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## Synthesis and crystal structure of the complex double salt $[\text{Re}(\text{NCC}_6\text{H}_4\text{Me-4})_2\text{-}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2][\text{ReF}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2][\text{BF}_4]_2$

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### Abstract

Reaction of  $\text{NCC}_6\text{H}_4\text{Me-4}$  with  $\text{trans}[\text{ReCl}(\text{N}_2)(\text{dppe})_2]$  ( $\text{dppe} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ ) in the presence of  $\text{TIBF}_4$  has given the formation of  $\text{trans}[\text{Re}(\text{NCC}_6\text{H}_4\text{Me-4})_2(\text{dppe})_2][\text{BF}_4] \cdot \text{trans}[\text{ReF}_2(\text{dppe})_2][\text{BF}_4]$ , the crystal structure of which has been determined.

The coordination chemistry of organonitriles is of wide interest [1] because of the widespread use of nitrile complexes as starting materials and of the  $\text{C}\equiv\text{N}$  stretching band in the IR as an indicator of the electron density at a ligated metal centre.

In pursuit of our interest in the reactions of small molecules at dinitrogen-binding centres [2] we recently prepared the series  $\text{trans}[\text{ReCl}(\text{NCR})(\text{dppe})_2]$  ( $\text{R} = \text{alkyl}$  or  $\text{aryl}$ ;  $\text{dppe} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ ) and showed that nitriles bound at this centre are susceptible to protic attack to give ligating methyleneamido groups [3].

In general, RCN ligands are relatively poor  $\pi$ -acids and normally ligate electron-rich centres in combination with a stronger  $\pi$ -acid, e.g. in  $\text{trans}[\text{Re}(\text{N}_2)(\text{NCR})(\text{dppe})_2]^+$  [4],  $\text{trans}[\text{Mo}(\text{N}_2)(\text{NCR})(\text{dppe})_2]$  [5] and  $[\text{M}(\text{CO})_{6-n}(\text{NCMe})_n]$  ( $\text{M} = \text{Cr}$ ,  $\text{Mo}$  or  $\text{W}$ ;  $n = 1, 2$  or  $3$ ) [6]. However, we have now succeeded in preparing a dinitrile complex of  $\text{Re}(\text{I})$ ,  $\text{trans}[\text{Re}(\text{NCC}_6\text{H}_4\text{Me-4})_2(\text{dppe})_2]^+$ , and during its preparation have also obtained an unusual difluoride cation of  $\text{Re}^{\text{III}}$ ,  $[\text{ReF}_2(\text{dppe})_2]^+$ , as described below.

After treatment of  $\text{trans}[\text{ReCl}(\text{N}_2)(\text{dppe})_2]$  in refluxing tetrahydrofuran (THF) with  $\text{NCC}_6\text{H}_4\text{Me-4}$  (3 molar equivalents) in the presence of  $\text{TIBF}_4$  (2 molar equivalents) we obtained an orange crystalline compound. It has a  $\text{C}\equiv\text{N}$  IR band at  $2140 \text{ cm}^{-1}$ , lower by circa  $80 \text{ cm}^{-1}$  than that for the free nitrile, pointing to the electron-rich nature of the  $\{\text{Re}(\text{dppe})_2\}^+$  site, i.e. to considerable electron release from metal to ligand [1,2].

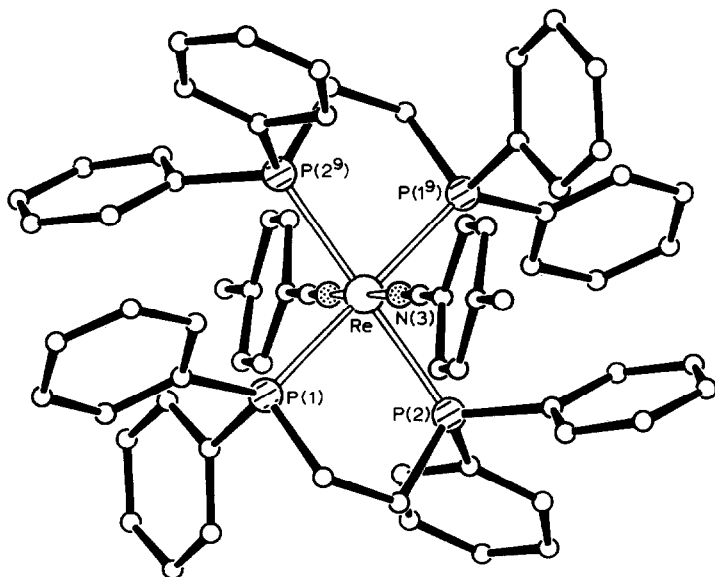


Fig. 1. Molecular structure of the  $trans\text{-}[\text{Re}(\text{NCC}_6\text{H}_4\text{Me-4})_2(\text{dppe})_2]^+$  moiety. Selected dimensions (with e.s.d.'s in parentheses):  $\text{Re}(1)\text{-N}(3)$  2.063(7),  $\text{N}(3)\text{-C}(30)$  1.102(13),  $\text{C}(30)\text{-C}(31)$  1.417(14),  $\text{Re}(1)\text{-P}(1)$  2.392(3),  $\text{Re}(1)\text{-P}(2)$  2.409(2) Å.  $\text{Re}(1)\text{-N}(3)\text{-C}(30)$  178.6 (6),  $\text{N}(3)\text{-C}(30)\text{-C}(31)$  177.2(12),  $\text{P}(1)\text{-Re}(1)\text{-N}(3)$  85.8(2),  $\text{P}(2)\text{-Re}(1)\text{-N}(3)$  85.6(2)°.

The X-ray structure of this molecule reveals, moreover, that not only does it contain the desired dinitrile cation  $[\text{Re}(\text{NCC}_6\text{H}_4\text{Me-4})_2(\text{dppe})_2]^+$  but also the unusual difluoride cation  $[\text{ReF}_2(\text{dppe})_2]^+$ , i.e. the species is  $trans\text{-}[\text{Re}(\text{NCC}_6\text{H}_4\text{Me-4})_2(\text{dppe})_2][\text{BF}_4] \cdot trans\text{-}[\text{ReF}_2(\text{dppe})_2][\text{BF}_4]$ . The molecular structure of the dinitrile cationic species is shown in Fig. 1, together with selected bond lengths and angles\*.

Both complex cations show a distorted octahedral coordination and the  $\text{Re}\text{-N}$  distance for the virtually linear nitrile ligands in the dinitrile complex [2.063(7) Å] is a little longer than the 1.978(5) Å observed [7] for the neutral compound  $trans\text{-}$

\* Crystal data for  $trans\text{-}[\text{Re}(\text{NCC}_6\text{H}_4\text{Me-4})_2(\text{dppe})_2][\text{BF}_4] \cdot trans\text{-}[\text{ReF}_2(\text{dppe})_2][\text{BF}_4]$ .

$(\text{C}_{68}\text{H}_{62}\text{N}_2\text{P}_4\text{Re})^+(\text{C}_{52}\text{H}_{48}\text{F}_2\text{P}_4\text{Re})^+ 2(\text{BF}_4)^-$ ,  $M$  2412.0. Triclinic, space group  $P\bar{1}$  (no. 2),  $a$  13.606(1),  $b$  21.148(2),  $c$  10.714(1) Å,  $\alpha$  98.111(9),  $\beta$  117.151(7),  $\gamma$  94.152(8)°,  $V$  = 2682.6 Å<sup>3</sup>.  $Z$  = 1,  $D_c$  = 1.493 g cm<sup>-3</sup>,  $F(000)$  = 1214,  $\mu(\text{Mo-K}\alpha)$  = 24.7 cm<sup>-1</sup>,  $\lambda(\text{Mo-K}\alpha)$  = 0.71069 Å.

An orange-yellow irregular needle (ca. 0.10 × 0.14 × 0.30 mm) was photographed, then transferred to our Enraf-Nonius CAD4 diffractometer (with monochromated radiation) for accurate cell dimensions and intensity data ( $\theta_{\text{max}}$  = 25°; 9415 independent reflections). Corrections were applied for Lorentz and polarisation effects, absorption and to eliminate negative intensities.

Structure determination was by heavy-atom methods in the SHELX system [10]. For the centrosymmetrical cation  $[\text{Re}(\text{NCC}_6\text{H}_4\text{Me-4})_2(\text{dppe})_2]^+$ , all the C, N, P and Re atoms were allowed anisotropic thermal parameters, and H atoms (except those in the methyl group) were included in idealised positions. The second cation, also lying about a centre of symmetry, shows considerable thermal motion (or disorder) and less satisfactory refinement. From large-block-matrix least-squares refinement, final  $R$  = 0.073,  $R_g$  = 0.094 [10] for 8311 reflections (those with  $I > \sigma_I$ ) weighted  $w = (\sigma_F^2 + 0.00170 F^2)^{-1}$ .

Tables of atomic parameters and molecular dimensions have been deposited at the Cambridge Crystallographic Data Centre.

$[\text{ReCl}(\text{NCMe})(\text{dppe})_2]$ , in which there is a *trans* influence of the  $\pi$ -donor chloride ligand.

The cation *trans*- $[\text{ReF}_2(\text{dppe})_2]^+$  shows considerable thermal motion, or possibly disorder, in the phenyl rings. The Re–P distances in this cation (average of 2.453(4) Å) and in the related cation *trans*- $[\text{ReCl}_2(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)_2]^+$  (average of 2.438(2) Å) [8] are somewhat longer than those in the dinitrile-rhenium(I) complex cation (average of 2.401(3) Å). The Re–F bond length, 2.045(10) Å, is not too different from that reported [9] for the complex *trans*- $[\text{ReF}(\text{CCH}_2\text{Bu}^t)(\text{dppe})_2][\text{BF}_4]$ , 2.134(4) Å.

Although we have previously observed the ability of  $[\text{BF}_4]^-$  to mono-fluorinate the  $\{\text{Re}(\text{dppe})_2\}^+$  centre [9], the double fluorination observed here, which occurs despite the presence of a nitrile substrate, is rather surprising, and we are studying the mechanism of this reaction and its generality.

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## References

- 1 For reviews see, e.g. (a) Yu.N. Kukushkin, *Koordinat. Khim.*, 7 (1981) 323; (b) B.N. Storhoff and H.C. Lewis, Jr., *Coord. Chem. Rev.*, 23 (1977) 1.
- 2 A.J.L. Pombeiro, in J. Chatt, L.M.C. Pina and R.L. Richards (Eds.), *New Trends in the Chemistry of Nitrogen Fixation*, Chap. 10, Academic Press, New York, 1980; A.J.L. Pombeiro, in U. Schubert (Ed.), *Advances in Metal Carbene Chemistry*, NATO ASI Series, Kluwer Acad. Publ., Dordrecht, The Netherlands, 1989, p. 79; A.J.L. Pombeiro and R.L. Richards, *Coord. Chem. Rev.*, 104 (1990) 13; D.L. Hughes, A.J.L. Pombeiro and R.L. Richards, in H. Bothe, F.J. Bruin and W.E. Newton (Eds.), *Nitrogen Fixation: Hundred Years After*, Gustav Fischer, New York, 1988, p. 66.
- 3 A.J.L. Pombeiro, D.L. Hughes and R.L. Richards, *J. Chem. Soc., Chem. Commun.*, (1988) 1052.
- 4 G.J. Leigh, R.H. Morris, C.J. Pickett and D.R. Stanley, *J. Chem. Soc., Dalton Trans.*, (1981) 800.
- 5 T. Tatsumi, M. Hidai and Y. Uchida, *Inorg. Chem.*, 14 (1975) 2530.
- 6 J.M. Kelly, D.V. Bent, H. Herrmann, D. Schulte-Frohlinde and E.K. von Gustorf, *J. Organomet. Chem.*, 69 (1974) 259; J.M. Graham and M. Kilner, *ibid.*, 77 (1974) 247.
- 7 A.J.L. Pombeiro, M.F.C.G. Silva, D.L. Hughes and R.L. Richards, *Polyhedron*, 8 (1989) 1872.
- 8 J.L. Vanderheyden, M.J. Heeg and E. Deutsch, *Inorg. Chem.*, 24 (1985) 1666.
- 9 A.J.L. Pombeiro, A. Hills, D.L. Hughes and R.L. Richards, *J. Organomet. Chem.*, 352 (1988) C5.
- 10 G.M. Sheldrick, *SHELXN*, Modified version of SHELX-76 program for crystal structure determination, University of Cambridge, 1976.