Inorganica Chimica Acta, 76 (1983) L225–L226

Reaction of the Dinitrogen Complex $[Re(\eta^2\text{-}S_2PPh_2)(N_2)(PMe_2Ph)_3]$ with Methylisocyanide. Preparation and X-ray Structure of the Mixed Dinitrogen–Isocyanide Complex *mer*-$[Re(\eta^1\text{-}S_2PPh_2)(N_2)(CNMe)(PMe_2Ph)_3]$

ARMANDO J. L. POMBEIRO*

Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, 1000 Lisbon, Portugal

PETER B. HITCHCOCK and RAYMOND L. RICHARDS

School of Molecular Sciences, The University of Sussex, Brighton, U.K.

Received December 1, 1982

A comparative study of the reactivity of dinitrogen and the isoelectronic ligand methylisocyanide is the subject of our interest, and an analogy of behaviour appears to be followed by these species. When they bind analogous metal sites, both undergo electrophilic attack when ligating an electron-rich metal centre or when susceptible to a nucleophilic attack when they coordinate an electron-poor site [1, 2].

However, the stronger electron π-acceptance of the isocyanide constitutes a destabilizing influence on the metal–dinitrogen bond, and previous attempts to isolate mixed dinitrogen-isocyanide complexes of M(0) or W(0) with phosphine co-ligands have failed, although electrochemical and spectroscopic evidence suggested the formation in solution of the unstable complex *cis*-$[Mo(N_2)(CNMe)(PMe_2Ph)_4]$ in the reaction of *cis*-$[Mo(N_2)_2(PMe_2Ph)_4]$ with CNMe [3]. Nevertheless, the presence of a suitable electron releasing ligand in the *trans* position relative to a metal–dinitrogen bond helps in its stabilization, and *mer*-$[ReCl(N_2)(CNMe)\{P(OMe)_3\}_3]$, with Cl *trans* to N_2 has been prepared [4].

In the present study, $SPPh_2$ has proved a stabilizing influence on the metal–dinitrogen bond in a rare example of a N_2 binding centre with a sulphur ligand. Thus, treatment of $[Re(\eta^2\text{-}S_2PPh_2)(N_2)(PMe_2Ph)_3]$ (*1*) with CNMe in THF under argon and tungsten filament light gave, upon careful crystallization from THF-diethyl ether–pentane, the complex *mer*-$[Re(\eta^1\text{-}S_2PPh_2)(N_2)(CNMe)(PMe_2Ph)_3]$ (*2*) as a yellow crystalline solid [ν(CN) 2100 cm^{-1}, $\nu(N_2)$ 1980 cm^{-1}] (reaction 1)

$$\underset{(1)}{[Re(\eta^2\text{-}S_2PPh_2)(N_2)(PMe_2Ph)_3]} + CNMe \longrightarrow$$

$$\longrightarrow mer\text{-}\underset{(2)}{[Re(\eta^1\text{-}S_2PPh_2)(N_2)(CNMe)(PMe_2Ph)_3]} \qquad (1)$$

The molecular structure of complex (*2*) is shown in Fig. 1. The phosphine ligands display a meridional arrangement in agreement with ^{31}P NMR data in CD_2Cl_2 (doublet for the two *trans* phosphine; doublet of triplets with half total intensity for the unique phosphine–phosphorus which couples to the other phosphine- and phosphinato-phosphorus atoms).

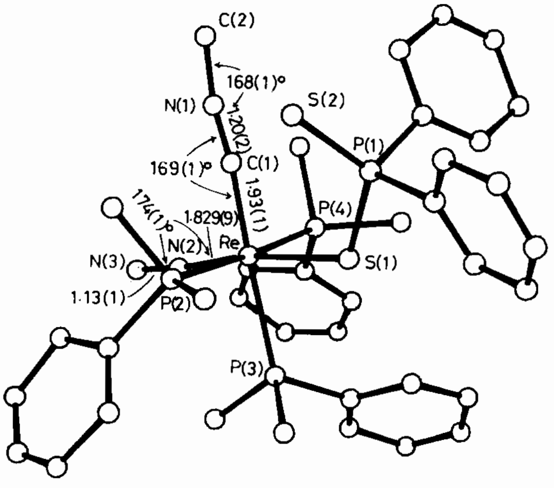

Fig. 1. The molecular structure of *mer*-$[Re(\eta^1\text{-}S_2PPh_2)(N_2)(CNMe)(PMe_2Ph)_3]$, (*2*).

The dithiophosphinato-ligand is *trans* to N_2 and the Re–N and N–N bond lengths [1.83(1) and 1.13(1) Å, respectively] are somewhat shorter and longer, respectively, than those of *mer*-$[ReCl(N_2)(CNMe)\{P(OMe)_3\}_3]$ (*3*) [corresponding values 1.98(1) and 1.04(2) Å] [4]. In accord, $\nu(N_2)$ for complex (*2*) (1980 cm^{-1}) occurs at a lower value than for (*3*) (2030 cm^{-1}).

These relative features of the two complexes result from the stronger net electron-donor character of the phosphine/dithiophosphinato-ligands relative to the phosphite/chloro ligand combination, the former stabilizing to a greater extent the bonds from the metal to the dinitrogen π-acceptor co-ligand.

Other isocyanide complexes appear to be formed in reaction (1). These and other dinitrogen–monophosphine complexes with different sulphur ligands are being studied to improve our understanding of the influence of the electron richness of metal sites and of co-ligands on the reactivity of ligating dinitrogen and isocyanide.

---

*Author to whom all correspondence should be addressed.

0020-1693/83/0000-0000/$03.00

Acknowledgements

We gratefully acknowledge the support given by the Instituto Nacional de Investigação Científica (to A.J.L.P.), the Junta Nacional de Investigação Científica e Technológica (to A.J.L.P., research contract N^{er} 216.80.55) and a NATO research grant (N^{er} 1604, to A.J.L.P. and R.L.R.).

References

1 A. J. L. Pombeiro, 'Reactions of Ligands Analogous to Dinitrogen on Dinitrogen Binding Sites', Ch. 10, in 'New Trends in the Chemistry of Nitrogen Fixation', J. Chatt, L. M. C. Pina, R. L. Richards, eds., Academic Press, 1980, and references therein.

2 A. J. L. Pombeiro and R. L. Richards, *Trans. Metal Chem., 5,* 55 (1980); *ibid,* 281; J. Chatt, A. J. L. Pombeiro and R. L. Richards, *J. Chem. Soc., Dalton Trans.*, 492 (1980); *ibid,* 1585 (1979); *J. Organometal. Chem., 184,* 357 (1980).

3 A. J. L. Pombeiro, C. J. Pickett, R. L. Richards and S. A. Sangokoya, *J. Organometal. Chem., 202,* C15 (1980).

4 M. F. N. N. Carvalho, O. Orama, C. J. Pickett, A. J. L. Pombeiro, R. L. Richards and U. Schubert, *J. Organometal. Chem.*, in press.

5 J. Chatt, A. J. L. Pombeiro and R. L. Richards, *J. Organometal. Chem., 190,* 297 (1980).