure of $[(PMe_2Ph)_4ClReN_2MoCl_4(OMe)]$

By MARY MERCER
(*Rothamsted Experimental Station, Molecular Structures Department, Inveresk House, Strand, London* WC2R 0HG)
and ROBERT H. CRABTREE and RAYMOND L. RICHARDS*
(*A.R.C. Unit of Nitrogen Fixation, University of Sussex, Brighton* BN1 9QJ)

Summary The complex $[(PMe_2Ph)_4ClReN_2MoCl_4(OMe)]$ has been prepared; it has $\nu(N_2)$ at 1660 cm^{-1} and the N–N (1·21 Å), Re–N (1·79 Å), and Mo–N (1·89 Å) bond distances, determined by *X*-ray crystallography are consistent with a linear Re–N–N–Mo delocalised bonding scheme.

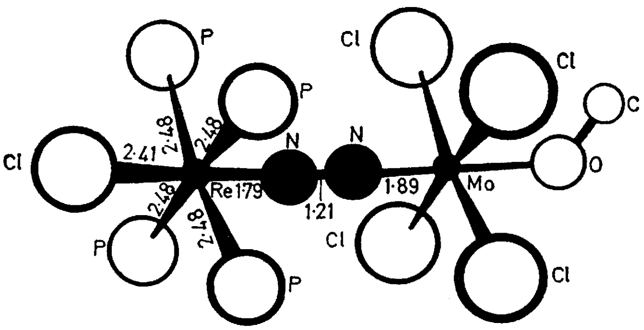
THE N–N bond distances in all complexes of dinitrogen, whether mononuclear or dinuclear, whose structures have been accurately determined, are within 0·03 Å of that in molecular nitrogen (1·10 Å).[1] Some asymmetrically bridged dinitrogen complexes have low $\nu(N_2)$[2] and it is of interest to see whether they contain long N–N bonds. Such complexes are usually sensitive to moisture, but complex (A) has now been prepared [$\nu(N_2)$ 1660 cm^{-1}] which is stable to air, obtained according to reaction (1). Complex (A) has

$$[ReCl(N_2)(PMe_2Ph)_4] + [MoCl_4(thf)_2] \text{ (excess)} \xrightarrow[MeOH]{CH_2Cl_2} \underset{(A)}{[(PMe_2Ph)_4ClReN_2MoCl_4(OMe)]} \qquad (1)$$

μ_{eff} = 1·85 B.M., m.p. 100° (decomp.), and crystallises as purple-black crystals from dry MeOH.

Crystal data. Monoclinic, a = 14·918, b = 11·176, c = 28·162 Å, β = 92·6°, Z = 4, Mo-K_α radiation, λ = 0·7107 Å; space group $P2_1/c$ 3595 diffractometer observations, R = 0·06%.

The Figure shows the more important dimensions of one complete molecule. The lengthening of the N–N bond is accompanied by a shortening of the two metal-nitrogen bonds *cf.* Re–N in $[ReCl(N_2)(PMe_2Ph)_4]$[3] (1·97 Å) and



FIGURE

Mo^{V}–N single bond distances[4,5] (*ca.* 2·23 Å). The Re–N–N–Mo system is linear and thus its π-system is delocalised as postulated[6] for the analogous [(PMe$_2$Ph)$_4$ClReN$_2$CrCl$_3$-(thf)]. Although the N–N distance of (A) is that of a formal double bond, the bonding scheme is essentially the same as that of the [(NH$_3$)$_5$Ru–N$\equiv$N–Ru–(NH$_3$)$_5$]$^{4+}$ ion (N–N = 1·124 Å)[7] and the long N–N distance of (A) arises because the two 3*e*-orbitals,[6] which are bonding on nitrogen, are vacant. The corresponding molecular orbitals in the ruthenium compound are filled.

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