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Preliminary communication

Formation of oxo-phosphonato complexes of rhenium from reactions of $[ReOCl_3(PPh_3)_2]$ with methyl phosphites. Crystal structure of $[ReOCl(OMe)\{P(O)(OMe)_2\}(PPh_3)_2]$

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Abstract

The oxo-phosphonato complexes $[ReOClX\{P(O)(OMe)_2\}(PPh_3)_2]$ (II, X = Cl; III, X = OMe) have been obtained by reaction of $[ReOCl_3(PPh_3)_2]$ (I) with $P(OMe)_3$ (for II) or with $P(OMe)_2OH/MeOH$ in the presence of a base (for III). The crystal structure of complex III is reported.

$[ReOCl_3(PPh_3)_2]$ (I) and its benzoyldiazenido derivative $[ReCl_2(NNCOPh)(PPh_3)_2]$ are key precursors for dinitrogen complexes of rhenium with a variety of phosphine or phosphite co-ligands [1,2]. However, in contrast to the chemistry of rhenium phosphine complexes [3], that of rhenium phosphite complexes is relatively underdeveloped. We are therefore investigating the reactions of organophosphites with the above-mentioned rhenium compounds. We previously described [2] the preparation of the benzoyldiazenido complexes $[ReCl_2(NNCOPh)(PPh_3)_x\{P(OR)_3\}_{3-x}]$ ($x = 0$, R = Me; $x = 1$, R = Et) by treatment of $[ReCl_2(NNCOPh)(PPh_3)_2]$ with the appropriate alkylphosphite in refluxing benzene, and we now report some preliminary results of our study of the reactions of organophosphites with the complex $[ReOCl_3(PPh_3)_2]$ (I).

This compound has been shown by others [4] to react with triethylphosphite, $P(OEt)_3$, to afford, in boiling benzene, *fac*-$[ReCl_3\{P(OEt)_3\}_3]$ and $P(O)Ph_3$, in quantitative yield. We have now shown that quite a different type of reaction may occur between compound I and trimethylphosphite, involving dealkylation of the latter to give an oxo-phosphonato complex, $[ReOCl_2\{P(O)(OMe)_2\}(PPh_3)_2]$ (II, eq. 1), as a brown solid.

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$$\underset{(\mathrm{I})}{[\mathrm{ReOCl_3(PPh_3)_2}]} + \mathrm{P(OMe)_3} \xrightarrow[\text{reflux}]{\mathrm{MeOH}} \underset{(\mathrm{II})}{[\mathrm{ReOCl_2\{P(O)(OMe)_2\}(PPh_3)_2}]} + \mathrm{MeCl} \tag{1}$$

The phosphonato ligand is possibly generated through a Michaelis–Arbuzov type rearrangement of ligating $P(OMe)_3$ in an ionic process [5] involving nucleophilic attack of liberated chloride ion at a C^{α} of the coordinated phosphite; this type of mechanism is favoured over the alternative radical pathway [6] in view of the high oxidation state of the metal.

The phosphonato complex $[ReOCl(OMe)\{P(O)(OMe)_2\}(PPh_3)_2]$ (III) has also been prepared (in ca. 10% yield), as a brownish-red solid, by reaction 2.

$$\underset{(\mathrm{I})}{[\mathrm{ReOCl_3(PPh_3)_2}]} + \mathrm{P(OMe)_2(O)H} + 2\mathrm{NEt_3} + \mathrm{MeOH} \xrightarrow[\text{reflux}]{}$$

$$\underset{(\mathrm{III})}{[\mathrm{ReOCl(OMe)\{P(O)(OMe)_2\}(PPh_3)_2}]} + 2[\mathrm{Et_3NH}]\mathrm{Cl} \tag{2}$$

In the absence of NEt_3, only the known [7] complex $[ReOCl_2(OMe)(PPh_3)_2]$ was isolated. Hence, the phosphonato ligand in III was probably derived by deprotonation (by NEt_3) of the pentavalent-phosphorus tautomeric form of the dialkyl phosphite, $P(OMe)_2(O)H$ (which predominates over the trivalent phosphorus form $P(OMe)_2(OH)$), thus following a route [8,9] to phosphonato complexes known for other metal systems.

Complexes II and III exhibit IR bands assigned to the phosphonato ligand, e.g., ν(P=O) at 1190 (II) and 1145 cm^{-1} (III), ν(Re=O) at 950 (II) and 945 cm^{-1} (III). In their ^1H NMR spectra (in CD_2Cl_2), the methyl proton resonance of the phosphonato ligand, $P(O)(OMe)_2$, appears as a doublet (δ 3.22, $^3J(PH)$ 13.5 Hz (II); δ 3.09 ppm, $^3J(PH)$ 10.7 Hz (III)).

The structure of complex III has been confirmed by an X-ray diffraction study*, and is depicted in Fig. 1; selected bond lengths and angles are given in Table 1. To our knowledge, this is the first structural characterization of a phosphonato complex of rhenium.

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* *Crystal data for compound III*: $C_{39}H_{39}ClO_5P_3Re \cdot nCH_4O$. M (n is estimated to be 2) = 966.4. Monoclinic, a 16.058(5), b 20.957(5), c 13.641(2) Å, β 114.64(2)°, V 4172.5 $Å^3$. Space group $P2_1/n$ (equivalent to no. 14). $Z = 4$, D 1.538 g cm^{-3}. $F(000) = 1944$. $\mu(Mo\text{-}K_{\alpha})$ 31.7 cm^{-1}. $\lambda(Mo\text{-}K_{\alpha})$ 0.71069 Å.

Crystals are deep orange-brown and approximately octahedral in form. After photographic examination, our crystal, size 0.50×0.45×0.30 mm, was mounted on an Enraf–Nonius CAD4 diffractometer, with monochromated Mo radiation, for measurement of cell parameters and intensity data. 3886 unique refections, with θ_{max} 20° were recorded and corrected for Lorentz-polarisation and absorption effects and for negative intensities. The structure was determined by the heavy atom method and refined by least-squares methods in the SHELX program to $R = 0.047$ and $R_w = 0.044$ for 3703 reflections (having $I > \sigma_I$) weighted $w = \sigma_I^{-2}$. The solvent (methanol) molecules are disordered and not satisfactorily resolved.

Scattering factors were from reference 10. Computer programs used in this analysis are listed in Table 4 of reference 11 and were run on the VAX 11/750 computer at G.C.R.I. Littlehampton.

The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (U.K.). Any request should be accompanied by the full literature citation for this communication

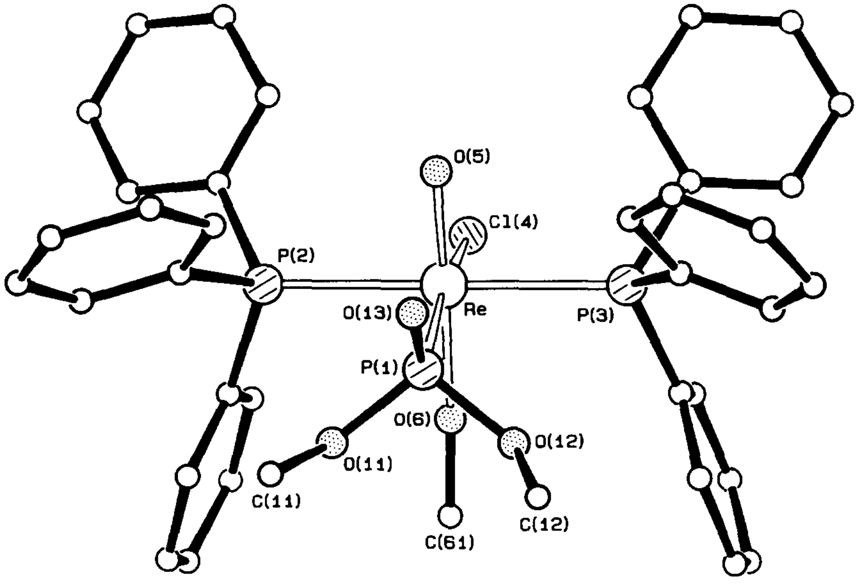

Fig. 1. The molecular structure of the Re complex $[ReOCl(OMe)\{P(O)(OMe)_2\}(PPh_3)_2] \cdot 2MeOH$ (III). The hydrogen atoms are omitted for clarity.

The compound contains a pseudo-mirror plane of symmetry which passes through the chloro, oxo, methoxy, and phosphonato ligands. The two phosphine ligands are mutually *trans*, as are the two coordinated oxygen atoms; the chloro ligand is *trans* to the phosphonato group. The Re–P(phosphonate) distance is 2.420(2) Å, i.e. it is slightly longer than the Re–P(phosphite) distance in other rhenium-phosphite complexes [2,12], as expected in view of the slightly poorer electron π-acceptor and/or σ-donor character of the phosphonate relative to the phosphite ligand [5,13,14].

Table 1

Selected molecular dimensions in compound III. Bond lengths are in Å, angles in degrees; e.s.d.s are in parentheses.

(a) About the Re atom			
Re–P(1)	2.420(2)	Re–Cl(4)	2.463(2)
Re–P(2)	2.502(3)	Re–O(5)	1.720(7)
Re–P(3)	2.498(3)	Re–O(6)	1.951(7)
P(2)–Re–P(3)	174.5(1)	O(5)–Re–O(6)	174.7(3)
P(1)–Re–Cl(4)	167.5(1)		
(b) In the ligands			
P(1)–O(11)	1.598(7)	O(11)–C(11)	1.430(12)
P(1)–O(12)	1.592(9)	O(12)–C(12)	1.397(18)
P(1)–O(13)	1.488(7)	O(6)–C(61)	1.330(16)
Re–P(1)–O(11)	106.6(3)	Re–P(1)–O(13)	120.5(3)
Re–P(1)–O(12)	104.9(2)	Re–O(6)–C(61)	165.7(7)

Within the phosphonato ligand, the phosphoryl P=O bond, 1.488(7) Å, is, as expected, shorter than the P–OC single bonds 1.598(7) and 1.592(9) Å, and the latter values are comparable to those reported [13] for other metal-phosphonato species.

The Re=O distance, 1.720(7) Å, is much shorter than the Re–OC distance, 1.951(7) Å, and, as suggested [3c,15] for other complexes, the rhenium–oxo bond appears to have a considerable triple bond character.

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