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Reactivity of rhenium(V) complexes containing different cores such as $[Re{\equiv}O]^{3+}$, $[Re{\equiv}NR]^{3+}$ and $[Re{\equiv}N]^{2+}$ toward bis(diphenylphosphino)methane: synthesis and crystal structures

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Abstract

The complexes *fac*-[$ReOCl_3$(dppm-*P,P'*)] (**1a**), *mer*-[$ReOCl_3$(dppm-*P,P'*)] (**1b**), *mer*-[$ReCl_3$(dppm-*P,P'*)(dppom-*P*)] (**2**), [$ReCl_4$(dppom-*P,O*)] (**3**) and *mer*-[$ReCl_3$(dppm-*P,P'*)PPh_3] (**4**) (dppm = $Ph_2PCH_2PPh_2$, dppom = $Ph_2PCH_2P(=O)Ph_2$) were obtained by reaction of [$ReOCl_3(PPh_3)_2$] or [$AsPh_4$][$ReOCl_4$] and dppm under different experimental conditions. Complex **1b** is probably obtained via the intermediate formation of complexes **2** or **4**. The complexes *fac*-[Re(NCH_3)Cl_3(dppm-*P,P'*] (**5**), *trans*-[$ReNCl_2$(dppm-*P*)PPh_3] (**6**) and [ReNCl(dppm-*P,P'*)$_2$]Cl (**7**) were also obtained starting from [Re(NCH_3)$Cl_3(PPh_3)_2$] and [$ReNCl_2(PPh_3)_2$], respectively. The structures of **1a** and **3** were determined by X-ray crystallography. Compound **1a** is monoclinic, space group $P2_1/c$, with $a = 11.156(4)$, $b = 17.264(5)$, $c = 14.467(5)$ Å and $\beta = 110.96(3)°$. The molecular complex is distorted octahedral. Selected bond distances (Å) are: Re–O(oxide) 1.671(6), Re–Cl(*trans* to O) 2.452(3), Re–Cl(*trans* to P) 2.365(4) and 2.373(3), Re–P 2.439(3) and 2.449(2). The P–Re–P chelation angle is 69.2(1)°. Compound **3** is orthorhombic, space group *Pccn*, with $a = 34.843(5)$, $b = 8.242(2)$ and $c = 19.342(4)$ Å. The molecular complex is roughly octahedral with the oxidized dppm ligand chelated through the P atom and the O atom of the P=O group. Selected bond distances (Å) are: Re–Cl(*trans* one other) 2.355 (mean), Re–Cl(*trans* to P) 2.353(3), Re–Cl(*trans* to O) 2.215(5), Re–O 2.087(7). The P–Re–O chelation angle is 80.7(2)°.

Introduction

Bis(diphenylphosphino)amine, $HN(PPh_2)_2$, and its derivatives $HN(XPPh_2)_2$ (X = O, S, Se) are useful systems to study as the ring size and the different donor group X affect the coordination properties. These ligands have been the subject of recent attention by us and two papers dealing with the reactivity of such ligands toward rhenium complexes containing the $[Re{\equiv}O]^{3+}$ core have been published [1].

The aim of this paper is to extend our studies on the reactivity of these ligands toward rhenium compounds containing different cores such as $[Re{\equiv}NMe]^{3+}$ and $[Re{\equiv}N]^{2+}$. In particular, we report here the reactivity of [$ReOCl_3(PPh_3)_2$], [$AsPh_4$][$ReOCl_4$], [Re(NCH_3)$Cl_3(PPh_3)_2$] and [$ReNCl_2(PPh_3)_2$] with bis(diphenylphosphino)methane (dppm), a potentially bidentate phosphine isoelectronic with $HN(PPh_2)_2$, in addition to a complete crystallographic study of mononuclear rhenium–dppm complexes having the metal in the different oxidation states +V and +IV.

Experimental

Materials

Solvents were purified and dried before use. Reactions, when necessary, were carried out in an atmosphere of argon using degassed solvents. The starting compounds [$ReOCl_3(PPh_3)_2$] [2], [$ReOCl_4$][$AsPh_4$] [3],

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[Re(NCH_3)Cl_3(PPh_3)$_2$] [4] and [ReNCl_2(PPh_3)$_2$] [5] were prepared following the literature methods. IR spectra were recorded on a Perkin-Elmer spectrometer. $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker AC 200 spectrometer operating at 81.01 MHz using an internal deuterium lock and 85% H_3PO_4 as external standard. ^1H NMR spectra were recorded on the same instrument and were calibrated with use of internal tetramethylsilane. Elemental analyses were performed on a Carlo Erba model 1106 elemental analyser. Magnetic susceptibilities of solid samples were measured on a Faraday balance as previously described [6]. Corrections for the ligands' diamagnetism were estimated from Pascal's constants. Conductivity measurements were performed with use of an Amel model 134 conductivity meter at 21 °C.

Preparations

*fac-[ReOCl$_3$(dppm-P,P'] (**1a**)*

A stoichiometric amount of dppm (0.18 mmol) was dissolved in degassed chloroform (30 ml), and added dropwise during a period of 10 min to a refluxing solution of [ReOCl_3(PPh_3)$_2$] (0.18 mmol) or [$AsPh_4$][ReOCl_4] in the same solvent (30 ml) purged with argon. In a few minutes the yellow colour of the solution turned green–blue and a precipitate slowly formed. After 20 min the pale blue solid was filtered and washed with ethanol and diethyl ether. The complex was recrystallized from hot CH_2Cl_2–CH_3NO_2, yield 85%. *Anal.* Found: C, 42.9; H, 2.8. Calc. for $C_{25}H_{22}Cl_3OP_2Re$: C, 43.3; H, 3.2%. ν(Re≡O) 990 cm^{-1} (Nujol). NMR ((CD_3)$_2$SO): $^{31}P\{^1H\}$, δ 21.0(s); ^1H, δ 4.15 (2H, t, ^2J(PH) 13.6 Hz).

*mer-[ReOCl$_3$(dppm-P,P')] (**1b**) and [ReCl$_4$(dppom-P,O] (**3**)*

(i) Complex **2** or **4** (see below) (0.18 mmol) was dissolved in toluene (30 ml) and refluxed for 10 min with a slow stream of oxygen passed through the solution. Heating was continued for 20 min, during which time the colour of the solution turned from yellow–orange to green. The green precipitate **1b** was collected by filtration, and washed with ethanol and diethyl ether. The complex was crystallized from hot dichloromethane–ethanol. Yield 80%.

(ii) A mixture of [ReOCl_3(PPh_3)$_2$] (0.18 mmol) and dppm, in 1:1 or 1:2 molar ratio in toluene (40 ml), was heated for 20 min, then oxygen was bubbled through it for 10 min, and the reflux protracted for 15 min, during which the green compound **1b** began to form in the reaction medium.

(iii) When the above reaction was carried out in toluene at reflux temperature in aerated conditions for 60 min, a mixture of **1b** and **3** was collected as green powder. We were unable to separate this mixture by fractional crystallization. Slow evaporation of a hot solution in dichloromethane–nitromethane gave good quality crystals of the mixture.

Complex **1b**. NMR [(CD_3)$_2$SO]: $^{31}P\{^1H\}$, δ 60.4(d), -17.7(d) (^2J(PP) 19.7 Hz). ^1H, δ 5.01 (CH_2, t, ^2J(PH) 11.6 Hz).

*mer-[ReCl$_3$(dppm-P,P')(dppom-P)] (**2**)*

This compound was prepared using a modified literature procedure [7]. A stoichiometric (2:1) amount of dppm was added to a $CHCl_3$ solution (30 ml) of [ReOCl_3(PPh_3)$_2$] or [$AsPh_4$][ReOCl_4] (0.18 mmol). The orange solution was refluxed for 30 min under argon, filtered and concentrated *in vacuo* to a small volume. Addition of diethyl ether gave a yellow precipitate which was crystallized from CH_2Cl_2–CH_3NO_2. Yield 75%. *Anal.* Found: C, 55.6; H, 4.0; Cl, 9.3. Calc. for $C_{50}H_{44}Cl_3OP_4Re$: C, 55.7; H, 4.1: Cl, 9.9%. μ_{eff} 2.16 μ_B (27 °C). For IR and NMR data see ref. 7.

*mer-[ReCl$_3$(dppm-P,P')PPh$_3$] (**4**)*

(i) A stoichiometric amount (1:1) of dppm was added to a refluxing solution of [ReOCl_3(PPh_3)$_2$] (0.18 mmol) in toluene (40 ml) and heating continued for 60 min under argon atmosphere. The yellow–orange solution was filtered and concentrated to a small volume. Addition of diethyl ether gave rise to a yellow precipitate. The product was purified by chromatography using a silica-gel plate (2 mm) (ethyl acetate/dichloromethane (4/96) as eluant). Crystallization from dichloromethane–ethanol gave orange crystals of **4**. Yield 70%.

(ii) A mixture of **1a** (0.18 mmol) and an excess of triphenylphosphine (1:4) in degassed toluene (40 ml), was refluxed for 30 min under argon. The yellow–orange solution was concentrated and crystallized as above without chromatography purification. Yield 85%. *Anal.* Found: C, 54.2; H, 4.0. Calc. for $C_{43}H_{37}Cl_3P_3Re$: C, 55.0; H, 4.0%. μ_{eff} 1.59 μ_B (21 °C). NMR ($CDCl_3$): $^{31}P\{^1H\}$, AMX spin system, δ_A 419.45(dd), δ_M 402.14(dd) (assignable to the PPh_3 and the *trans* disposed dppm-P atom; ^2J(P_AP_M) 301.4 Hz, ^2J(P_AP_X) 19.3 Hz, 2J(P_MP_X) 33.0 Hz); δ_X 299.50(dd). The attribution of P_A and P_M resonances could be reversed because of the uncertainty in their assignement; ^1H, δ 2.81 (CH_2, t, ^2J(PH) 8.6 Hz).

*fac-[Re(NCH$_3$)Cl$_3$(dppm-P,P')] (**5**)*

An excess of the dppm ligand (0.54 mmol) was added to a hot chloroform solution (40 ml) of [Re(NCH_3)Cl_3(PPh_3)$_2$] (0.18 mmol). Within about 5 min, at reflux temperature, a blue precipitate began to form. After 30 min the precipitate was removed by filtration, and washed with ethanol and diethyl ether. Slow evaporation of the solution obtained by adding ethanol to a hot nitromethane solution gave the complex

5 as a deep blue microcrystalline solid. Yield 80%. *Anal.* Found: C, 43.9; H, 3.2; N, 2.1. Calc. for $C_{26}H_{25}Cl_3NP_2Re$: C, 44.2; H, 3.6; N, 2.0%. NMR (CD_3NO_2): $^{31}P\{^1H\}$, δ −41.77(s); ^1H, δ 0.73 (3H, t, $^4J(PH)$ 4.8 Hz, NCH_3).

trans-[ReNCl$_2$(dppm-P)PPh$_3$] (6)

To a suspension of $[ReNCl_2(PPh_3)_2]$ (0.18 mmol) in chloroform (30 ml) at reflux temperature, was added dropwise during a period of 10 min a stoichiometric amount of dppm (0.18 mmol) dissolved in the same solvent (15 ml). The mixture was allowed to reflux for 40 min, during which the initial pale blue suspension turned to a orange solution. The solution was filtered, evaporated to a small volume and diethyl ether added until an orange precipitate formed. The product was crystallized from dichloromethane–ethanol. Yield 82%. *Anal.* Found: C, 55.8; H, 3.9; N, 1.5. Calc. for $C_{43}H_{37}Cl_2NP_3Re$: C, 56.2; H, 4.1; N, 1.5%. NMR ($CDCl_3$): $^{31}P\{^1H\}$, AMX spin system, δ_M 13.60 (dd), δ_A −35.12(d), δ_X −36.75 ($^2J(P_MP_A)$ 238.2 Hz, $^2J(P_MP_X)$ 19.7 Hz); ^1H: δ 5.61 (CH_2, t, $^2J(P_MH) \approx 2J(P_XH) \approx 10.6$ Hz).

[ReNCl(dppm-P,P′)$_2$]Cl (7)

A mixture of $[ReNCl_2(PPh_3)_2]$ (0.18 mmol) and dppm (0.40 mmol) in refluxing chloroform (40 ml) was stirred for 40 min. The yellow solution was filtered, evaporated to a small volume and diethyl ether added until a yellow precipitate formed. It was recrystallized from methanol–diethyl ether as yellow plates. Yield 80%. *Anal.* Found: C, 57.1; H, 4.2; N, 1.4. Calc. for $C_{50}H_{44}Cl_2NP_4Re$: C, 57.7; H, 4.3; N, 1.3%. The molar conductivity (Λ_m) in methanol (2.5×10^{-4} M) was 81 Ω^{-1} cm^2 mol^{-1} (21 °C), consistent with this complex having a mono-ionic structure. NMR ($CDCl_3$): $^{31}P\{^1H\}$: δ −25.23(s); ^1H: δ_A 5.98, δ_B 5.49 ($2CH_2$, m, $^2J(AB)$ 14.7 Hz, $J(AX)$ 3.0 Hz, $J(BX)$ 6.0 Hz).

X-ray data

Crystals of maximum dimension of 0.2 mm were mounted on the end of glass fibers and covered with epoxy-adhesive.

Crystal data

$C_{25}H_{22}Cl_3OP_2Re$ (**1a**), $M = 693$, monoclinic, space group $P2_1/c$, $a = 11.156(4)$, $b = 17.264(5)$, $c = 14.467(5)$ Å, $\beta = 110.96(3)°$, $U = 2602$ Å^3 (by least-squares refinement of 25 medium angle reflections, $\lambda = 0.7107$ Å), $Z = 4$, $D_c = 1.77$ g cm^{-3}, $F(000) = 1344$; μ(Mo Kα) = 51 cm^{-1}.

$C_{25}H_{22}Cl_4OP_2Re$ (**3**), $M = 728$, orthorhombic, space group $Pcnn$, $a = 34.843(5)$, $b = 8.242(2)$ and $c = 19.342(4)$ Å, (by least-squares refinement of 25 medium angle reflections, $\lambda = 0.7107$ Å), $Z = 8$, $D_c = 1.74$ g cm^{-3}, $F(000) = 2824$, μ(Mo Kα) = 47.4 cm^{-1}.

Data collection and processing

Philips four-circle diffractometer, θ–2θ mode, scan speed 2 min^{-1}, graphite-monochromated Mo Kα radiation, scan range $2 < \theta < 25°$. For **1a** a total of 13 728 independent reflections was recorded, of which 6729 were above background ($I > 3\sigma(I)$); for **3** a total of 5512, of which 2645 were above background. All samples used were stable under irradiation. Absorption corrections were applied [8].

Structure analysis and refinement

Patterson methods followed by normal heavy-atom procedures were used. Full-matrix least-squares refinement with non-hydrogen atoms anisotropic and hydrogens in calculated positions with a fixed U_{iso} (= 0.08 Å^2). Final *R* factors, based on observed reflections, were 0.038 for **1a** and 0.041 for **3**. Programs and

TABLE 1. Fractional coordinates of $[ReOCl_3(dppm\text{-}P,P')]$ (**1a**) with equivalent isotropic thermal parameters (Å^2)

Atom	*x*	*y*	*z*	U_{eq} ^{a}
Re(1)	0.15617(4)	0.14357(2)	0.48891(3)	0.0347(1)
P(1)	0.2845(2)	0.2044(1)	0.4035(2)	0.0318(7)
C(25)	0.1470(7)	0.2445(5)	0.3012(6)	0.031(3)
P(2)	0.0193(2)	0.1891(1)	0.3247(2)	0.0306(7)
Cl(1)	0.1344(2)	0.2828(1)	0.5128(2)	0.0448(9)
Cl(2)	−0.0022(3)	0.1197(2)	0.5588(2)	0.068(1)
Cl(3)	0.3070(3)	0.1392(2)	0.6533(2)	0.064(1)
O(1)	0.1785(6)	0.0584(4)	0.4425(5)	0.044(3)
C(2)	0.3352(7)	0.1266(5)	0.2506(5)	0.092(7)
C(3)	0.4082(7)	0.0773(5)	0.2154(5)	0.114(9)
C(4)	0.5150(7)	0.0396(5)	0.2817(5)	0.084(7)
C(5)	0.5488(7)	0.0512(5)	0.3833(5)	0.111(8)
C(6)	0.4757(7)	0.1005(5)	0.4185(5)	0.122(8)
C(1)	0.3690(7)	0.1382(5)	0.3522(5)	0.040(3)
C(8)	0.4047(6)	0.3474(4)	0.4097(4)	0.048(4)
C(9)	0.5005(6)	0.4020(4)	0.4535(4)	0.061(5)
C(10)	0.5904(6)	0.3888(4)	0.5480(4)	0.067(5)
C(11)	0.5844(6)	0.3210(4)	0.5987(4)	0.099(6)
C(12)	0.4886(6)	0.2665(4)	0.5549(4)	0.077(5)
C(7)	0.3988(6)	0.2797(4)	0.4604(4)	0.036(3)
C(14)	−0.0470(6)	0.1305(4)	0.1339(5)	0.052(4)
C(15)	−0.0879(6)	0.0722(4)	0.0627(5)	0.078(6)
C(16)	−0.1178(6)	−0.0011(4)	0.0890(5)	0.082(7)
C(17)	−0.1069(6)	−0.0160(4)	0.1864(5)	0.081(6)
C(18)	−0.0661(6)	0.0423(4)	0.2576(5)	0.055(4)
C(13)	−0.0361(6)	0.1155(4)	0.2314(5)	0.036(3)
C(20)	−0.2001(6)	0.2353(4)	0.3548(5)	0.063(5)
C(21)	−0.3065(6)	0.2825(4)	0.3413(5)	0.072(6)
C(22)	−0.3273(6)	0.3476(4)	0.2803(5)	0.078(6)
C(23)	−0.2417(6)	0.3654(4)	0.2329(5)	0.075(6)
C(24)	−0.1353(6)	0.3182(4)	0.2464(5)	0.059(4)
C(19)	−0.1145(6)	0.2531(4)	0.3074(5)	0.038(3)

^{a}U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE 2. Bond distances (Å) and angles (°) for **1a**

Re–P(1)	2.439(3)	Re–P(2)	2.449(2)
Re–Cl(1)	2.452(3)	Re–Cl(2)	2.365(4)
Re–Cl(3)	2.373(3)	Re–O	1.671(6)
P(1)–C(1)	1.802(9)	P(2)–C(13)	1.794(6)
P(1)–C(7)	1.800(6)	P(2)–C(19)	1.802(7)
P(1)–C(25)	1.843(6)	P(2)–C(25)	1.846(9)
Cl(1)–Re–Cl(2)	89.1(1)	Cl(1)–Re–O	162.8(1)
Cl(1)–Re–Cl(3)	87.7(1)	Cl(2)–Re–O	105.1(2)
Cl(1)–Re–P(1)	75.8(1)	Cl(3)–Re–O	102.7(2)
Cl(1)–Re–P(2)	76.3(1)	P(1)–Re–O	88.7(3)
Cl(2)–Re–Cl(3)	86.3(1)	P(2)–Re–O	91.3(3)
P(1)–Re–P(2)	69.2(1)	P(1)–C(25)–P(2)	97.7(4)
Re–P(1)–C(1)	115.1(3)	Re–P(2)–C(13)	115.5(2)
Re–P(1)–C(7)	121.8(2)	Re–P(2)–C(19)	122.0(2)
Re–P(1)–C(25)	95.6(3)	Re–P(2)–C(25)	95.2(3)
C(25)–P(1)–C(1)	108.4(4)	C(25)–P(2)–C(13)	108.0(4)
C(25)–P(1)–C(7)	110.3(4)	C(25)–P(1)–C(19)	108.2(4)
C(1)–P(1)–C(7)	104.9(4)	C(13)–P(2)–C(19)	106.5(3)

TABLE 3. Fractional coordinates of [ReCl$_4$(dppom-*P*,*O*)] (**3**) with equivalent isotropic thermal parameters (Å^2)

Atom	x	y	z	U_{eq} [a]
Re(1)	0.36207(1)	0.45807(6)	0.09360(3)	0.0328(1)
P(1)	0.38670(9)	0.2020(4)	0.0447(2)	0.0311(9)
P(2)	0.3647(1)	0.1318(4)	0.1907(2)	0.0298(9)
Cl(1)	0.42377(9)	0.5416(5)	0.1293(2)	0.053(1)
Cl(2)	0.3352(1)	0.6714(4)	0.1583(2)	0.043(1)
Cl(3)	0.30056(9)	0.3591(4)	0.0694(2)	0.050(1)
Cl(4)	0.3686(2)	0.5900(6)	−0.0055(2)	0.085(2)
O(1)	0.3609(3)	0.3149(9)	0.1825(4)	0.033(3)
Cl(5)	0.7208(2)	0.1260(7)	0.0036(3)	0.097(2)
C(25)	0.3687(3)	0.049(2)	0.1049(5)	0.031(3)
C(2)	0.4547(3)	0.289(1)	−0.0110(5)	0.056(6)
C(3)	0.4945(3)	0.305(1)	−0.0149(5)	0.068(7)
C(4)	0.5178(3)	0.221(1)	0.0319(5)	0.073(7)
C(5)	0.5012(3)	0.123(1)	0.0825(5)	0.072(7)
C(6)	0.4614(3)	0.108(1)	0.0864(5)	0.050(5)
C(1)	0.4381(3)	0.191(1)	0.0396(5)	0.042(5)
C(8)	0.3421(3)	0.202(1)	−0.0767(5)	0.057(6)
C(9)	0.3299(3)	0.134(1)	−0.1390(5)	0.067(6)
C(10)	0.3475(3)	−0.006(1)	−0.1641(5)	0.080(8)
C(11)	0.3772(3)	−0.078(1)	−0.1268(5)	0.092(9)
C(12)	0.3894(3)	−0.010(1)	−0.0645(5)	0.079(8)
C(7)	0.3718(3)	0.130(1)	−0.0395(5)	0.043(5)
C(14)	0.4296(3)	0.2026(9)	0.2656(5)	0.048(5)
C(15)	0.4636(3)	0.1619(9)	0.2998(5)	0.076(7)
C(16)	0.4746(3)	−0.0002(9)	0.3052(5)	0.071(7)
C(17)	0.4518(3)	−0.1217(9)	0.2764(5)	0.063(6)
C(18)	0.4178(3)	−0.0811(9)	0.2423(5)	0.051(5)
C(13)	0.4068(3)	0.0811(9)	0.2369(5)	0.042(5)
C(20)	0.3285(2)	−0.013(1)	0.3015(4)	0.053(5)
C(21)	0.2962(2)	−0.065(1)	0.3379(4)	0.064(6)
C(22)	0.2599(2)	−0.054(1)	0.3078(4)	0.060(6)
C(23)	0.2560(2)	0.010(1)	0.2414(4)	0.060(6)
C(24)	0.2883(2)	0.062(1)	0.2050(4)	0.044(5)
C(19)	0.3245(2)	0.050(1)	0.2350(4)	0.037(4)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE 4. Bond distances (Å) and angles (°) for **3**

Re–P(1)	2.467(3)	Re–O(1)	2.087(7)
Re–Cl(1)	2.361(3)	Re–Cl(3)	2.340(3)
Re–Cl(2)	2.353(3)	Re–Cl(4)	2.215(5)
P(1)–C(25)	1.83(1)	P(2)–C(25)	1.80(1)
P(1)–C(7)	1.81(1)	P(2)–C(13)	1.77(1)
P(1)–C(1)	1.80(1)	P(2)–C(19)	1.77(8)
		P(2)–O(1)	1.523(8)
P(1)–Re–O(1)	80.7(2)	Cl(2)–Re–O(1)	88.6(2)
P(1)–Re–Cl(1)	92.6(1)	Cl(2)–Re–Cl(1)	89.4(1)
P(1)–Re–Cl(3)	86.8(1)	Cl(2)–Re–Cl(3)	90.1(1)
P(1)–Re–Cl(4)	93.0(1)	Cl(2)–Re–Cl(4)	97.7(1)
Cl(1)–Re–O(1)	86.7(2)	Cl(3)–Re–O(1)	87.1(2)
Cl(1)–Re–Cl(4)	90.9(2)	Cl(3)–Re–Cl(4)	95.3(2)
Re–P(1)–C(1)	114.2(3)	Re–O(1)–P(2)	130.1(4)
Re–P(1)–C(7)	121.7(3)	O(1)–P(2)–C(13)	111.1(4)
Re–P(1)–C(25)	103.1(4)	O(1)–P(2)–C(19)	110.8(4)
P(1)–C(25)–P(2)	110.8(6)	O(1)–P(2)–C(25)	106.6(5)

computers used and sources of scattering factors data are given in refs. 9–11. Fractional atomic coordinates and temperature factors for the two compounds are reported in Tables 1 and 3; selected bond distances and angles are listed in Tables 2 and 4.

Results and discussion

Complexes containing the [Re≡O]$^{3+}$ core

The rhenium(V) complex *fac*-[ReOCl$_3$(dppm-*P*,*P'*)] (**1a**) was easily obtained as a pale blue precipitate when [ReOCl$_3$(PPh$_3$)$_2$] or [AsPh$_4$][ReOCl$_4$] was made to react in a 1:1 molar ratio with dppm in refluxing chloroform for a short time (15–20 min). This compound was previously obtained by prolonged heating of [ReCl$_4$(dppm-*P*,*P'*] in acetone [12], and more recently by Shaw and co-workers from the reaction of [ReOCl$_3$(AsPPh$_3$)$_2$ with dppm [7]. Complex **1a** is scarcely soluble in usual organic solvents. Nevertheless, we were able to grow suitable crystals for a diffraction study by slow evaporation of a solution obtained by adding nitromethane to a hot solution of **1a** in dichloromethane. In keeping with the spectroscopic (IR and NMR) data, the X-ray analysis confirms the already postulated *fac* configuration [7] (see below). In order to record significative NMR spectra of **1a**, a sufficient solubility for this purpose was only obtained in dimethyl sulfoxide. However, the pale blue colour of a freshly prepared solution of **1a** turned green within few minutes. The broad band proton decoupled ^{31}P NMR spectrum of this solution established the presence of two closely related species in approximatively equal amount. Indeed, a narrow singlet at 21.0 ppm and a couple of doublets at 60.4 and −17.7 ppm (^2J(PP) = 19.7 Hz) were consistent with the presence of both *fac*- (**1a**) and *mer*-[ReOCl$_3$(dppm-*P*,*P'*] (**1b**) isomers.

In line with the $^{31}P\{^{1}H\}$ NMR spectral data, the ^{1}H NMR spectrum showed two triplets centered at 5.01 ($^{2}J(HP)=11.6$ Hz) and 4.15 ($^{2}J(HP)=13.6$ Hz) ppm which may be safely assigned to the methylene protons of the chelating dppm ligand in the two geometrical isomers **1a** and **1b**.

When the reaction was carried out in a 1:2 molar ratio, under the same experimental conditions which afford **1a**, the yellow rhenium(III) complex *mer*-[ReCl$_3$(dppm-*P*,*P*′)(dppom-*P*)] (**2**) (dppom = Ph$_2$PCH$_2$P(=O)Ph$_2$) was precipitated when diethyl ether was added to the concentrated reaction mixture. Both IR and NMR (CDCl$_3$) spectra of **2** are in excellent agreement with those previously published [7]. Complex **2** is paramagnetic in the solid state and exhibits a bulk magnetic moment of 2.16 μ_B at 27 °C. The observed magnetic moment is lower than the spin-only value expected for a d^4 complex, but it is close to those reported for other rhenium(III) octahedral complexes [13].

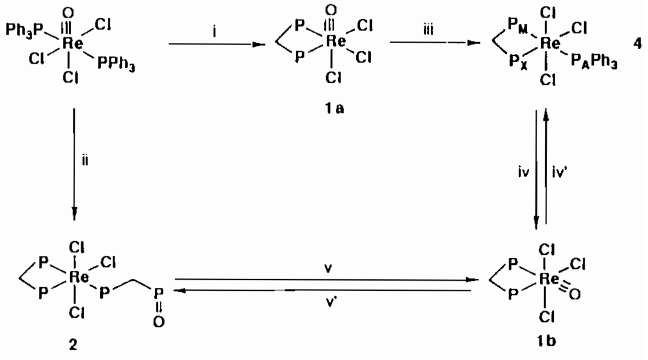
When we reacted the Re(V) precursor, [ReOCl$_3$(PPh$_3$)$_2$], with dppm ligand in a higher boiling solvent such as toluene, in aerated conditions, a green precipitate was collected irrespectively of the molar ratio employed (1:1 or 1:2). The same green precipitate was also obtained in refluxing toluene solution of **2**. Although the solubility of this green material is very reduced in common organic solvents, we had success in growing crystals suitable for an X-ray diffraction analysis under the same conditions used for complex **1a**.

In order to obtain a solution for NMR studies, we dissolved the green product in (CD$_3$)$_2$SO. The multinuclear NMR analysis of this product revealed the presence of two compounds, one of which, in minor amounts, was paramagnetic. The two doublets in the $^{31}P\{^{1}H\}$NMR spectrum, ($\delta=60.4$ and -17.7), and the presence of a triplet at 5.01 ppm in the proton NMR spectrum, indicated that the diamagnetic species in the green mixture was the *mer*-isomer **1b**.

We were unable to separate the components of the mixture in order to identify the paramagnetic species. However, when we decided to undertake a crystallographic study on a crystalline batch of the green material, we were capable of picking out a crystal of the paramagnetic compound. The X-ray data showed that the paramagnetic species is the novel Re(IV) complex [ReCl$_4$(dppom-*P*,*O*)] (**3**) in which the diphosphine-monoxide ligand is coordinated to the metal through a phosphorus and an oxygen atom thus forming a five-membered chelate ring.

When the precedent reactions were carried out under argon atmosphere using degassed toluene, we did not observe the formation of the complexes **1b** and **3**. In contrast, when only one equivalent amount of dppm was used, a yellow–orange compound was collected. We also observed that this complex was obtained more readily and efficiently starting from the *fac*-isomer **1a** in the presence of an excess of triphenylphosphine (see 'Experimental'). The formation of this complex takes place by subsequent reaction between the *fac*-isomer **1a** and the free triphenylphosphine generated in the reaction medium as a consequence of the formation of **1a**. The higher boiling temperature of toluene most likely allows this second step of the reaction (see Scheme 1) to occur.

On the grounds of elemental analysis, magnetic susceptibility measurements ($\mu_{eff}=1.59$ μ_B at 21 °C) and especially, NMR spectra, we propose that this complex is *mer*-[ReCl$_3$(dppm-*P*,*P*′)PPh$_3$] (**4**). It shows the same donor set as compound **2**, in which, instead of PPh$_3$, the dppom molecule is bonded as a monodentate ligand, through its non-oxidized P atom. The magnetic moment of **4** is lower than that found for **2**, but matches well the values reported for other d^4 species such as ReX$_3$L$_3$ and OsX$_4$L$_3$ (X = halides, L = tertiary phosphine) [14]. This relatively low magnetic moment is most likely responsible for the occurrence of narrow resonances in the ^{1}H NMR spectrum which, in addition, maintain their coupling connections to the phosphorus nuclei coordinated to the paramagnetic rhenium atom. As an example, the methylene resonance of dppm does not consist of the broad signal usually featured in the proton NMR spectrum of paramagnetic dppm–Re complexes [7], but appears as a narrow triplet at δ 2.81 owing to fortuitous coincidence of the coupling constants to the two non-equivalent dppm phosphorus atoms ($^{2}J(HP)$ 8.6 Hz). This observation prompted us to record the $^{31}P\{^{1}H\}$ NMR spectrum of complex **4** hoping to observe well defined ^{31}P resonances instead of the usually undetectable, extremely broad signals, which indicate phosphorus atoms directly coordinated to a paramagnetic d^4 Re(III) metal center. In keeping with our expectations, the $^{31}P\{^{1}H\}$ NMR spectrum of **4** in CDCl$_3$



Scheme 1. Reaction conditions: (i) dppm 1 equiv., refluxing CHCl$_3$; (ii) dppm 2 equiv., refluxing CHCl$_3$; (iii), PPh$_3$, Ar, refluxing toluene; (iv), O$_2$, refluxing toluene; (iv′), PPh$_3$, refluxing toluene; (v), O$_2$, refluxing toluene; (v′), dppm, refluxing CHCl$_3$.

exhibited a first order AMX spin system greatly shifted to low field (δ_A 419.45, δ_M 402.14, δ_X 299.50). This behaviour has already been observed for some d^4 Osmium compounds showing similar unusually low magnetic moment values [15]. The large value of the coupling constant ($^2J(P_AP_M)$ 301.4 Hz) [16] is indicative of the *trans* disposition of the triphenylphosphine molecule and one phosphorus of the dppm ligand.

When the above reaction was carried out in the 1:2 molar ratio, under the same experimental conditions, complex **2** was obtained as the main product with a small amount of complex **4**, whereas the complexes **1b** and **3** were not formed, even when the heating was continued for 2 h. From a mechanistic point of view these results suggest that the presence of dioxygen is necessary to form **1b** and **3** (see below) and that the monodentate diphosphine-monoxide ligand in **2** does not play any effective role in the formation of complex **3**. It also indicates the higher efficiency of dppm in reducing the Re–oxo core with respect to triphenylphosphine; after the first step of formation of the *fac*-isomer **1a**, the dppm present in the reaction medium, in addition to PPh_3, is able to reduce **1a** in toluene as well as in the lower boiling point chloroform.

A good amount of the *mer*-isomer **1b** was collected in a short time when oxygen was bubbled through a solution containing indifferently **2** or **4** in refluxing toluene. **1b** is then probably produced by the action of dioxygen on the dppom or triphenylphosphine ligands of the complexes **2** or **4**, respectively; $(OPPh_2)_2CH_2$ or $OPPh_3$ is therefore eliminated and an oxygen atom is finally bonded *trans* to one of the phosphorus atoms of the chelate dppm ligand. On the other hand the complex **1b** can be reduced to **2** or **4** by adding an excess of the appropriate phosphine to a refluxing solution of **1b** in toluene (for complex **4**) or in chloroform (for complex **2**).

We never observed the presence of the complex $[ReCl_4(dppom$-$P,O)]$ (**3**) when the reactions were carried out under oxygenated conditions. This behaviour suggests that the formation of **3** should be promoted by the presence in solution of the *mer*-isomer **1b**.

In **1b** the strong *trans* influence of the $Re{\equiv}O_{oxo}$ bond ought to give rise to a lengthening of the Re–P bond. This fact would favour the transformation of the highly strained four-membered chelate ring into the five-membered chelate ring in **3**. The fourth chlorine atom should originate from a little decomposition owing to the high reflux temperature of the solution. Probably the oxidative conditions, together with a shorter reaction time, inhibit the decomposition of **1b** to **3**.

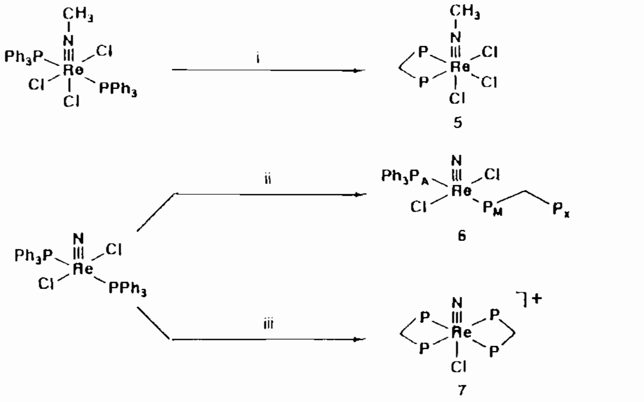
Complexes containing the $[Re{\equiv}NCH_3]^{3+}$ *and* $[Re{\equiv}N]^{2+}$ *cores*

Organo-imido and nitrido complexes, containing $[Re{\equiv}NR]^{3+}$ and $[Re{\equiv}N]^{2+}$ cores, respectively, form a second important class of rhenium(V) halides which are isoelectronic with the oxo complexes characterized by the $[Re{\equiv}O]^{3+}$ core.

In order to compare their chemical behaviour, we decided to study the reactivity of $[Re(NCH_3)Cl_3(PPh_3)_2]$ and $[ReNCl_2(PPh_3)_2]$ toward the potentially bidentate dppm ligand under similar conditions to those used for the related species containing the $[Re{\equiv}O]^{3+}$ core. The different products obtained and the experimental conditions used are presented in Scheme 2.

The deep blue complex *fac*-$[Re(NCH_3)Cl_3(dppm$-$P,P')]$ (**5**) was readily isolated as a precipitate in the reaction medium on heating the methylimido complex $[Re(NCH_3)Cl_3(PPh_3)_2]$ with dppm in chloroform or toluene. The monosubstituted compound was obtained irrespectively of the molar ratio used. Complex **5**, although scarcely soluble in common organic solvents, could be crystallized by adding ethanol to a hot nitromethane solution. It was characterized by elemental analysis and NMR spectra. The *fac*-stereochemistry was confirmed by the presence in its $^{31}P\{^1H\}$ NMR spectrum (CD_3NO_2) of a singlet resonance at -41.77 ppm due to the phosphorus atoms of the chelate dppm ligand. In the ^1H NMR spectrum recorded in the same solvent, the methyl group of the organo-imido ligand appeared as a triplet at 0.73 ppm ($^4J(PH)$ 4.8 Hz). When a similar reaction was accomplished with the rhenium(V) nitrido complex, $[ReNCl_2(PPh_3)_2]$, different products were obtained depending on the stoichiometric ratio. In particular when only one equivalent amount of dppm was used, the yellow complex $[ReNCl_2(dppm$-$P)PPh_3]$ (**6**) was obtained, while with two equivalents of dppm the ionic disubstituted complex $[ReNCl(dppm$-$P,P')_2Cl$ (**7**) was obtained in good yield. These compounds were characterized by elemental analyses, molar conductivity measurements and NMR spectroscopy.

The correct formulation of **6**, as well as its stereochemical arrangement, was safely inferred by analysis



Scheme 2. Reaction conditions: (i) dppm, refluxing $CHCl_3$; (ii) dppm 1 equiv., refluxing $CHCl_3$; (iii) dppm 2 equiv., refluxing $CHCl_3$.

of the $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$) which appears as a first order AMX spin system with no detectable coupling connection between the triphenylphosphine resonance (P_A) and one of the resonances (P_X) due to the dppm phosphorus atoms. This feature is indicative that dppm does not behave as a chelating ligand and then coordinates to rhenium through only one of its phosphorus donors (P_M), whose resonance appears as a doublet of doublets at δ 13.4 ($^2J(P_AP_M)$ 238.4 Hz; $^2J(P_MP_X)$ 17.7 Hz). The magnitude of the coupling constant between P_A and P_M clearly indicates that the two rhenium-bonded phosphorus atoms (P_A and P_M) are lying *trans* to each other [16].

In 7, the $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$) showing a singlet resonance at -25.23 ppm was consistent with an octahedral geometry in which the two chelate dppm ligands are in *trans* position to each other on the equatorial plane of the coordination polyhedron. According to this stereochemical assignment, the proton NMR spectrum ($CDCl_3$) presented (see trace (a) in Fig. 1) two well resolved multiplets (δ_A 5.98, δ_B 5.49). They may be assigned to the four methylene hydrogens which are virtually coupled to the four dppm-phosphorus atoms, so that, an $AA'BB'X_2X'_2$ spin system ($X = {}^{31}P$) results. Indeed, when the resolution of these NMR resonances is enhanced through a Gaussian multiplication procedure, both signals resolve into a couple of quintuplets (see trace (b) in Fig. 1) which exhibit a geminal coupling, J(AB), of 14.7 Hz and coupling constants to the X nuclei of 3.0 (J(AX)) and 6.0 (J(BX)) Hz, respectively [17].

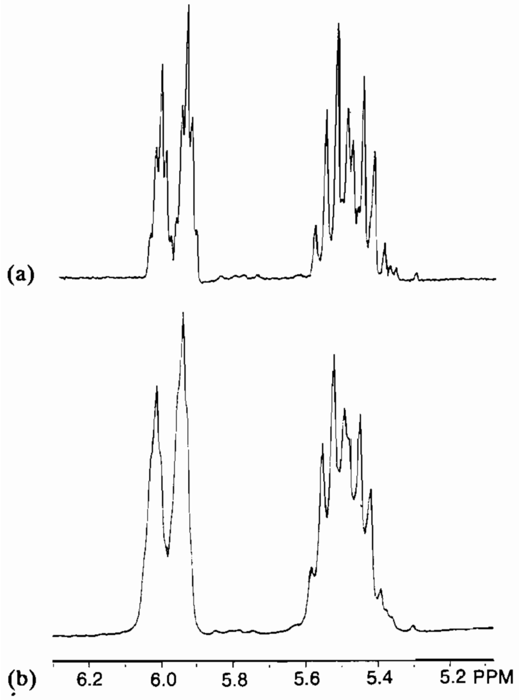


Fig. 1. ^1H NMR methylene resonances of 7: (a) normal spectrum; (b) resolution enhanced spectrum by Gaussian multiplication.

X-ray crystal structures

Complex 1a

As shown in Figs. 2 and 3, *fac*-[ReOCl$_3$(dppm-*P*,*P*′)] is a rather distorted octahedral molecular complex with approximate *Cs* symmetry. Major asymmetries in bond lengths are mainly due to the nature of the bonded atoms; distortions in bond angles being due to geometrical constraints of the chelate ligand, which subtends an angle of 69° at the metal atom, and to the fact that the metal ion is strongly bound to oxygen. The Re–O distance of 1.671(6) Å indicates the presence of a triple bond and compares well with values found in other Re(V)–oxo– complexes [18]. The high concentration of electronic density along the Re–O axis strongly influences the positions of the adjacent chlorine atoms, which are pushed away (the mean of the O–Re–Cl angles is 104°), while this is not the case for the less electronegative P atoms. At the same time all Cl–Re–Cl angles maintain roughly normal values (mean 88°) so

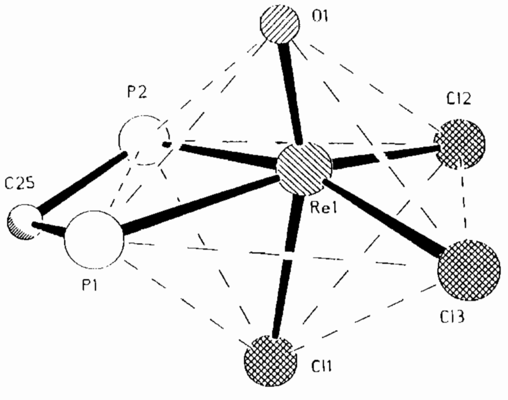


Fig. 2. The molecular structure of [ReOCl$_3$(dppm-*P*,*P*′)] (**1a**).

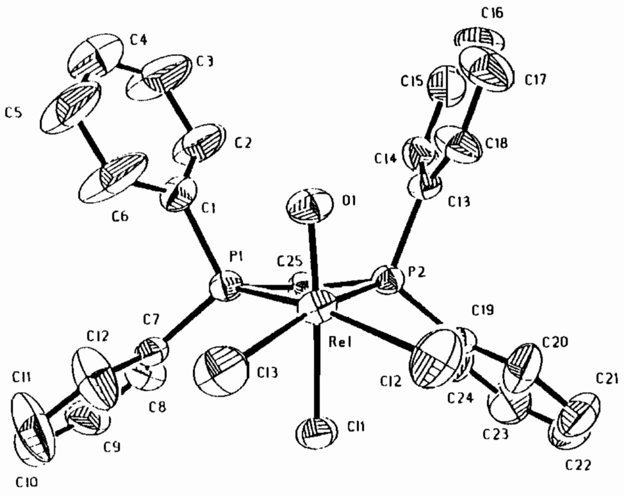


Fig. 3. The coordination polyhedron of Re(V) in **1a**.

that the rather rigid system formed by the three Cl atoms is bent toward the P atoms (the mean of the Cl(1)–Re–P angles is 76°). This feature also causes a strong deviation from linearity of the O–Re–Cl(1) sequence (162.8(2)). The Re–Cl distances are significantly different: the lengthening of the Re–Cl(1) bond (2.452(3) Å) *trans* to the multiply bonded oxygen can be ascribed to *trans* weakening, which is negligible in the Re–Cl bonds *trans* to phosphorus (mean 2.369 Å). The Re–P distances are equivalent and comparable with values found in other Re(V) octahedral complexes.

Bond distances in the chelate ligand show a significant difference between the P–C(aliphatic) (1.843(7) and 1.846(9) Å) and P–C(aromatic) (mean 1.800 Å) bonds. In addition, the Re–P–C(25) angles (95.2(3) and 95.6(3)°) are much smaller than the corresponding Re–P–C(phenyl) ones (mean 119°) and the P–C–P angle (97.7(4)°) is exceptionally small for a C(sp^3) atom. These features, as well as the small chelation angle, are reasonably ascribed to coordination, because of the impossibility of the ligand to form with Re a tetra-atomic metallacycle maintaining ideal values for bond angles. A mean plane calculation shows that the tetra-atomic cycle is almost planar and that C(25) is displaced by 0.33(1) Å from the ReP_2 plane.

Complex 3

The crystal structure of [$ReCl_4$(dppom-*P*,*O*)] is shown in Fig. 4 with the used numbering scheme. In this case the dppm molecule, though oxidized at P(1), acts as a chelating ligand forming, with the metal atom, a five-membered metallacycle. As expected, the P–O distance (1.523(8) Å) is longer than the corresponding distance (1.485(7) Å) of the monodentate ligand in **2**, where the P=O arm of the ligand remains uncoordinated [7]. As far as the Re–O bond is concerned, we can assume a bond order of one, or even less. In fact, the Re–O distance (2.087(7) Å) is longer than 2.04 Å which is assumed to be the theoretical value for an Re–O single bond [19]. On the other hand, the relative weakness of this bond is suggested by the fact that the Re–Cl(*trans* to O) distance (2.215(5) Å) is significantly shorter than all other Re–Cl distances in this compound (mean 2.351 Å). The Re–P bond length of 2.467(3) Å is comparable with values found in other Re(IV) complexes. It is noteworthy that all P–C bonds involving P(2), which is directly bonded to O, are 0.03 Å shorter than the corresponding P–C bonds involving P(1), which is directly bonded to Re.

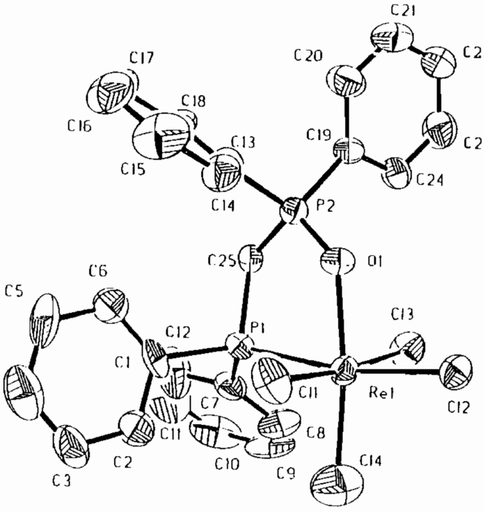


Fig. 4. The molecular structure of [$ReCl_4$(dppom-*P*,*O*)] (**3**).

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