# Preparation and *X*-Ray Structure of a Trinuclear Dinitrogen-bridged Complex, *trans*-[$MoCl_4\{(N_2)ReCl(PMe_2Ph)_4\}_2$]

By Peter D. Cradwick*
(*The Macaulay Institute for Soil Research, Craigiebuckler, Aberdeen* AB9 2QJ)
and Joseph Chatt, Robert H. Crabtree, and Raymond L. Richards
(*A.R.C. Unit of Nitrogen Fixation, University of Sussex, Brighton* BN1 9QJ)

*Summary* The compound *trans*-[$MoCl_4\{(N_2)ReCl(PMe_2Ph)_4\}_2$] has been prepared and is shown by *X*-ray diffraction to contain a linear Re–N–N–Mo–N–N–Re chain.

In certain of its metal complexes, *e.g.* *trans*-[$ReCl(N_2)(PMe_2Ph)_4$], the dinitrogen ligand is sufficiently basic to ligate to a second acceptor molecule, giving dinitrogen-bridged, binuclear complexes.[1] Generally only one rhenium dinitrogen complex binds to the acceptor group, but early transition-metal acceptors sometimes take two. A titanium dirhenium complex, unsuitable for *X*-ray structure determination, has recently been described.[2] Similar molybdenum and tungsten dirhenium complexes have now been prepared and the structure of a bis-($\mu$-dinitrogen) complex determined by *X*-ray diffraction.

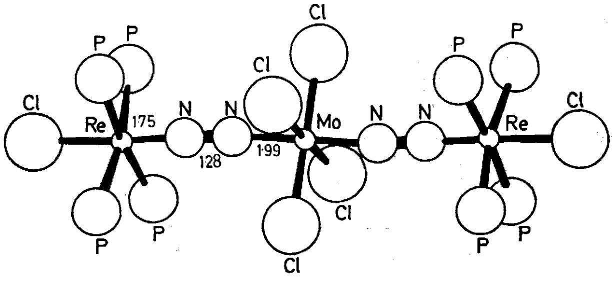

Figure. Rhenium and molybdenum co-ordination with bond lengths in Å; the standard deviations in the bond lengths shown are Re–N, Mo–N, ±0·04; N–N, ±0·05.

*Crystal data*. $[\mathrm{MoCl_4\{(N_2)ReCl(PMe_2Ph)_4\}_2}]$ $a$ = 16·710, $b$ = 14·164, $c$ = 19·084 Å, $\beta$ = 114·3°, $Z$ = 2; the molybdenum atom lies on a centre of symmetry in space group $P2_1/c$. The new trinuclear complexes are *trans*-$[\mathrm{MCl_4\{(N_2)ReCl(PMe_2Ph)_4\}_2}]$, where M = Mo or W. The molybdenum complex has the structure shown in the Figure. At present $R$ = 0·074 over 1306 film data and light-atom bond distances are insufficiently accurate for detailed discussion. Nevertheless, the novel, linear Re–$N_2$–Mo–$N_2$–Re system is unambiguously defined and, as found in a related binuclear complex,[1] the N–N distances are considerably longer than those of mononuclear complexes.

The molybdenum compound was first prepared by the interaction of $\mathrm{MoOCl_3}$ with an excess of *trans*-$[\mathrm{ReCl(N_2)(PMe_2Ph)_4}]$ in dichloromethane, but it and its tungsten analogue are better prepared as in reaction (1). Only one $N_2$-stretching band at *ca*. 1800 cm$^{-1}$ is observed in the i.r. spectra of these green, diamagnetic compounds, consistent with the proposed stereochemistry. The compounds are diamagnetic because two of the three $\pi$-type, non-bonding $d$-orbitals of the molybdenum interact with the bonding $\pi$-system of the dinitrogen ligands, leaving an essentially non-bonding $d$-orbital on molybdenum to accommodate its two electrons.

$$2\ trans\text{-}[\mathrm{ReCl(N_2)(PMe_2Ph)_4}] + [\mathrm{MCl_4(PPh_3)_2}] \xrightarrow{\mathrm{CH_2Cl_2}} trans\text{-}[\mathrm{MCl_4\{(N_2)ReCl(PMe_2Ph)_4\}_2}] + 2\mathrm{PPh_3} \qquad (1)$$

Thus *trans*-$[\mathrm{ReCl(N_2)(PMe_2Ph)_4}]$ behaves as an effective nitrogen $\sigma$- and $\pi$-donor ligand, and an extensive coordination chemistry of this and other dinitrogen complexes with early transition-metal acceptors is to be expected.

(*Received, 4th March* 1975; *Com.* 272.)

---

[1] M. Mercer, *J.C.S. Dalton*, 1974, 1637 and references therein.

[2] R. Robson, *Inorg. Chem.*, 1974, **13**, 475.