Rhenium carbonyl complexes with bis(diphenyl phosphino)methane. X-ray crystal structure of $[ReBr(CO)_2(Ph_2PCH_2PPh_2)(Ph_2PCH_2P'Ph_2)\cdot 0.43[ReBr(CO)_2(Ph_2PCH_2PPh_2)(Ph_2PCH_2P(O)Ph_2)]$

Gabino A. Carriedo*, M. Luz Rodríguez
Depto. Química Organometálica, Facultad de Química, Universidad de Oviedo, Oviedo (Spain)
Santiago García-Granda and **Angel Aguirre**
Depto. Química Física y Analítica, Facultad de Química, Universidad de Oviedo, Oviedo (Spain)

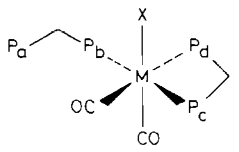
(Received July 23, 1990)

Abstract

The reaction of *fac*-$[ReBr(CO)_3(dppm)]$ (dppm $= Ph_2PCH_2PPh_2$) with dppm in refluxing xylene gave the dicarbonyl *cis-mer*-$[ReBr(CO)_2$(dppm-P)(dppm-P,P')] (**Id**) in which one dppm is monodentated. This compound reacted with oxygen in xylene at room temperature to give first the P-oxide derivative *cis-mer*-$[ReBr(CO)_2$(dppm-P)(dppm-P,PO)] (**II**), that subsequently decomposes with formation of $Ph_2P(O)CH_2P(O)PPh_2$. The X-ray structure of **I** has been determined in a crystal containing 30% of **II**. The reaction of **I** with $TlPF_6$ in CH_2Cl_2 gave the cationic *cis*-$[Re(CO)_2(dppm\text{-}P)_2]PF_6$ (**III**).

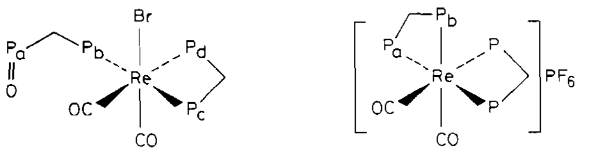
Introduction

Dicarbonyl complexes of the type $[MX(CO)_2$(dppm-P)(dppm-P,P')] (Fig. 1) (dppm $= Ph_2PCH_2PPh_2$, X = Cl, M = Mn (Ia) or Re (Ic)), having one monodentated dppm are useful precursors for the synthesis of bimetallic compounds with bridging dppm ligands [1].



I

M	X	
Mn	Cl	(**Ia**)
Mn	Br	(**Ib**)
Re	Cl	(**Ic**)
Re	Br	(**Id**)



II **III**

Fig. 1. The rhenium carbonyl complexes with dppm.

Earlier we reported the synthesis of the bromo complexes of manganese (**Ib**) from $MnBr(CO)_5$ and dppm [2], that could be used for the preparation of the CN and NCS derivatives, and other manganese carbonyls [2, 3]. Herein we report the synthesis and characterization of the rhenium analogue (**Id**).

Experimental

Unless otherwise stated all manipulations were performed under dry nitrogen. IR spectra were recorded on a Perkin-Elmer FT 1720-x spectrometer. ^{31}P NMR (^1H decoupled) are given in δ to high frequency of external 85% H_3PO_4 (J in Hz) and were recorded on a Bruker AC-300 instrument.

The compound *fac*-$[ReBr(CO)_3(dppm)]$ [4] was prepared as indicated below.

Preparation of fac-$[ReBr(CO)_3(dppm)]$

The compound $ReBr(CO)_5$ (1.1 g, 2.71 mmol) and the ligand dppm (1.04 g, 2.71 mmol) were stirred in toluene (20 ml) at 80–85 °C (water bath) for 14 h. Concentration *in vacuo* to *c*. 5 ml and addition of hexane in excess gave a white crystalline precipitate that was recrystallized from CH_2Cl_2/hexane. Yield

---

*Author to whom correspondence should be addressed.

0020-1693/90/$3.50

1.88 g (94.6%); m.p. 218 °C. *Anal.* Found: C, 45.4; H, 3.0. Calc.: C, 45.8; H, 3.0%. IR ν(CO) in CH_2Cl_2: 2031s, 1947s, 1907s cm^{-1}. ^{31}P NMR (CH_2Cl_2): -36 ppm (lit. -38.5 in $CHCl_3$ [4]).

Preparation of cis-mer-[ReBr(CO)$_2$(dppm-P)(dppm-P,P')] (Id)

A mixture of the complex *fac*-[ReBr(CO)$_3$(dppm)] (0.29 g, 0.395 mmol) and dppm (0.455 g, 1.185 mmol) in distilled and deoxygenated dry xylene (15 ml) was refluxed for 30 h. (Very small amounts of unreacted *fac*-tricarbonyl still remained but prolonged reaction times led to [Re(CO)$_2$(dppm)$_2$]Br and lowered the yield.) The resulting solution was concentrated to *c.* 8 ml and excess hexane was added to give **Id** as a white crystalline precipitate (0.32 g, 74.3%), that was recrystallized from CH_2Cl_2/hexane (final yield 62%); m.p. 250 °C. *Anal.* Found: C, 56.9; H, 4.1. Calc.: C, 57.2; H, 4.0%. Molar conductivity in 5×10^{-4} M acetone solution: 1.7 Ω^{-1} cm^2 mol^{-1}. IR ν(CO) in CH_2Cl_2: 1941s, 1862s (1946, 1871 in xylene; 1938, 1869 cm^{-1} in nujol). ^{1}H NMR in $CDCl_3$: 5.45m, 4.9m (CH_2, dppm-P), 3.91m, 2.84m (dppm-PP'). ^{31}P NMR in CH_2Cl_2 (see Fig. 1): -46.7 (doublet, Pd), -27.1 (doublet Pa), -23.3 (doublet, Pc), 6.22 (doublet of doublet of doublet, Pb); ^2J(ab) 43, ^2J(bc) 178, ^2J(bd) 26.

Preparation of cis-mer-[ReBr(CO)$_2$(dppm,P)(dppm-P,PO)] (II)

A solution of **Id** (0.2 g, 0.18 mmol) in xylene (30 ml) (with some suspension) was bubbled with dry air at room temperature for 12 days (checking by ^{31}P NMR revealed that some unreacted **Id** still remained). The solvent was evaporated and the residue was dissolved in CH_2Cl_2 (15 ml). Hexane (30 ml) was added slowly and the solution was concentrated *in vacuo* to *c.* 20 ml, causing the initiation of crystallization. The precipitation was completed by adding hexane (30 ml) with stirring. The liquid was decanted and the white residue was washed with hexane and dried *in vacuo*; yield 0.15 g, 75%; m.p. 255 °C. *Anal.* Found: C, 55.5; H, 4.2. Calc.: C, 56.4; H, 4.0%. IR ν(CO) in CH_2Cl_2: 1943s, 1867s, (1947, 1875 in xylene and 1938, 1869 cm^{-1} in nujol); ν(P=O): 1197 cm^{-1}. ^{1}H NMR (in $CDCl_3$): 5.5m, 4.9m (CH_2, dppm, P); 4.5m, 2.4m (CH_2, dppm-P,PO). ^{31}P NMR (in CH_2Cl_2) (Fig. 1): -44.8 (doublet, Pd), -23.5 (doublet, doublet, Pc), 3.6 (doublet, triplet, Pb), 24.6 (doublet, doublet, O=Pa), ^2J(ab) 27, ^2J(bc) 179, ^2J(bd) 27, ^4J(ac) 7.

From the mother liquor, by cooling at -20 °C, 0.012 g of a mixture of **II** and **Id** was recovered.

Preparation of cis-[Re(CO)$_2$(dppm)$_2$]PF$_6$ (III)

A mixture of *fac*-[ReBr(CO)$_3$(dppm)] (0.66 g, 0.80 mmol) and dppm (1.2 g, 3.12 mmol) in xylene (25 ml) was refluxed for 35 h to give **Id** mixed with some [Re(CO)$_2$(dppm)$_2$]Br. The solvent was removed *in vacuo* and the residue was dissolved in CH_2Cl_2 (25 ml). $TlPF_6$ (0.32 g, 0.9 mmol) was added to the solution and the mixture was stirred at room temperature for 7 days. The precipitate was removed by filtration, the solution was concentrated to *c.* 5 ml, and enough diethyl ether was added with stirring to give **III** as a crystalline precipitate (0.90 g). The compound was recrystallized from CH_2Cl_2/Et_2O; yield 0.78 g, 75.1%.

The compound was also prepared from pure **Id** and $TlPF_6$; m.p. 305 °C dec. *Anal.* Found: C, 54.5; H, 3.8. Calc.: C, 54.0; H, 3.8%. Molar conductivity (5×10^{-4} M acetone solution): 142 Ω^{-1} cm^2 mol^{-1}. IR ν(CO) in CH_2Cl_2: 1972s, 1914s; in nujol: 1945s, 1888s, 820 cm^{-1} (PF_6). ^{31}P NMR in CH_2Cl_2: -46.0 (triplet, Pb), -33.6 (triplet, Pa), J(ab) 34.

Structure determination of [ReBr(CO)$_2$(dppm-P)(dppm-P,P')]·0.43[ReBr(CO)$_2$(dppm-P)(dppm,P-PO)]

Crystal data: $C_{52}H_{44}BrO_{2.3}Re$, $M_r=971.8$, monoclinic, space group $P2_1/c$, $a=13.8832(2)$, $b=13.0460(2)$, $c=25.4374(3)$ Å, $\beta=94.869(1)°$, $V=4590.6$ Å^3, $Z=4$, $D_c=1.41$ Mg/m^3. Mo Kα radiation (graphite crystal monochromator, $\lambda=0.71073$ Å), μ(Mo Kα) = 35.81 cm^{-1}, $F(000)=1936$, $T=293$ K. Final conventional R factor = 0.024, $R_w=0.026$ for 6101 'observed' reflections and 546 variables.

Colorless crystal, $0.44\times0.27\times0.20$ mm in size. Mo Kα radiation used with a graphite crystal monochromator, ENRAF Nonius-CAD4 single crystal diffractometer. Unit cell dimensions determined from the angular settings of 25 reflections, $20°<\theta<25°$. Space group $P2_1/c$ from the systematic absences. A total of 8699 reflections measured, *hkl* range (-16, 0, 0) to (16, 15, 30), theta limits ($0°<\theta<25°$); ω–2θ scan technique with a variable scan rate and a maximum scan time of 60 s per reflection. Intensity of the primary beam checked by monitoring three standard reflections every 60 min. Drift correction factors between 0.99 and 1.03. On all reflections profile analysis performed [5]. Some double measured reflections were averaged, $R_{int}=\Sigma(I-\langle I\rangle)/\Sigma I=0.070$, 8099 unique reflections, 6101 'observed' with $I>3\sigma(I)$. Semi-empirical absorption correction, based on Ψ-scans, was applied [6], with minimum and maximum of 0.41 and 1.00. Lorentz and polarization corrections applied and the data were reduced to $|F_o|$ values. The structure was solved by Patterson methods using SHELXS86 [7] and Fourier synthesis Isotropic least-squares refinement, using SHELX [8], converged to $R = 0\ 064$ At this stage empirical absorption correction applied [9], maximum and minimum absorption corrections of 1 16 and 0 86

During least-squares refinement high electronic density close to P2 was observed from Fourier difference synthesis This peak was assigned to an oxygen atom (O3), due to a partial oxidation of the dppm ligand In order to determine the occupation factor of the oxidized ligand, the isotropic thermal factor of the oxygen was fixed to 0 07 Å^2 and its occupation factor was refined, converging to 0 30 Further anisotropic refinements followed by a Fourier difference synthesis allowed the location of some hydrogen atoms The positions of the hydrogen atoms were geometrically calculated and refined riding on their parent atoms with a common, refined, isotropic thermal parameter Final conventional agreement factors were $R = 0\ 024$, $R_w = 0\ 026$ for 6101 'observed' reflections and 546 variables The function minimized $\Sigma w(F_o - F_c)^2$, $w = 1/(\sigma^2(F_o) + 0\ 0003F_o^2)$, $\sigma(F_o)$ from counting statistics Maximum shift over error ratio in the last full matrix least-squares cycle less than 0 04 Final difference Fourier map showed no peaks higher than 0 62 e/Å^3 and deeper than $-0\ 64$ e/Å^3 Atomic scattering factors taken from the International Tables for X-ray Crystallography [10] Plots made with PLUTO program [11] Geometrical calculations made with PARST [12]

Results and discussion

The complex *fac*-[ReBr(CO)$_3$(dppm)] reacted slowly with dppm in refluxing xylene to give the dicarbonyl *cis-mer*-[ReBr(CO)$_2$(dppm-P)(dppm-P,P')] (**Id**) as a white crystalline solid in good yield This compound was easily characterized from the analytical and spectroscopic properties (see 'Experimental'), that closely resembled those of the chloro-derivative **Ic** [1] The IR spectrum in nujol mull of **Id** showed two strong ν(CO) absorptions at 1938 and 1869 cm^{-1} that differ markedly from those corresponding to the neutral chloro-compound with the same stoichiometry [ReCl(CO)$_2$(dppe)$_2$] (1837s, 1795s) that was not structurally characterized [13]

Although the compound **Id** could be recovered unaffected after bubbling air through a dichloromethane solution at room temperature for 7 days, it reacted slowly with dry air in xylene at room temperature to give the P-oxide derivative [ReBr(CO)$_2$(dppm,P)(dppm-P,PO)] (**II**) (Fig 1), in high yield If this reaction, that is faster in refluxing xylene, is continued further, the compound **II** de-

TABLE 1 Fractional positional parameters with e s d s in parentheses for **Id** 0 43 **II**

Atom	*x*	*y*	*z*
Re1	0 19386(1)	0 01958(1)	0 17583(1)
Br1	0 24060(3)	−0 07001(3)	0 08797(2)
O1	−0 0228(2)	−0 0203(3)	0 1543(1)
C2	0 0586(3)	−0 0040(3)	0 1602(2)
O2	0 1344(3)	0 1272(3)	0 2738(1)
C3	0 1586(3)	0 0864(3)	0 2369(2)
P1	0 20223(7)	0 18016(7)	0 12870(4)
C4	0 3143(3)	0 1926(3)	0 0951(2)
P2	0 33105(8)	0 29945(9)	0 04979(4)
P3	0 36632(7)	−0 00130(8)	0 20832(4)
C5	0 3561(3)	−0 1415(3)	0 2161(2)
P4	0 22203(7)	−0 14665(8)	0 21426(4)
C6	0 4083(3)	0 0494(4)	0 2728(2)
C7	0 3773(3)	0 1450(4)	0 2871(2)
C8	0 4148(4)	0 1894(5)	0 3341(2)
C9	0 4819(4)	0 1354(7)	0 3672(2)
C10	0 4763(3)	−0 0024(4)	0 3063(2)
C11	0 5127(4)	0 0405(6)	0 3530(2)
C12	0 4744(3)	0 0200(3)	0 1730(2)
C13	0 5297(3)	0 1065(4)	0 1837(2)
C14	0 6112(4)	0 1245(4)	0 1568(2)
C15	0 6371(4)	0 0580(5)	0 1195(2)
C16	0 5818(4)	−0 0268(5)	0 1079(2)
C17	0 4992(3)	−0 0467(4)	0 1337(2)
C18	0 1808(3)	−0 2605(3)	0 1775(2)
C19	0 2429(4)	−0 3304(4)	0 1579(2)
C20	0 2055(5)	−0 4138(4)	0 1278(2)
C21	0 1086(4)	−0 4260(4)	0 1190(2)
C22	0 0464(4)	−0 3587(4)	0 1393(2)
C23	0 0826(4)	−0 2741(4)	0 1674(2)
C24	0 1954(3)	−0 1752(3)	0 2818(2)
C25	0 2189(4)	−0 1037(4)	0 3208(2)
C26	0 2045(5)	−0 1248(5)	0 3729(2)
C27	0 1638(4)	−0 2172(5)	0 3862(2)
C28	0 1397(3)	−0 2871(4)	0 3481(2)
C29	0 1554(3)	−0 2682(3)	0 2960(2)
C30	0 1050(3)	0 2071(3)	0 0769(1)
C31	0 0511(3)	0 1271(3)	0 0540(2)
C32	−0 0195(3)	0 1461(4)	0 0129(2)
C33	−0 0334(4)	0 2445(4)	−0 0063(2)
C34	0 0212(4)	0 3238(4)	0 0160(2)
C35	0 0902(3)	0 3058(3)	0 0579(2)
C36	0 1999(3)	0 2917(3)	0 1722(1)
C37	0 1109(3)	0 3207(4)	0 1891(2)
C38	0 1066(4)	0 3939(4)	0 2282(2)
C39	0 1896(4)	0 4385(4)	0 2509(2)
C40	0 2775(4)	0 4120(4)	0 2336(2)
C41	0 2825(3)	0 3380(3)	0 1945(2)
C42	0 4555(3)	0 2798(4)	0 0332(2)
C43	0 5142(4)	0 3651(5)	0 0292(2)
C44	0 6051(4)	0 3555(6)	0 0104(3)
C45	0 6383(4)	0 2622(5)	−0 0041(2)
C46	0 5818(4)	0 1793(5)	−0 0003(2)
C47	0 4924(4)	0 1862(4)	0 0180(2)
C48	0 2681(3)	0 2590(3)	−0 0129(2)
C49	0 2337(3)	0 1617(4)	−0 0252(2)
C50	0 1903(3)	0 1398(5)	−0 0741(2)
C51	0 1804(4)	0 2159(5)	−0 1127(2)
C52	0 2140(4)	0 3115(5)	−0 1013(2)
C53	0 2563(4)	0 3356(4)	−0 0512(2)
O3	0 3186(8)	0 3984(9)	0 0649(4)

composes giving [$Ph_2P(O)CH_2P(O)PPh_2$] and other products not identified The compound **II** could be characterized by the analytical and spectroscopic data (see 'Experimental') Thus, the ^{31}P NMR was similar to that of **Id**, except for the chemical shift of the phosphorus bearing the oxygen atom (Pa) that was 51 7 ppm higher

In order to determine the structure of **Id**, an amount of this product was crystallized from CH_2Cl_2/hexane and one of the single crystals was chosen for an X-ray diffraction study The results (see 'Experimental' and Tables 1–3) clearly showed that in the crystal, the molecules of **Id** were packed together with molecules of **II** in a proportion of 7 3* Therefore, the structure shown in Fig 2 is the average molecular structure of **Id** 70% and **II** (30%) However, this structure should not be very different to that of **Id**, except for the parameters around the non-coordinated PPh_2 group, that bears the O atom in **II**

TABLE 2 Bond lengths Å with e s d s in parentheses for **Id** 0 43 **II**

Re1–Br1	2 604(1)
Re1–C2	1 944(4)
Re1–C3	1 846(4)
Re1–P1	2 417(1)
Re1–P3	2 548(1)
Re1–P4	2 411(1)
O1–C2	1 160(5)
O2–C3	1 130(5)
P1–C4	1 782(4)
C4–P2	1 824(4)
P2–O3	1 358(12)
P3–C5	1 845(4)
C5–P4	1 863(4)

TABLE 3 Bond angles (°) with e s d s in parentheses for **Id** 043 **II**

Br1–Re1–C2	89 7(1)
Br1–Re1–C3	178 1(1)
C2–Re1–C3	89 5(2)
Br1–Re1–P1	87 2(1)
C2–Re1–P1	94 7(1)
C3–Re1–P1	91 2(1)
Br1–Re1–P3	89 8(1)
C2–Re1–P3	163 2(1)
C3–Re1–P3	91 5(1)
P1–Re1–P3	102 0(1)
Br1–Re1–P4	84 5(1)
C2–Re1–P4	95 6(1)
C3–Re1–P4	97 3(1)
P1–Re1–P4	166 7(1)
P3–Re1–P4	67 7(1)
Re1–C2–O1	175 5(4)
Re1–C3–O2	178 0(4)
P1–C4–P2	119 0(2)
C4–P2–O3	122 1(5)
Re1–P3–C5	93 9(1)
P3–C5–P4	96 3(2)
Re1–P4–C5	98 0(1)

The coordination around the Re atom is nearly octahedral, but some angles, like P1–Re–P4 (166 7(1)°) and C2–Re–P3 (163 2(1)°) are very different from 180°, and the Re atom is not coplanar with the atoms P1, P3, P4 and C2, because P1 and P4 are 0 152(1) and 0 170(1) Å, respectively from the mean plane (the other deviations are $-0\ 0156(2)$ (Re), 0 004(4) (C2) and $-0\ 031(1)$ (P4)) In this 'equatorial plane' there are important distortions in the angles caused by the small bite angle P3–Re–P4 (67 7(1)) of the chelating dppm This angle and the torsion angle C5–P3–Re–P4 ($-13\ 9(1)$°) are normal for a chelating dppm [14] While the Re–Br and Re–P distances are within the expected values [15], a clear *trans* effect can be observed in the longer Re–P3 distance (2 548(1) Å) as compared with the other two Re–P distances (average 2 414(1)), and in the Re–C2 distance (1 944(4)), that is longer than the Re–C3 distance (1 846(4)) Perhaps the longer Re–P3 bond is related to the reactivity of the compounds of this type, that can generate bimetallic complexes with two bridgings dppm [1]

Similarly to the Mn analogue, compound **Id** reacted readily with $TlPF_6$ in CH_2Cl_2 at room temperature with precipitation of TlBr originating a vacant site that was occupied by the uncoordinated PPh_2 group, to give the cationic dicarbonyl *cis*-[$Re(CO)_2(dppm)_2$]PF_6 (**III**) The spectroscopic data were consistent with this formulation (see 'Experimental') The ν(CO) stretching frequencies were close to those reported for the long known salts of the analogous dicarbonyl cation with $Ph_2PCH_2CH_2PPh_2$(dppe) [16], and were *c* 25 cm^{-1} lower in the nujol mull spectrum than those measured in CH_2Cl_2 solution This rather large difference was also observed in the analogous [$Mn(CO)_2(dppm)_2$]PF_6 [2]

Acknowledgement

We thank the Spanish DGICYT for support

---

*Redissolving all the remaining crystals it was found by ^{31}P NMR that they were a mixture of **Id** (80%) and **II** (20%) Clearly the sample used for the crystallization had been made without careful exclusion of air

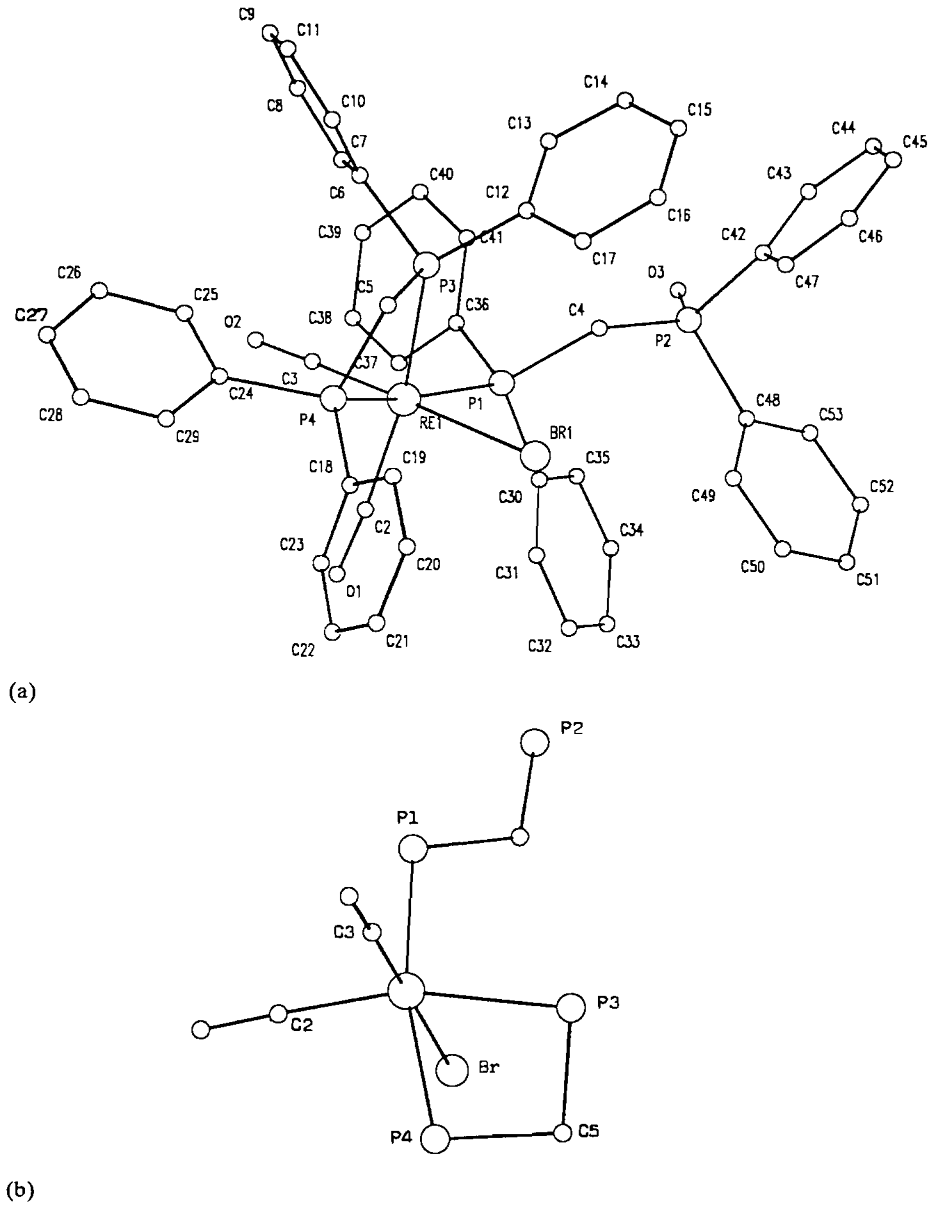


Fig 2 (a) Average molecular structure of **Id** (70%) and **II** (30%) with the atom numbering (b) Schematic view of the coordination around the rhenium atom

References

1 S W Carr, B L Shaw and M Thornton-Pett, *J Chem Soc, Dalton Trans*, (1987) 1763

2 G A Carriedo, V Riera and J Santamaría, *J Organomet Chem*, *234* (1982) 175

3 G A Carriedo, J B Parra-Soto, V Riera, M L Valín, D Moreiras and X Solans, *J Organomet Chem*, *326* (1987) 201

4 D A Edward and J Marshalsea, *J Organomet Chem*, *131* (1977) 73

5 D F Grant and E J Gabe, *J Appl Crystallogr*, *11* (1978) 114, M S Lehman and F K Larsen, *Acta Crystallogr, Sect A*, *30* (1974) 580

6 A C T North, D C Philips and F S Mathews, *Acta Crystallogr, Sect A*, *24* (1968) 351

7 G M Sheldrick, *Crystallographic Computing 3*, Clarendon Press, Oxford, 1985, p 175

8 G M Sheldrick, *SHELX*, a program for crystal structure determination, University Chemical Laboratory, Cambridge, U K, 1976

9 N Walker and D Stuart, *Acta Crystallogr, Sect A*, *39* (1983) 158

10 *International Tables for X-ray Crystallography*, Vol IV, Kynoch Press, Birmingham, 1974

11 W D S Motherwell, *PLUTO*, a Program for plotting molecular and crystal structures, University of Cambridge, U K, 1976
12 M Nardelli, *Comput Chem*, *7* (1983) 95
13 C A Hertzer, R E Myers, P Brant and R A Walton, *Inorg Chem*, *17* (1978) 2383
14 R J Puddephatt, *Chem Soc Rev*, *12* (1983) 99
15 A G Orpen, L Brammer, F H Allen, O Kennard, D G Watson and R Taylor, *J Chem Soc*, *Dalton Trans*, (1989) S1
16 M Freni, V Valenti and D Giusto, *J Inorg Nucl Chem*, *1* (1965) 2635