

Preliminary communication

PREPARATION OF NEW DINITROGEN COMPLEXES OF RHENIUM(I) WITH ORGANOPHOSPHITE AND ISOCYANIDE LIGANDS. X-RAY STRUCTURE OF *mer*-[ReCl(N₂)(CNMe){P(OMe)₃]₃]

FERNANDA N.N. CARVALHO, ARMANDO J.L. POMBEIRO*,

Centro de Quimica Estrutural, Complexo I, Instituto Superior Técnico, 1000 Lisboa (Portugal)

OLLI ORAMA*, ULRICH SCHUBERT,

Anorganisch Chemisches Institut der Technischen Universität München, D-8046 Garching (West Germany)

CHRISTOPHER J. PICKETT and RAYMOND L. RICHARDS

Unit of Nitrogen Fixation, University of Sussex, Brighton (Great Britain)

(Received August 9th, 1982)

Summary

The mixed dinitrogen-isocyanide complexes *mer*-[ReCl(N₂)(CNMe)-{P(OMe)₃]₃] (I) and [ReCl(N₂)(CNMe)(PPh₃){P(OEt)₃]₂] (II) are obtained by a novel route through reactions of CNMe with the organodiazenido species [ReCl₂(NNCOPh){P(OMe)₃]₃] and [ReCl₂(NNCOPh)(PPh₃){P(OEt)₃]₂] (III, newly synthesized), whereas *mer*-[ReCl(N₂)(PPh₃){P(OMe)₃]₃] (IV) (which gives I by reaction with CNMe) is formed in the reaction of [ReCl₂(NNCOPh)(PPh₃)₂] with P(OMe)₃; the structure of complex I is authenticated by X-ray analysis.

Isocyanides bound to transition metal centres show a diversity of reactivity towards electrophiles and nucleophiles which depends on the nature of the metal centre [1]. They have also been used as convenient probes in the study of the isoelectronic dinitrogen molecule [2] and of the electronic properties of metal centres which it ligates [3]. Hence, series of isocyanide complexes which are analogous to dinitrogen species have been prepared by replacement reactions of ligating N₂, e.g., in [M(N₂)₂L] (M = Mo or W, L = monophosphine or 0.5 dppe) [4] and [ReCl(N₂)(dppe)₂] [5,3], and their chemical behaviour

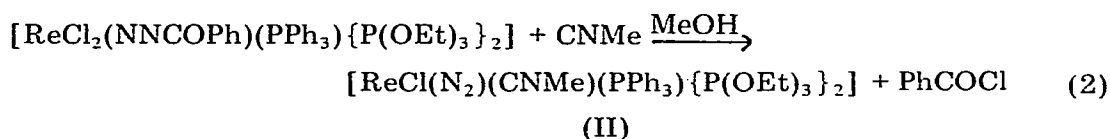
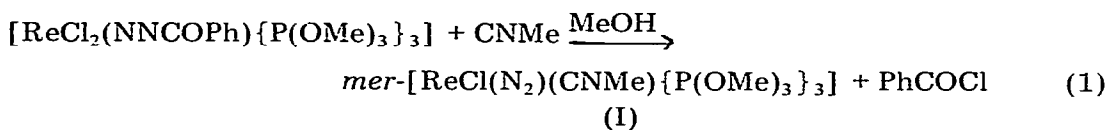
*Permanent address: Department of Chemistry, University of Helsinki (Finland).

compared [6,5]. Moreover, in a limited number of dinitrogen complexes, a co-ligand can undergo displacement by isocyanide with retention of ligating N_2 , e.g., formation of *mer*-[Re(η^1 -S₂PPh₂)(N₂)(CNMe)(PMe₂Ph)₃] from reaction of [Re(η^2 -S₂PPh₂)(N₂)(PMe₂Ph)₃] with CNMe [7].

The displacement routes described above for the preparation of isocyanide complexes require the previous synthesis of the parent dinitrogen complexes. We wish now to report the preliminary results of our attempts to develop a novel and more direct route for the synthesis of isocyanide complexes with a dinitrogen binding site.

The benzoylazo complex [ReCl₂(NNCOPh)(PPh₃)₂] is a known [8] precursor for a variety of organodiazenido and derived dinitrogen complexes, and we have studied the reactions of methyl isocyanide with the benzoyldiazenido [ReCl₂(NNCOPh){P(OMe)₃}₃] and [ReCl₂(NNCOPh)(PPh₃){P(OEt)₃}₂] species.

In these reactions, carried out in methanol, ligating N₂ is generated in situ from the benzoyldiazenido ligand and the isocyanide binds the metal site to give (eq. 1 and 2) the mixed dinitrogen isocyanide complexes *mer*-[ReCl(N₂)(CNMe){P(OMe)₃}₃] (I) and [ReCl(N₂)(CNMe)(PPh₃){P(OEt)₃}₂] (II) which are isolated as yellow crystalline solids on concentration and addition of diethyl ether. Their IR spectra exhibit strong bands at 2140 (I) and 2074 cm⁻¹ (II) which are assigned to ν (CN), whereas ν (N₂) appears at 2030 (I) and 2010 cm⁻¹ (II). The IR frequencies for the diphosphite complex are somewhat lower than the corresponding ones for the triphosphite species (I), in agreement with the stronger electron-donor character of triphenylphosphine relative to the phosphite ligand.



Complex (I) exhibits in its ³¹P NMR spectrum a triplet: doublet pattern (with 1/2 relative intensity) characteristic of a meridional phosphine arrangement, and its molecular structure (depicted in Fig. 1) has been confirmed by X-ray analysis.

Crystal data: C₁₁H₃₀ClN₃O₉P₃Re, *M* = 663.0, orthorhombic, space group *Pnam*, *a* 22.040(6), *b* 8.413(2), *c* 12.536(4) Å, *V* 2324.5 Å³, *Z* = 4, *D_c* 1.89 g cm⁻³, μ (Mo-*K* α) 59.0 cm⁻¹. Graphite-monochromated Mo-*K* α radiation, λ 0.71069 Å. 1914 independent reflections ($2^\circ \leq 2\theta \leq 48^\circ$); empirical absorption correction. Full-matrix least squares refinement with anisotropic thermal parameters for all non-hydrogen atoms resulted in *R* = *R_w* = 0.058 (all reflections used).

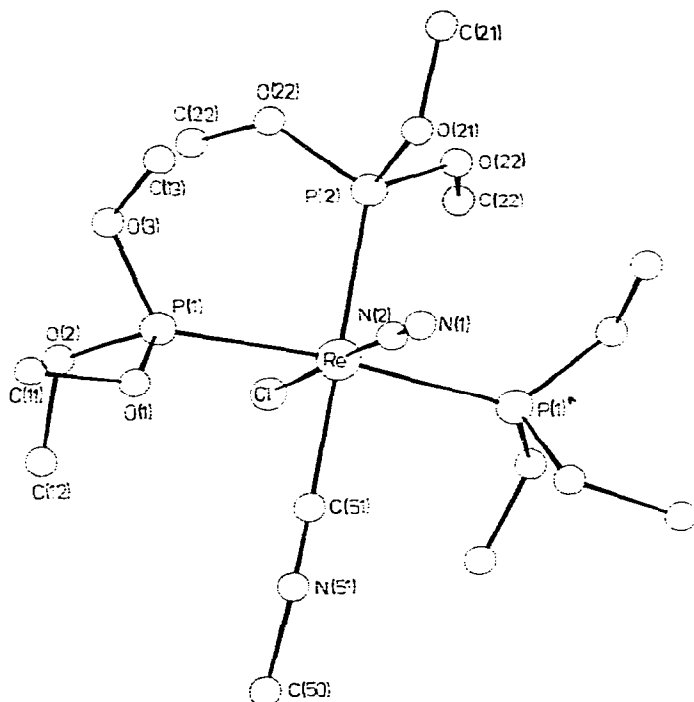


Fig. 1. The molecular structure of *mer*-[ReCl(N₂)(CNMe){P(OMe)₃}₃] (I). The hydrogen atoms are omitted for clarity. Crystallographic mirror symmetry with Re, P(2), Cl, the N₂ and the CNMe ligand in the mirror plane.

Selected bond length and angles are given in Table 1.

The isocyanide ligand does not deviate considerably from the linearity at the nitrogen atom (169(1)°) and the C—N isocyanide bond length (1.11(2) Å) is very close to that found [9] in *trans*-[Mo(CNMe)₂(dppe)₂] (1.10(1) Å); the CNMe angle in the latter (156(1)°) is much smaller than in complex I, thus evidencing the lower electronrichness of the rhenium(I) metal site compared to the {Mo(dppe)₂} centre.

The Re—N and N—N bond lengths (1.98(1) and 1.04(2) Å) are identical to those observed [10] for the related complex *trans*-[ReCl(N₂)(PMe₂Ph)₄] (1.97(2) and 1.06(3) Å, respectively). Presumably the binding of the dinitrogen ligand is stabilized by the electron releasing character of the Cl ligand in the *trans* position, which compensates the presence of a strong electron-acceptor competitor such as methyl isocyanide, and the relatively poorly electron-donating P(OMe)₃ ligand.

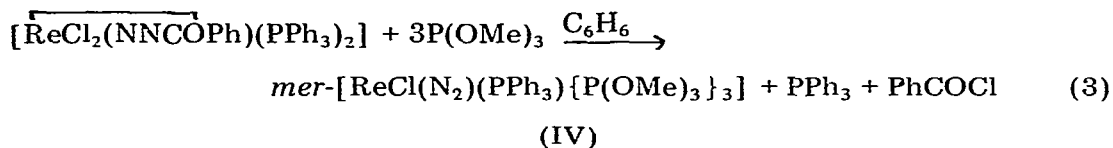
Complex II has not yet been obtained in a spectroscopically pure state, being contaminated to varying extents, by other products and by the parent benzoyl-diazenido species [ReCl₂(NNCOPh)(PPh₃){P(OEt)₃}₂] (III), which was newly prepared by reaction of [ReCl₂(NNCOPh)(PPh₃)₂] with P(OEt)₃ in refluxing benzene, a route which is analogous to the known [8] synthesis of

TABLE 1

BOND LENGTHS (Å) AND BOND ANGLES (°)

Bond lengths (Å)		Bond angles (°)	
Re—P (1)	2.357(2)	P(1)—Re—P(2)	93.1(1)
Re—P(2)	2.387(4)	P(1)—Re—P(1)*	173.81(9)
Re—Cl	2.530(4)	P(1)—Re—Cl	89.8(1)
Re—N(2)	1.98(1)	P(2)—Re—Cl	91.0(1)
Re—C(51)	2.07(2)	P(1)—Re—N(2)	90.1(3)
N(1)—N(2)	1.04(2)	P(2)—Re—N(2)	90.7(4)
C(51)—N(51)	1.12(2)	Cl—Re—N(2)	178.4(4)
N(51)—C(50)	1.45(2)	P(1)—Re—C(51)	86.9(4)
mean P—O	1.594(8)	P(2)—Re—C(51)	177.3(4)
		Cl—Re—C(51)	86.3(4)
		N(2)—Re—C(51)	92.0(5)
		Re—N(2)—N(1)	179(1)
		Re—C(51)—N(51)	179(1)
		C(51)—N(51)—C(50)	169(1)

[ReCl₂(NNCOPh){P(OMe)₃}₃]. In the latter preparation, a new dinitrogen complex, *mer*-[ReCl(N₂)(PPh₃){P(OMe)₃}₃] (IV), was isolated from the mother liquor (reaction 3) as a yellow crystalline solid.



Compound (IV) displays $\nu(\text{N}_2)$ as a strong band at 2010 cm⁻¹ in its IR spectrum. In this complex, triphenylphosphine is replaced by CNMe in thf at ambient temperature to give the mixed complex (I).

The reactions described above suggest a versatile route for the preparation of series of isocyanide complexes with a wide variety of co-ligands, namely dinitrogen, and their study will allow a direct comparison of the chemical reactivity of dinitrogen and isocyanide when activated simultaneously by a common metal centre.

Acknowledgements

We gratefully acknowledge the support given by the Instituto Nacional de Investigação Científica (to F.N.N.C. and A.J.L.P.), the Junta Nacional de Investigação Científica e Tecnológica (research contract No. 216.80.56), a NATO research grant (No. 1604, to A.J.L.P. and R.L.R.), and the Deutscher Akademischer Austauschdienst for a scholarship (to O.O.). We are also indebted to Mr. and Mrs. Oiney of the University of Sussex and Mr. L. Vieira of the Centro de Química Estrutural for microanalyses.

References

- 1 Y. Yamamoto, *Coord. Chem. Rev.*, **32** (1980) 193; F. Bonati and G. Minghetti, *Inorg. Chim. Acta*, **9** (1974) 95.

- 2 A.J.L. Pombeiro, Reactions of Ligands Analogous to Dinitrogen on Dinitrogen Binding Sites. Ch. 10 in J.Chatt, L.M.C. Pina and R.L. Richards (Eds.), *New Trends in the Chemistry of Nitrogen Fixation*, Academic Press, London, 1980.
- 3 A.J.L. Pombeiro, C.J. Pickett and R.L. Richards, *J. Organometal. Chem.*, 224 (1982) 285.
- 4 J.Chatt, C.M. Elson, A.J.L. Pombeiro, R.L. Richards and G.H.D. Royston, *J. Chem. Soc. Dalton Trans.*, (1978) 165; J. Chatt, A.J.L. Pombeiro and R.L. Richards, *J. Organometal. Chem.*, 190 (1980) 297.
- 5 A.J.L. Pombeiro, M.F.N.N. Carvalho, P.B. Hitchcock and R.L. Richards, *J. Chem. Soc., Dalton Trans.*, (1981) 1629.
- 6 A.J.L. Pombeiro and R.L. Richards, *Trans. Metal Chem.*, 5 (1980) 55 and ref. therein; *ibid.*, 5 (1980) 281; J. Chatt, A.J.L. Pombeiro and R.L. Richards, *J. Organometal. Chem.*, 184 (1980) 357; *J. Chem. Soc., Dalton Trans.*, (1980) 492; *ibid.*, (1979) 1585.
- 7 A.J.L. Pombeiro and R.L. Richards, studies in progress.
- 8 G.J. Leigh, R.H. Morris, C.J. Pickett, D.R. Stanley and J. Chatt, *J. Chem. Soc., Dalton Trans.*, (1981) 800.
- 9 J. Chatt, A.J.L. Pombeiro, R.L. Richards, G. Royston, K. Muir and R. Walker, *J. Chem. Soc., Chem. Commun.*, (1975) 708.
- 10 B.R. Davis and J.A. Ibers, *Inorg. Chem.*, 10 (1971) 584.