Journal of Organometallic Chemistry, 430 (1992) C56–C59
Elsevier Sequoia S.A., Lausanne
JOM 22741PC

Preliminary communication

Syntheses of low-valent nitrosyl complexes of rhenium and X-ray structure of *trans*-$[ReCl(NO)(Ph_2PCH_2CH_2PPh_2)_2][NO_3]_2$ with nitrosyl derived nitrates

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(Received January 24, 1992)

Abstract

The nitrosyl complexes *trans*-$[ReCl(NO)(dppe)_2]A_2$ (**1**; A = BF_4 or NO_3; dppe = $Ph_2PCH_2CH_2PPh_2$) and *trans*-$[ReCl(NO)(dppe)_2][BF_4]$ (**2**) have been prepared from the reactions of $NO[BF_4]$ or NO with *trans*-$[ReCl(N_2)(dppe)_2]$. An unusual facile oxidation of NO to nitrate is involved in the formation of (**1**, A = NO_3), the X-ray structure of which is reported.

In spite of the known versatile coordination chemistry of nitrogen monoxide (NO) [1,2] and its possible role in the biological nitrogen cycle, NO is not a substrate of nitrogenase but is an inhibitor of its activity [3]. Therefore, at the active site of nitrogenase, it behaves quite differently from related unsaturated species such as dinitrogen, isocyanides, alkynes, etc., which are substrates of the enzyme and isoelectronic with NO^+, a common form of ligated NO. Since we have been studying the coordination chemistry of those substrates at electron-rich dinitrogen binding metal sites, in particular *trans*-$\{ReCl(dppe)_2\}$ [4], we have attempted to extend this investigation to NO and NO^+. We now report the preliminary results obtained from the study of the reactions of $NO[BF_4]$ and NO with *trans*-$[ReCl(N_2)(dppe)_2]$.

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Upon treatment of a THF solution of this dinitrogen complex with NO[BF$_4$] we observed an initial oxidation of the rhenium compound to *trans*-[ReCl(N$_2$)(dppe)$_2$][BF$_4$] (eq. 1), a known [5] complex which was isolated as a dark purple solid with properties identical to those previously reported. The oxidizing role of the nitrosonium cation is in agreement with the high value (1.28 V *vs.* SCE [6]) of its reversible redox potential, well above that (0.28 V) [7] for the reversible oxidation of the neutral dinitrogen complex.

However, if the reaction is allowed to proceed further in the presence of an excess of NO[BF$_4$], replacement of N$_2$ by NO$^+$ occurs to give *trans*-[ReCl(NO)(dppe)$_2$]A$_2$ (**1**, A = BF$_4$) (eq. 2), which was isolated as a yellow solid (above 50% yield) with ν(NO) = 1680 cm^{-1}, indicative [8] of linear NO$^+$ coordination.

A related salt, *trans*-[ReCl(NO)(dppe)$_2$][NO$_3$]$_2$ (**1**, A = NO$_3$) [ν(NO) = 1700 cm^{-1}], was isolated (*ca.* 70% yield) as a pale green species (recrystallized from CH$_2$Cl$_2$/Et$_2$O) from the reaction of NO with *trans*-[ReCl(N$_2$)(dppe)$_2$] in THF. The unexpected nature of this compound was fully elucidated only by an X-ray diffraction study [9*]. Its formation involves not only the replacement of N$_2$ by NO, but also the oxidation of the latter to nitrate.

In contrast, simple substitution of N$_2$ by NO without oxidation of the latter occurs in *trans*-[ReCl(N$_2$)(dppe)$_2$][BF$_4$], giving *trans*-[ReCl(NO)(dppe)$_2$][BF$_4$] (**2**), which was isolated (*ca.* 75% yield) as a yellow solid with ν(NO) = 1690 cm^{-1}, also suggesting linearly coordinated NO$^+$; complex **2** is isoelectronic with *trans*-[MX(NO)(dppe)$_2$] (M = Mo or W; X = H, OH, or NCO) [10], which have been prepared by reaction of *trans*-[M(N$_2$)$_2$(dppe)$_2$] with some NO precursors, *e.g.*, MeN(NO)C(O)NH$_2$ and Et$_2$NNO.

$$trans\text{-}[\mathrm{ReCl(N_2)(dppe)_2}] \xrightarrow{\mathrm{NO[BF_4]}} trans\text{-}[\mathrm{ReCl(N_2)(dppe)_2}][\mathrm{BF_4}] \qquad (1)$$

$$trans\text{-}[\mathrm{ReCl(N_2)(dppe)_2}][\mathrm{BF_4}] \xrightarrow{\mathrm{NO[BF_4]}, -\mathrm{N_2}} trans\text{-}[\mathrm{ReCl(NO)(dppe)_2}][\mathrm{BF_4}]_2 \qquad (2)$$

$$(\mathbf{1}, \mathrm{A} = \mathrm{BF_4})$$

The structure of the cationic complex of (**1**, A = NO$_3$) is depicted in Fig. 1, together with the most important bond distances and angles. The Re atom displays an octahedral coordination involving four P atoms from the two chelating dppe ligands in the equatorial positions, and a Cl atom and an N atom from the NO group occupying the apical positions. The complex has crystallographically imposed C_i symmetry, so that the apical ligands are disordered in the two positions with equal occupancy factor. The NO is almost linearly coordinated [Re–N(1)–O(1) = 174.7(11)°] with N–O and Re–N bond lengths of 1.24(2) and 1.730(13) Å respectively; the former is within the expected range (1.10–1.25 Å [1,2]), for a linear nitrosyl ligand, and the latter is comparable with the Re–N distance, 1.76(2) Å [11], found in [ReF(CO)(NO)(PPh$_3$)$_3$][BF$_4$].

Moreover, the X-ray analysis revealed the unexpected presence of the NO$_3^-$ counterions, derived from the oxidation of NO at the Re. Although the mechanism of this conversion of nitric oxide to nitrate has not yet been elucidated, it can be

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

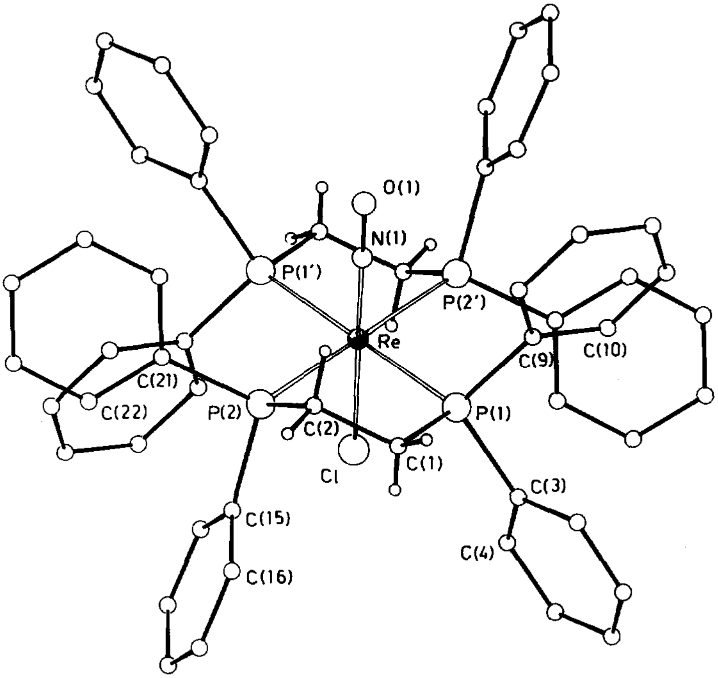

Fig. 1. View of the structure of the cation *trans*-$[ReCl(NO)(dppe)_2]^{2+}$ of **1** with the atomic labelling scheme. The Cl and NO are disordered between the two apical positions, one of the two forms being represented in the figure. Selected bond distances (Å) and angles (°): Re–P(1) 2.479(1), Re–P(2) 2.458(2), Re–Cl 2.388(5), Re–N(1) 1.730(13), N(1)–O(1) 1.24(2); P(1)–Re–P(2) 80.6(1), P(1)–Re–N(1) 85.5(4), P(2)–Re–N(1) 87.5(4), Cl–Re–N(1) 178.8(4), Re–N(1)–O(1) 174.7(11).

envisaged as resulting from the oxidation (by oxygen) of NO activated by the electron-rich Re centre in the hypothetical intermediate $[ReCl(NO)(dppe)_2]$, following an overall $2NO/2O_2$ process. In fact, the activation of a NO ligand towards electrophilic attack by O_2 to give nitrate or nitrite has been documented in a limited number of cases, in particular with some Group 8 [12] or 6 [13] transition metal-phosphine complexes, and has been shown to be promoted by electron release (*e.g.*, by base addition to the metal [14] or by electrochemical reduction [13]) from the metal to the NO. Although adventitious air might be the source of O_2 in our system, we cannot yet rule out the possibility that bound NO can undergo deoxygenation [15], also facilitated by the transfer of electron density to the ligand [16]; moreover, the catalytic disproportionation of NO into N_2 and O_2 is also a known [15] reaction.

Acknowledgements. This work has been partially supported by the Orient Foundation, JNICT and INIC (Portugal).

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9 Crystal data for 1, $C_{52}H_{48}ClN_3O_7P_4Re$, $M = 1172.52$, triclinic, space group $P\bar{1}$, $a = 10.118(3)$, $b = 11.060(4)$, $c = 12.705(4)$ Å, $\alpha = 71.29(2)$, $\beta = 74.06(2)$, $\gamma = 69.21(2)°$, $V = 1238.0(7)$ Å^3, $Z = 1$, $D_c = 1.573$ g cm^{-3}, $F(000) = 589$, graphite-monochromated Mo-K_α radiation, $\bar{\lambda} = 0.71073$ Å, $\mu = 27.21$ cm^{-1}. The intensity data were collected on a Philips PW 1100 diffractometer, using the θ–2θ scan technique at room temperature. 6008 Unique reflections were measured, with θ in the range 3–28°, 5972 having $I \geqslant 2\sigma(I)$, 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 all the non-hydrogen atoms. The Cl and NO ligands were found disordered and distributed between the two apical positions with equal occupancy factor in order to justify the crystallographically imposed C_i symmetry of the cationic complex. A refinement of the structure in the non centrosymmetric space group $P1$ with each of two ligands occupying an apical position gave worse results. The hydrogen atoms were clearly localized in the final ΔF map and refined isotropically. The R and R_w values were 0.0489 and 0.0603. Atomic coordinates have been deposited at Cambridge Crystallographic Data Centre.

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