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NEW NITROSYL DERIVATIVES OF RHENIUM

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Summary

The synthesis of the new rhenium nitrosyls $Re(CO)_2(NO)(PPh_3)_2$ and $Re(H)(NO)_2(PPh_3)_2$, and the reactions of these low-oxidation state complexes with reagents such as X_2 (X = Cl, Br, I) and RX (X = halogen; R = H, CH_3, CH_3CO, C_6H_5CO) are described. The products include some new rhenium halonitrosyl derivatives.

Introduction

Recently *N*-methyl-*N*-nitrosotoluene-*p*-sulphonamide has been shown to be a useful reagent for the synthesis of nitrosyl derivatives of transition metals in low oxidation states [1, 2]. We have extended its use to the synthesis of formally rhenium(—I) nitrosyl derivatives [3], $Re(CO)_2(NO)(PPh_3)_2$ and $Re(H)(NO)_2(PPh_3)_2$. Although analogous manganese derivatives have been known for some time [4], no similar rhenium complexes have been previously reported.

Results and discussion

Synthesis of $Re(CO)_2(NO)(PPh_3)_2$ and $Re(H)(NO)_2(PPh_3)_2$

The direct reaction under nitrogen of $Re(PPh_3)_2Cl_4$ [5] or $Re(PPh_3)_2(O)(OC_2H_5)I_2$ [6] with *N*-methyl-*N*-nitrosotoluene-*p*-sulphonamide in the presence of triphenylphosphine and sodium borohydride in ethanol, gave $Re(H)(NO)_2(PPh_3)_2$ (I), which is diamagnetic in the solid state. This compound decomposes in air within a few hours, even in the solid state. The IR spectrum of (I) exhibits two intense bands at 1620 and 1580 cm^{-1}, which can be assigned to $\nu(NO)$, and a weak band at 1780 cm^{-1} which we assign to a Re—H stretching mode. The analogous manganese complex obtained by reducing a preformed halo-nitrosyl derivative with $NaBH_4$ [4] shows $\nu(NO)$ at 1684 and 1640 cm^{-1}, but no Mn—H stretching vibration was reported. The nitrosyl bands of (I) are in the same region (1600—1650 cm^{-1}) as those of the related complexes of formula $Re(X)(NO)_2(PPh_3)_2$ (X = Cl, Br, I) [7a, 7b].

Attempted deuteration of the rhenium compound was unsuccessful, and the ^{1}H NMR spectrum was not conclusive owing to the marked instability of this compound in solvents such as chloroform. However, the reactions of the new rhenium hydrido compound are consistent with its formulation (see below). The unusually low ν(Re—H) in $Re(H)(NO)_2(PPh_3)_2$ is not easy to explain. A *trans*-bond weakening effect of the NO σ-donor ligand on substituents such as chlorine has been invoked [8] but this explanation cannot be simply extended to our case. In fact, we cannot yet decide on a structure for (I) and it would not be justifiable to discuss the nature of the coordinated NO ligand on the basis of the infrared spectrum alone [3]. Moreover it should be noted we are considering here the effect of the ligand on a substituent which is itself *trans*-weakening.

When $Re(H)(CO)_2(PPh_3)_3$ [9] is treated with *N*-methyl-*N*-nitrosotoluene-*p*-sulphonamide in benzene under reflux the quite stable compound $Re(CO)_2(NO)(PPh_3)_2$ (II) is obtained in good yield. Its IR spectrum shows two carbonyl bands at 1950 and 1870 cm^{-1} and a nitrosyl band at 1620 cm^{-1}. These absorptions are in the same region as are those of the analogous manganese derivative [10]. The X-ray structure of the manganese derivative $Mn(CO)_2(NO)(PPh_3)_2$ shows a trigonal bipyramidal arrangement with the linear nitrosyl group in the equatorial plane [11]. Presumably $Re(CO)_2(NO)(PPh_3)_2$ has an analogous structure, as is suggested by the positions of the IR absorptions, which in this case can be used diagnostically with confidence, since they are being compared for two complexes having strictly analogous structures.

Reactions

On treatment with chlorine and bromine in solvents such as benzene $Re(CO)_2(NO)(PPh_3)_2$ gave rise to $[Re(CO)(NO)(PPh_3)_2X]X_3$ derivatives ($X = Cl, Br$) (III, IV), which are insoluble in the reaction medium. Compound (IV) shows the molar conductivity in nitrobenzene of a typical 1/1 electrolyte.

Fresh solutions of compound (III) in nitrobenzene show rather low molar conductivities, which decrease with time, down to those of a non-conducting solution. This is in agreement with the behaviour of (III) in polar solvents such as acetone, in which it easily loses chlorine to give the new derivative $Re(CO)(NO)(PPh_3)_2Cl_2$ (V). It is well known that the Cl_3^- anion is a very unstable species [12]. The same reaction is possible with the analogous bromine derivative (IV), but in this case different reaction conditions (see Experimental) are necessary in order to bring about complete dehalogenation to give $Re(CO)(NO)(PPh_3)_2Br_2$ (VI). Compounds (V) and (VI) were also formed as by-products in the benzene solution of the direct halogenation of (II). This transformation is accompanied by a lowering of ν(CO) and ν(NO) in the IR spectra, the latter vibration being more sensitive to the electron density on the metal [13]. A series of related non-ionic complexes containing ligands such as pyridine and triphenylarsine instead of triphenylphosphine have been previously reported, and show IR absorptions similar to those of (V) and (VI) [14].

When $Re(H)(NO)_2(PPh_3)_2$, suspended in alcohol, is treated with chlorine, the known $Re(NO)_2(PPh_3)_2Cl_2$ [7a] is formed. A different product was obtained from the reaction with excess bromine, the diamagnetic $[Re(NO)_2(PPh_3)_2$-

TABLE 1

IR DATA FOR RHENIUM NITROSYL DERIVATIVES [a]

For complete formulae of compounds (I) — (X) see Table 2.

Compound	ν(NO)	ν(CO)
(I) [b]	1580, 1620	
(II)	1620	1870, 1950
(III)	1810	2050
(IV)	1805	2050
(V)	1730	2000
(VI)	1740	2010
(VII)	1800, 1890	
(VIII)	1670, 1725	
(IX) [c]	1370, 1720	
(X)	1380, 1745	

[a] In cm^{-1}; measured as Nujol mulls. All absorptions reported are strong. [b] ν(Re—H) 1780 m cm^{-1}.
[c] ν(Re—Cl) 302 w, 380 w cm^{-1}.

$Br_2]Br_3$ (VII) being isolated. In this case gas evolution (probably HBr) was observed. This perbromide derivative, which behaves as a 1/1 electrolyte in nitrobenzene, loses bromine when heated in ethanol or spontaneously in acetone at room temperature, giving the known $Re(NO)_2(PPh_3)_2Br_2$ [7a]. This interesting reaction is a type of internal redox reaction, the final product showing a marked lowering of ν(NO) (see Table 1), as expected. A third type of reaction was observed with iodine. When a slight excess of halogen was used, $Re(NO)_2(PPh_3)_2I$ was formed, while the presence of HI was detected in the mother liquor. This complex, which has been previously reported [7], reacts with a large excess of iodine to give the new $Re(NO)_2(PPh_3)_2I_2$ (VIII). The corresponding chloro and bromo derivatives [7] have ν(NO) in the same region as the diiodide complex (VIII).

Although different products have been isolated from the reactions with the various halogens they probably follow a common reaction path (eqn. 1).

$$Re(H)(NO)_2(PPh_3)_2 \xrightarrow{X_2} \underset{(A)}{Re(NO)_2(PPh_3)_2X} \xrightarrow{X_2} \underset{(B)}{[Re(NO)_2(PPh_3)_2X_2]X_3} \rightarrow$$

$$\rightarrow \underset{(C)}{Re(NO)_2(PPh_3)_2X_2} \quad (1)$$

Only in the case of X = Br, could species (B) be isolated in a pure form, owing to its high stability, and for X = Cl and I, the species (B) were detected only by means of the IR spectra of the reaction mixtures. The oxidation of a monohalorhenium derivative to give compounds similar to (B) has already been reported [15].

$Re(H)(NO)_2(PPh_3)_2$ was also treated with iodomethane, acetyl and benzoyl chloride, with the aim of isolating compounds incorporating the organic moiety, but the formation of such derivatives was not in fact observed, $Re(NO)_2(PPh_3)_2I$ and $Re(NO)_2(PPh_3)_2Cl_2$ being the only products isolated. Similarly, $Re(CO)_2(NO)(PPh_3)_2$ when treated with RCOCl (R = CH_3, C_6H_5) gave $Re(CO)(NO)(PPh_3)_2Cl_2$ (V) and $Re(CO)_3(PPh_3)_2Cl$.

An interesting reaction was observed when $Re(H)(NO)_2(PPh_3)_2$ was treated with gaseous HCl. In this case one of the nitrosyl groups was protonated, and the rhenium derivative $Re(NO)(HNO)(PPh_3)_2Cl_2$ (IX) was obtained. This type of reaction has been previously reported for low-valent nitrosyl complexes of rhodium [16] and osmium [17].

The ν(NO) for the unusual ligand HNO lies at 1370 cm^{-1}, in agreement with the value found for $Os(CO)(HNO)(PPh_3)_2Cl_2$ [17], while the remaining nitrosyl group showed the usual shift to higher wavenumber. No ν(NH) was observed in the IR spectrum above 3100 cm^{-1}, but this could possibly be due to hydrogen bonding. The insolubility of this compound in common organic solvents precluded any ^{1}H NMR measurements.

The osmium derivative mentioned above is known to lose HCl spontaneously in solution. In our case we observed this behaviour only in the presence of bases such as $NaHCO_3$, and under these conditions $Re(NO)_2(PPh_3)_2Cl$ was formed. The reaction is reversible, and by treating $Re(NO)_2(PPh_3)_2Cl$ with gaseous HCl, the original HNO derivative can be isolated. The reaction path must thus be as shown in eqn. (2). This has been confirmed by treating the monoiodo derivative $Re(NO)_2(PPh_3)_2I$ with HCl, to give $Re(NO)(HNO)(PPh_3)_2(I)(Cl)$ (X). Complex (X), although slightly impure (see elemental analyses) showed the expected bands in its IR spectrum. These results enable us to conclude that the protonation of nitrosyl groups leading to HNO derivatives is possible only in the case of nitrosyl complexes showing particularly low ν(NO), i.e. with a high negative charge delocalised on the NO ligand. Although from the reaction between $Re(CO)_2(NO)(PPh_3)_2$ and HCl in alcohol or ethyl ether we were unable to isolate a pure product, even in these cases the reaction mixture showed absorptions assignable to the presence of a compound presumed to be $Re(CO)_2(HNO)(PPh_3)_2Cl$ (see Experimental). In this more complex reaction we have also detected by IR $Re(CO)(NO)(PPh_3)_2Cl_2$ (V) and, strangely enough, even $Re(CO)_3(PPh_3)_2Cl$ [9] (see reactions with RCOCl).

$$Re(H)(NO)_2(PPh_3)_2 \xrightarrow{HCl} Re(NO)_2(PPh_3)_2Cl \xrightleftharpoons[NaHCO_3]{HCl} Re(NO)(HNO)(PPh_3)_2Cl_2 \qquad (2)$$

$Re(CO)_2(HNO)(PPh_3)_2Cl$ shows chemical behaviour similar to that of $Os(CO)(HNO)(PPh_3)_2Cl_2$ reported above, spontaneously losing HCl when in solution. Thus, when the mixture of products of the protonation reaction in a benzene suspension is allowed to stand, the HNO derivative slowly loses HCl, to re-form the original $Re(CO)_2(NO)(PPh_3)_2$, which decomposes in solution, in the presence of air. The protonated compound reacts with CO in a way similar to the osmium derivative; thus carbonylation of the same reaction mixture converted the $Re(CO)_2(HNO)(PPh_3)_2Cl$ into $Re(CO)_3(PPh_3)_2Cl$. When we conducted the reaction with HCl in a carbon monoxide atmosphere, $Re(CO)_2(HNO)(PPh_3)_2Cl$ was not detected, while the amounts of $Re(CO)_3(PPh_3)_2Cl$ increased.

The reactions of the new nitrosyl rhenium derivatives towards other reagents are under investigation.

TABLE 2

ANALYTICAL DATA

Compound	Colour	M.p. (°C)	Analyses, found (calcd.) (%)		
			C	H	N
(I) $Re(H)(NO)_2(PPh_3)_2$	Brick-red	145	56.6 (56.0)	4.0 (4.0)	3.4 (3.63)
(II) $Re(CO)_2(NO)(PPh_3)_2$	Brick-red	180 (dec.)	57.4 (57.2)	3.65 (3.76)	1.72 (1.76)
(III) $[Re(CO)(NO)(PPh_3)_2Cl]Cl_3$	Pale-yellow	>250	48.6 (48.8)	3.2 (3.3)	1.3 (1.54)
(IV) $[Re(CO)(NO)(PPh_3)_2Br]Br_3$ [a,b]	Yellow	>250	41.2 (41.0)	2.74 (2.75)	1.35 (1.3)
(V) $Re(CO)(NO)(PPh_3)_2Cl_2$	Pink	>250	52.9 (53.0)	3.7 (3.58)	1.6 (1.67)
(VI) $Re(CO)(NO)(PPh_3)_2Br_2$	Pale-yellow	>250	47.35 (47.8)	3.15 (3.23)	1.41 (1.51)
(VII) $[Re(NO)_2(PPh_3)_2Br_2]Br_3$ [c,d]	Brown	181	37.3 (37.0)	2.5 (2.57)	2.34 (2.39)
(VIII) $Re(NO)_2(PPh_3)_2I_2$	Light-green	177	41.54 (42.1)	2.68 (2.92)	2.65 (2.73)
(IX) $Re(NO)(HNO)(PPh_3)_2Cl_2$ [e]	Yellow	180	50.74 (51.3)	3.59 (3.68)	3.13 (3.32)
(X) $Re(NO)(HNO)(PPh_3)_2(I)(Cl)$	Yellow	187	44.9 (46.2)	3.16 (3.32)	2.72 (3.0)

[a] Br (found/calcd.) = 28.8/29.4. [b] Λ_m (in nitrobenzene) = 21.0. [c] Br (found/calcd.) = 32.1/34.2. [d] Λ_m: 20.0. [e] Cl (found/calcd.): 8.5/8.43.

Experimental

All reactions were carried out under nitrogen with stirring. Solvents were distilled before use. IR spectra were recorded on Perkin—Elmer model 237 and 621 instruments. Conductivity data were obtained with a Philips conductivity bridge PR 9500.

$Re(PPh_3)_2Cl_4$, $Re(PPh_3)_2(O)(OC_2H_5)I_2$ and $Re(H)(CO)_2(PPh_3)_3$ were prepared according to literature procedures [5, 6, 9]. Elemental analyses were carried out by the analytical laboratories of Milan University (Table 2).

$Re(H)(NO)_2(PPh_3)_2$ (I)

To a refluxing ethanol solution (25 ml) of triphenylphosphine (0.204 g), $Re(PPh_3)_2(O)(OC_2H_5)I_2$ (0.4 g), *N*-methyl-*N*-nitrosotoluene-*p*-sulphonamide (0.25 g) and an ethanol solution (15 ml) of $NaBH_4$ (0.3 g) were added in rapid succession with stirring. After 15 min the brick-red product was filtered off under nitrogen, washed with degassed ethanol, and dried in vacuo. The product showed very low solubility in polar solvents and in benzene, and reacted with halogenated solvents.

$Re(CO)_2(NO)(PPh_3)_2$ (II)

To a degassed benzene solution (60 ml) of $Re(H)(CO)_2(PPh_3)_3$ (0.6 g), *N*-methyl-*N*-nitrosotoluene-*p*-sulphonamide (0.65 g) was added and the solution refluxed for 30 min. The resulting deep-red solution was evaporated to dryness and the residue treated with 50 ml of degassed warm ethanol. The insoluble brick-red compound was filtered, washed with degassed ethanol and dried in vacuo.

$[Re(CO)(NO)(PPh_3)_2Cl]Cl_3$ (III)

Dry Cl_2 was bubbled for 10 min through cold benzene (20 ml) and then (II) (0.3 g) was slowly added to the stirred solution. Gas evolution was noted while a pale-yellow precipitate formed. The precipitate was filtered off, washed with a little benzene and dried in vacuo.

$[Re(CO)(NO)(PPh_3)_2Br]Br_3$ (IV)

The yellow compound was prepared as described for (III), a mixture (1/1) of cold hexane—benzene (9 ml) and Br_2 (0.25 ml) being used.

$Re(CO)(NO)(PPh_3)_2Cl_2$ (V)

This compound was obtained as a by-product of the reaction of (II) with chlorine, by evaporating to dryness the filtrated benzene solution, and treating the residue with ethanol. It can also be prepared by stirring (III) for 2 h in acetone, in which (V) is insoluble, or by conducting the reaction of (II) with chlorine using a larger amount of benzene (about 50—60 ml). In this case a clear solution is obtained, from which (V) can be recovered as above.

$Re(CO)(NO)(PPh_3)_2Br_2$ (VI)

Analogously to compound (V), compound (VI) was obtained as a by-product of the preparation of (IV), by evaporating to dryness the mother liquor, but was not pure. It was treated with acetone under stirring, and the acetone insoluble product was crystallised from benzene—ethanol.

(VI) was also obtained by stirring (IV) in ethanol for two days in the presence of $NaBPh_4$. The insoluble material was then crystallised from benzene—ethanol. The use of $NaBPh_4$ as a very clean dehalogenating agent was discovered incidentally during attempted replacement of the Br_3^- anion.

$[Re(NO)_2(PPh_3)_2Br_2]Br_3$ (VII)

To an ethanol suspension (10 ml) of (I) (0.08 g), an ethanolic solution (3 ml) of bromine (0.2 ml) was added with stirring. Gas evolution (probably HBr) was noted. After 30 min the brown product was filtered off, washed with ethanol and dried in vacuo. It is diamagnetic in the solid state and conducting in nitrobenzene. When suspended in alcohol and refluxed for 1 h or in acetone at room temperature for 10 min, (VII) was shown to lose bromine to give the known $Re(NO)_2(PPh_3)_2Br_2$ [7a].

$Re(NO)_2(PPh_3)_2I_2$ (VIII)

The light-green compound was similarly prepared as described for (VII). When a slight excess of I_2 was used (ratio 1/4), after 10 h the known $Re(NO)_2(PPh_3)_2I$ [7] separated. It was identified by its IR spectrum, melting point and elemental analysis. When more iodine was added, after 20 h the new nitrosyl derivative (VIII) was obtained. It was filtered off, washed with ethanol and dried in vacuo.

$Re(NO)(HNO)(PPh_3)_2Cl_2$ (IX)

To an ethereal solution of gaseous HCl, (I) (0.08 g) was added with stirring. After 30 min the yellow compound was filtered off, washed several times with ether and dried in vacuo. It is stable in the solid state and little soluble in the common organic solvents.

$Re(NO)(HNO)(PPh_3)_2(I)(Cl)$ (X)

This reaction was carried out as described for (IX) using $Re(NO)_2(PPh_3)_2I$ obtained as described above, or by the reaction of (I) with CH_3I (see later).

Reaction of (I) with Cl_2, CH_3COCl, C_6H_5COCl

(a). With Cl_2. To (I) (0.08 g) an ethereal solution of chlorine was added with stirring. After 20 h a light-brown product was filtered off, washed several times with ether and dried in vacuo. It was identified as the known $Re(NO)_2(PPh_3)_2Cl_2$ [7a] from its IR spectrum, melting point and elemental analysis.

(b). With CH_3COCl *and* C_6H_5COCl. To (I) was added acetyl or benzoyl chloride. After 30 min or 20 h respectively, $Re(NO)_2(PPh_3)_2Cl_2$ was recovered by adding dry ethyl ether to the resulting suspension, filtering off, and drying in vacuo.

(c). With CH_3I. To (I) (0.08 g) iodine-free iodomethane (5 ml) was added and the suspension refluxed for ca. 1 h. The resulting brown solution was evaporated to dryness and the residue washed with degassed ethanol and dried for 6 h under reduced pressure. An orange product was collected, and identified as $Re(NO)_2(PPh_3)_2I$ [7].

Reactions of (IX) with $NaHCO_3$

To an ethanolic suspension of (IX), an aqueous solution of $NaHCO_3$ was added. Gas evolution was noted. After 16 h a yellow-brown compound was filtered off, washed with water ethanol and dried in vacuo. Its IR spectrum, melting point and elemental analysis were consistent with those of the known $Re(NO)_2(PPh_3)_2Cl$ [7]. When suspended in ether previously saturated with gaseous HCl, the product reverted to (IX).

Reaction of (II) with HCl

(II) (0.2 g) was added to an ether or alcohol solution of gaseous HCl. The pale-green mixture formed was filtered off, washed with ether and dried in vacuo. The IR spectrum of this mixture showed the presence of $Re(CO)(NO)(PPh_3)_2Cl_2$ (V), $Re(CO)_3(PPh_3)_2Cl$ [9] and a third compound which presumably is $Re(CO)_2(HNO)(PPh_3)_2Cl$. The latter complex has absorptions at 1880 and 1980 [ν(CO)] and 1380 cm^{-1} [ν(NO)]. Other properties of the HNO derivative are described in the main text.

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References

1 J.J. Levison and S.D. Robinson, J. Chem. Soc. A, (1970) 2947.
2 C.A. Reed and W.R. Roper, J. Chem. Soc. A, (1970) 3054.
3 D.M.P. Mingos and J.A. Ibers, Inorg. Chem., 10 (1971) 1479.

4 W.H. Hieber and H. Tengler, Z. Anorg. Allg. Chem., 318 (1962) 136.
5 M. Freni and V. Valenti, Gazz. Chim. Ital., 91 (1961) 1357.
6 J. Chatt and G.A. Rowe, J. Chem. Soc., (1962) 4019.
7 (a) M. Freni, D. Giusto and V. Valenti, Gazz. Chim. Ital., 94 (1964) 797;
(b) D. Giusto and G. Cova, Gazz. Chim. Ital., 102 (1972) 265.
8 D.A. Snyder and D.L. Weaver, Inorg. Chem., 9 (1970) 2760.
9 M. Freni, D. Giusto and P. Romiti, J. Inorg. Nucl. Chem., 33 (1971) 4093.
10 H. Wawersik and F. Basolo, J. Amer. Chem. Soc., 89 (1967) 4626.
11 J.H. Enemark and J.A. Ibers, Inorg. Chem., 6 (1967) 1575.
12 V. Gutman (Ed.), Halogen Chemistry, Academic Press, London, 1967, Vol. 1, p. 228.
13 G. La Monica, S. Cenini, G. Navazio and P. Sandrini, J. Organometal. Chem., 31 (1971) 89.
14 A. Trovati, P. Uguagliati and F. Zingales, Inorg. Chem., 10 (1971) 851.
15 W.J. Kirkham, A.G. Osborne, R.S. Nyholm and M.H.B. Stittard, J. Chem. Soc., (1965) 550.
16 J.P. Collman, N.W. Hoffman and D.E. Morris, J. Amer. Chem. Soc., 91 (1969) 5659.
17 K.R. Grundy, C.A. Reed and W.R. Roper, Chem. Commun., (1970) 1501.