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Preliminary Communication

Synthesis of *trans*-[Re(NO)$_2$(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$][BF$_4$], a formal dinitrosyl complex of rhenium(-I) and its protic denitrosylation. X-Ray structure of *trans*-[ReF(NO)(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$][BF$_4$]

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Abstract

Treatment of a THF solution of *trans*-[ReCl(N$_2$)(dppe)$_2$] (dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$) with NO, in the presence of Tl[BF$_4$], forms *trans*-[Re(NO)$_2$(dppe)$_2$][BF$_4$], a rare formal 20-electron d^8-rhenium nitrosyl complex which, by reaction with HX (X = BF$_4$, Cl or HSO$_4$), gives *trans*-[ReF(NO)(dppe)$_2$][BF$_4$] (**2**) (the X-ray structure of which is reported) or *trans*-[ReX(NO)(dppe)$_2$]X (**3**, X = Cl or HSO$_4$), respectively, as well as nitrous oxide.

Key words: Rhenium; Nitrosyl; X-ray structure; Electrophilic attack; Nitric oxide; Denitrosylation

The activation of nitric oxide by electron-rich dinitrogen-binding metal centres has not yet been adequately explored [1], in spite of its developed coordination chemistry at a variety of other metal sites [2] and its potential for the understanding of the versatile biological role of NO, as in the nitrogen cycle [3] and in the human body [4]. For example, NO is a conceivable intermediate in biological nitrite reduction [5], in nitrate assimilation pathways to ammonia and in the formation of nitrous oxide (N$_2$O) by nitrate reductases [3], although the mechanisms have not yet been elucidated.

Therefore, and also in pursuit of our interest on the activation of small unsaturated molecules of biological significance by N$_2$-binding sites, [6], we have recently initiated the study of the coordination chemistry of NO at *trans*-{ReCl(dppe)$_2$} (dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$). For example we reported [7] the formation of *trans*-[ReCl(NO)(dppe)$_2$][NO$_3$]$_2$, from the reaction of NO with *trans*-[ReCl(N$_2$)(dppe)$_2$], which involves an unusual, facile oxidation of NO to nitrate.

We now report the synthesis of *trans*-[Re(NO)$_2$(dppe)$_2$][BF$_4$] (**1**) (which, as far as we are aware, is the first example of a formal 20-electron d^8-rhenium dinitrosyl complex), as well as the protic reduction of one of the NO to nitrous oxide. Unsuccessful attempts to prepare related Group 6 metal dinitrosyl complexes [M(NO)$_2$(dppe)$_2$] (M = Mo or W) were reported by others [8]. Moreover, only few d^8-rhenium nitrosyls are known and they include the 18-electron complexes [ReX(NO)$_2$(PPh$_3$)$_2$] (X = H [9] or halide [10]) and [Re(NO)(CO)$_2$(PPh$_3$)$_2$] [9].

Complex **1** can be obtained by treatment of a THF solution of *trans*-[ReCl(N$_2$)(dppe)$_2$] with NO, in the presence of Tl[BF$_4$], under W-filament light irradiation (eqn. (1)).

$$\textit{trans}\text{-}[\mathrm{ReCl(N_2)(dppe)_2}] + 2\mathrm{NO} + \mathrm{Tl[BF_4]} \rightarrow$$

$$\underset{(\mathbf{1})}{\textit{trans}\text{-}[\mathrm{Re(NO)_2(dppe)_2}][\mathrm{BF_4}]} + \mathrm{N_2} + \mathrm{TlCl} \qquad (1)$$

It was isolated (*ca.* 70% yield) as a yellow solid with the expected elemental analysis and with a single strong band in the IR spectrum assigned to ν(NO) at 1650 cm^{-1}, suggesting the linear NO$^+$ coordination [11] for both nitrosyls. Therefore complex **1** appears to contain a formal d^8 rhenium centre with a 20-electron configuration. The alternative formulation as an 18-electron complex with one linear (3-electron donor) and one bent (1-electron donor) nitrosyl group would not fit the IR data. The *trans* geometry in solution was confirmed by the singlet resonance observed in the ^{31}P NMR spectrum (in CDCl$_3$) at δ −118.8 ppm rel. P(OMe)$_3$.

Complex **1** readily reacts with acid, HX (X = BF$_4$, Cl, or HSO$_4$), in CH$_2$Cl$_2$, to give the corresponding mononitrosyl species *trans*-[ReF(NO)(dppe)$_2$][BF$_4$] (**2**) or *trans*-[ReX(NO)(dppe)$_2$]X (**3**, X = Cl or HSO$_4$), respectively, as well as nitrous oxide (N$_2$O) (although in

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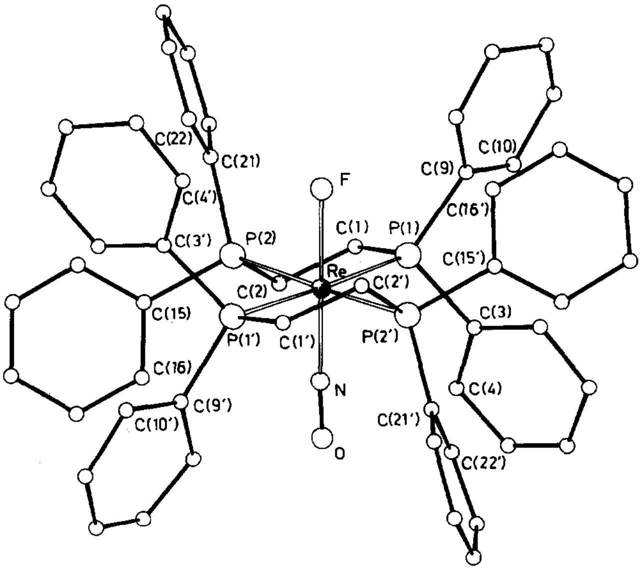

Fig. 1. View of the structure of the cation $[ReF(NO)(dppe)_2]^+$ of **2** with the atomic labelling scheme. The F and NO are disordered between the two apical positions, one form being represented in the figure. Selected bond distances (Å) and angles (°): Re–P(1) 2.497(8), Re–P(1') 2.428(7), Re–P(2) 2.478(4), Re–P(2') 2.410(4), Re–F 1.945(10), Re–N 1.874(10), N–O 1.11(2); P(1)–Re–P(2) 79.5(2), P(1)–Re–P(2') 99.8(2), P(2)–Re–P(1') 98.7(2), P(1')–Re–P(2') 82.0(2), P(1)–Re–N 84.5(3), F(2)–Re–N 84.5(3), F–Re–N 176.9(5), Re–N–O 175.6(14).

lower yields, ca. 10–15%) which has been detected by gas chromatography. Compound **3** (X = Cl) is analogous to *trans*-$[ReCl(NO)(dppe)_2][BF_4]$ which was obtained [7] by N_2 replacement by NO in *trans*-$[ReCl(N_2)(dppe)_2][BF_4]$.

Complexes **2** and **3** have been isolated (yields *ca.* 95–80%) as yellow solids, with adequate elemental analyses. The IR spectra exhibit a strong ν(NO) band at *ca.* 1670–1700 cm^{-1}, indicative [11] of linear NO^+ coordination. The *trans* geometry of these complexes has been clearly established by ^{31}P NMR spectroscopy. For **3** (X = Cl) a singlet is observed at δ −123.3 ppm rel. $P(OMe)_3$, whereas, for **2**, the expected doublet $[^2J(PF)] = 41$ Hz] occurs at δ −116.7 ppm and its ^{19}F NMR spectrum exhibits the fluoride resonance as a corresponding quintet at δ −57.9 ppm rel. $CFCl_3$.

The molecular structure of **2** has been confirmed by an X-ray diffraction analysis [12*]. The complex cation is depicted in Fig. 1, with relevant bond distances and angles. The Re atom exhibits a distorted octahedral coordination with the four P atoms in equatorial positions, and the F atom and the N atom occupying the apical positions. The structure is approximately centrosymmetric. The apical ligands are disordered in the two positions with equal occupancy factor.

As expected, the NO is almost linearly coordinated [Re–N(1)–O(1) = 175.6(14)°] with a N–O bond length of 1.11(2) Å which is within the usual range (1.10–1.25 Å) [2] for a linear nitrosyl ligand.

The susceptibility of complex **1** to undergo ready protonation contrasts with the behaviour of all the mononitrosyl complexes of our studies, such as the 18- or 17-electron species *trans*-$[ReCl(NO)(dppe)_2]^{n+}$ (n = 1 [this work] or 2 [7], respectively). The higher electron count (20-electrons) in **1** and its lower ν(NO) frequency, in comparison with the other complexes, are consistent with this. Nevertheless, examples of protonation of a linear nitrosyl are rare. Examples include the 18-electron species $[ReCl(NO)_2(PPh_3)_2]$ and $[Ir(NO)(PPh_3)_3]$ which react with HCl to give $[ReCl_2(HNO)(NO)(PPh_3)_2]$ [9] and $[IrCl_3(NH_2OH)(PPh_3)_2]$ [13], respectively.

In our system, the evolution of N_2O can be tentatively explained by considering the protonation of one NO to give nitroxyl (HNO) which, upon displacement by fluoride [from BF_4^- which is a known [14,15] fluorinating agent of $\{Re(dppe)_2\}^+$] would allow the formation of complex **2**. Nitrous oxide is a product [16] of the decomposition of nitroxyl in water.

In addition, rare examples of denitrosylation processes in the presence of acid have also been reported, such as at $[M(NO)_2(PPh_3)_2]$ (M = Ru or Os) which, by reaction with a perfluorocarboxylic acid (RCO_2H), form $[Ru(O_2CR)_3(NO)(PPh_3)_2]$ or $[OsH(O_2CR)_2(NO)(PPh_3)_2]$ [17]. However, these reactions in contrast with our system, require drastic conditions (boiling toluene or boiling 2-methoxyethanol). Moreover, liberation of nitrous oxide appears to occur upon decomposition of $[Ni(NO)(CN)_3]^{2-}$ by acid or water [16a,18].

Our studies have extended the activation of unsaturated molecules by coordination to an electron-rich rhenium centre towards protonation to NO. Such a process is already known to occur for isocyanides [19], nitriles [20], vinylidenes [15,21], and η^2-allenes [22]. Although for all the latter species the d^6-rhenium centre $\{ReCl(dppe)_2\}$ was the common activating site and the protonated products were stabilized by coordination, for NO the formal d^8-rhenium moiety $\{Re(NO)(dppe)_2\}$ was the active centre.

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* Reference number with asterisk indicates a note in the list of references.

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12 Crystal data for 2 $[C_{52}H_{48}FNOP_4Re][BF_4]$, $M = 1118.85$, monoclinic, space group Cc, $a = 12.309(4)$, $b = 17.381(3)$, $c = 22.523(8)$ Å, $\beta = 90.35(2)°$, $V = 4819(2)$ Å^3, $Z = 4$, $D_c = 1.542$ g cm^{-3}, $F(000) = 2240$, niobium-filtered Mo-Kα radiation, $\lambda = 0.71073$ Å, $\mu = 27.43$ cm^{-1}. The intensity data were collected on a Siemens AED diffractometer, using the θ–2θ scan technique at room temperature. 4276 Unique reflections were measured, with θ in the range 3–25°, 3366, having $I > 2\sigma(I)$, were used in the refinement. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares, with anisotropic thermal parameters in the last cycles of refinement for the Re and P atoms, the methylene carbons of the dppe and the atoms of the BF_4^-. The F and NO were found disordered and distributed in the apical positions with equal occupancy factor. The hydrogen atoms were placed at their geometrically calculated positions (C–H = 1.00 Å) and refined "riding" the corresponding carbon atoms. The R and R_w values were 0.0400 and 0.0541. Atomic coordinates and related data have been deposited at Cambridge Crystallographic Data Centre.

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