Structural and Electronic Comparison of 15- to 17-Electron Dichloro-complexes of Molybdenum and Rhenium: Electrochemical Behaviour and Crystal Structures of *trans*-$[ReCl_2(dppe)_2]A$ (A = Cl or BF_4; dppe = $Ph_2PCH_2CH_2PPh_2$), *trans*-$[ReCl_2(dppe)_2]$ and $[NBu^n{}_4]_2$[*trans*-$MoCl_2(dppe)_2][BF_4]_3$†

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The molecular structures of the complexes *trans*-$[ReCl_2(dppe)_2]A$ **1** (A = Cl or BF_4, dppe = $Ph_2PCH_2CH_2PPh_2$), *trans*-$[ReCl_2(dppe)_2]$ **2** and $[NBu^n{}_4]_2$[*trans*-$MoCl_2(dppe)_2][BF_4]_3$ **3** have been determined by X-ray crystallography. The metal–phosphorus and -chloride bond lengths are sensitive to the number of metal d electrons. The M–P (M = Mo or Re) distances *contract* by *ca.* 0.1 Å for each electron added. In contrast, the Re–Cl distances *increase* by *ca.* 0.1 Å upon addition of one electron (d^5 to d^6) but the Mo–Cl distances increase by less than 0.02 Å on addition of an electron (d^3 to d^4). These results are interpreted mainly in terms of π effects. Reduction of these complexes leads to cleavage of the metal–chloride bond which has been tracked by ramp-clamp voltammetry.

The reactivity of chloride-phosphine complexes of transition metals is often determined by the stability of their M–Cl and -P bonds towards dissociation. Therefore, investigation of the electronic factors which can labilize these bonds is of paramount importance in developing an understanding of the reactions of such complexes, particularly in catalysis where vacant co-ordination positions have to be made available for the activation of the substrate by the metal centre.[1]

X-Ray structural data can provide information relevant to the length and strength of such bonds, whereas electrochemical methods can be used to investigate the lability of metal–ligand bonds upon change in the metal oxidation state. In the present work we have used a combination of crystallographic and electrochemical measurements to investigate how the length and lability of M–P and -Cl bonds depend upon the d-electron count of the metal for a series of dichloride, 15- to 18-electron, phosphine complexes of molybdenum or rhenium with d^3 to d^6 metal centres. We have succeeded, as far as we are aware for the first time, in tracking the weakening of the M–Cl bond until its cleavage, upon stepwise reduction of the complexes along such a series.

Results and Discussion

Synthesis and Characterization.—The complex *trans*-$[ReCl_2(dppe)_2]A$ **1** (A = Cl, dppe = $Ph_2PCH_2CH_2PPh_2$) was prepared by a literature method,[2] and the tetrafluoroborate analogue **1** (A = BF_4) was obtained by replacement of the counter ion by use of $[Et_2OH][BF_4]$. The complex *trans*-$[ReCl_2(dppe)_2]$ **2** was isolated as a side-product in various reactions of *trans*-$[ReCl(N_2)(dppe)_2]$ with different substrates (such as nitriles), and therefore the original literature method, involving reduction of **1** (A = Cl)[3] with $NaBH_4$, was not followed.

The compound $[NBu^n{}_4]_2$[*trans*-$MoCl_2(dppe)_2][BF_4]_3$ **3** was produced by electrochemical oxidation of the parent *trans*-$[MoCl_2(dppe)_2]$ **4** which was prepared by a known method.[4]

The yellow complex salts **1** have a singlet resonance in their ^{31}P NMR spectra at δ 114.7 [in CD_2Cl_2, relative to $P(OMe)_3$], whereas **2** and **3**, also yellow, are paramagnetic, the former presenting a rhombic EPR spectrum showing hyperfine coupling to Re [$g_1 = 3.27$ ($A_1 < 30$G), $g_2 = 1.95$ ($A_2 = 235$G) and $g_3 = 1.31$ ($A_3 = 470$G)]. In their IR spectra, medium (m) or weak (w) intensity (M–Cl) stretching bands are observed at 320m for **1** (A = BF_4), 342w and 375w for **1** (A = Cl) and at 280m cm^{-1} for **2**.

It is noteworthy that the *trans* geometry is maintained along the 15-, 16- and 17-electron series of this study, as is clearly shown by X-ray crystallography (see below), in spite of the known variation of the relative stabilities of geometrical isomers of octahedral-type complexes with π-donor (or with π-acceptor) ligands. In particular, some extended-Hückel calculations[5] predict a greater stability of the *cis* relative to the *trans* isomer for 16-electron phosphine complexes with two π-donor ligands, such as $[MoO_2(PH_3)_4]^{2+}$. These predictions might be thought also to apply to the isoelectronic compounds *trans*-$[MoCl_2(dppe)_2]$ **4** and *trans*-$[ReCl_2(dppe)_2]^+$ **1** of this study, which have π-donor chloride ligands, but in fact they possess *trans* geometry. This geometry appears to be exclusive for these dichlorides; although a *cis* conformation has been reported for the crystal structure of $[MoCl_2(dppe)_2]$,[6] this structure has been reformulated as of the dihydride $[MoH_2Cl_2(dppe)_2]$.[7]

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Non-SI unit employed: G = 10^{-4} T.

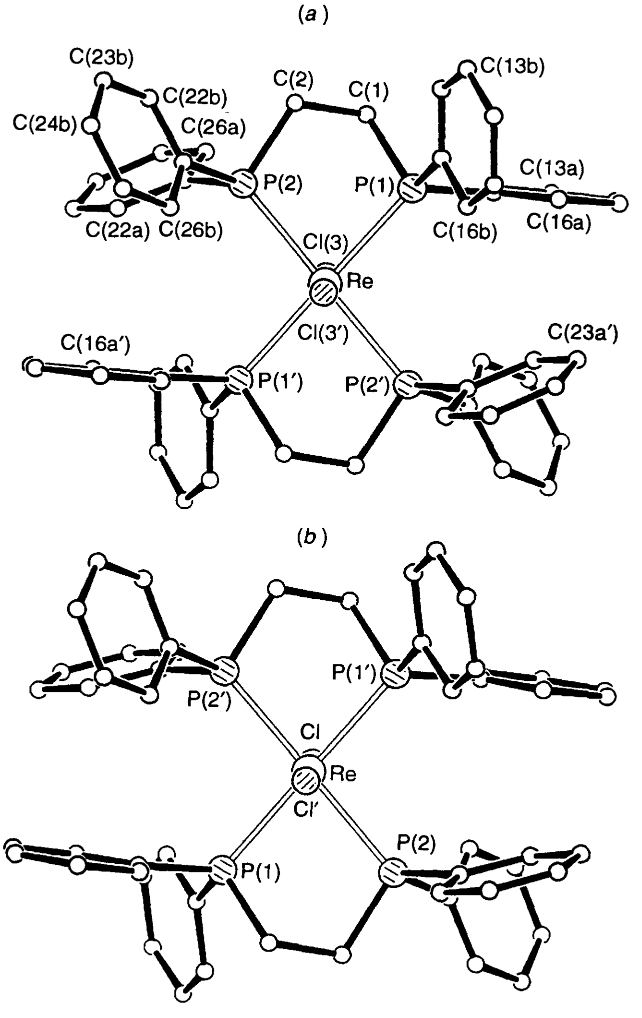

Fig. 1 Views of the rhenium complex cation 1 in (a) 1 (A = Cl) and (b) 1 (A = BF_4)

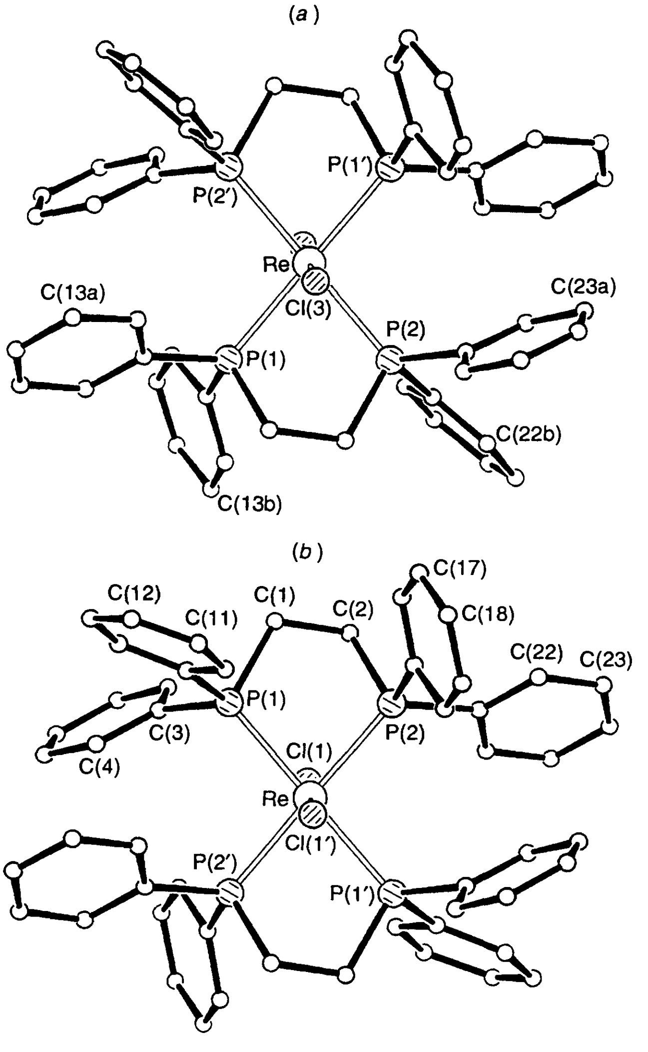

Fig. 2 Views of the rhenium complex molecules 2 in (a) 2·2thf and (b) 2·CD_2Cl_2

X-Ray Crystallography.—Structure of the rhenium complexes 1 (A = Cl *or* BF_4) *and* 2·*n*solv [solv = thf (*n* = 2) *or* CD_2Cl_2) (*n* = 1)]. The structure of the complex cations or molecules of Re in the four complexes 1 (A = Cl or BF_4) and 2·*n*solv [solv = tetrahydrofuran (thf) (*n* = 2) or CD_2Cl_2 (*n* = 1)] are depicted in Figs. 1 and 2. Atom coordinates are in Tables 1–4 and selected bond dimensions of these and related complexes are in Table 5.

Despite their common cation, the complexes *trans*-$[ReCl_2(dppe)_2]A$ 1 form crystals of quite different space-group symmetries (Table 6), clearly indicating the importance that the relatively small counter ions and the presence of solvent molecules can have in the packing of the molecules of these complexes. Differently solvated crystals of the neutral molecules, *trans*-$[ReCl_2(dppe)_2]$ 2, also have quite different packing arrangements depending on their solvents of crystallization.

The Re atom in each of the four rhenium complexes lies on a centre of symmetry and is six-co-ordinate with a distorted-octahedral ligand arrangement in which the bulky chelating dppe ligands form the equatorial plane and control the co-ordination geometry. In the uncharged complexes 2, the Re–Cl bond makes an angle of *ca.* 8.1° with the normal to the plane of the four P atoms, but in the cationic complexes 1 where the Cl atoms are drawn in closer to the Re atoms, that angle is reduced to *ca.* 4.2°.

In the two cationic complexes 1 the ligand conformations are very similar (Fig. 1). The phenyl rings of C(11a) and C(21a) [with atoms numbered as for 1 (A = Cl), Fig. 1(*a*)] are, very roughly, coplanar, and the rings of C(11b) and C(21b) of the opposite ligand, themselves approximately parallel, are perpendicular to the first pair and have H atoms directed towards the planes of the first pair, *e.g.* H(16b') is close to C(22a) and H(26b') is pointing towards C(12a). The channel around the Cl atoms is therefore U-shaped and the angular offset of the Cl atoms is determined by their various contacts with the phenyl rings.

The arrangements of the phenyl groups in the two uncharged complexes 2 are also virtually identical (Fig. 2) and differ from those of 1 principally in the orientations about the P–C bonds. There are, however, significant geometrical differences between complexes 1 and 2, particularly in the Re–P and Re–Cl distances which will be discussed below.

There are differences too in the torsion angles of the P–C–C–P linkages of the dppe ligands (Table 5). In each of the four complexes 1 and 2 the pair of dppe ligands is related by a centre of symmetry and thus has P–C–C–P torsion angles of opposite signs. All pairs may be described as *gauche* but those of complexes 1 have absolute values significantly larger than those of 2 resulting, presumably, from the differing interactions of the Cl atoms with the phenyl groups of the diphosphine ligands.

In complex 1 (A = BF_4) there are two independent sites occupied by the BF_4^- anions. In one, the B atom and one F atom lie on (or close to) a three-fold symmetry axis and each of the remaining F atoms is disordered over four possible sites. The second BF_4^- ion is not well resolved and lies, disordered, on one side or the other of a $\bar{3}$ symmetry site.

Table 1 Final atom coordinates (fractional × 10^4) for *trans*-$[ReCl_2(dppe)_2]Cl{\cdot}2MeOH$ **1** (A = Cl) with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
Re	0	0	0
P(1)	384.1(5)	334.1(4)	2161.1(4)
C(11a)	−784(2)	984(2)	2422(2)
C(12a)	−2209(3)	351(2)	2362(2)
C(13a)	−3118(3)	851(3)	2506(3)
C(14a)	−2597(3)	1979(3)	2742(3)
C(15a)	−1200(3)	2598(3)	2832(3)
C(16a)	−291(3)	2109(2)	2664(2)
C(11b)	2215(2)	1126(2)	2988(2)
C(12b)	2958(3)	714(2)	4262(2)
C(13b)	4328(3)	1381(3)	4862(3)
C(14b)	4952(3)	2447(2)	4217(3)
C(15b)	4222(3)	2859(2)	2965(2)
C(16b)	2869(2)	2193(2)	2339(2)
C(1)	56(2)	−1134(2)	3194(2)
C(2)	904(2)	−1860(2)	3098(2)
P(2)	659.3(5)	−1838.6(4)	1398.0(4)
C(21a)	−735(2)	−3192(2)	1050(2)
C(22a)	−684(3)	−3772(2)	211(2)
C(23a)	−1793(3)	−4772(2)	−109(3)
C(24a)	−2912(3)	−5182(2)	386(3)
C(25a)	−2964(3)	−4625(2)	1219(3)
C(26a)	−1874(3)	−3627(2)	1556(2)
C(21b)	2288(2)	−2209(2)	1598(2)
C(22b)	2638(2)	−3164(2)	2566(2)
C(23b)	3868(3)	−3464(2)	2745(3)
C(24b)	4732(3)	−2849(2)	1961(3)
C(25b)	4376(3)	−1931(2)	995(3)
C(26b)	3156(2)	−1602(2)	814(2)
Cl(3)	−2377.5(5)	−988.8(4)	−45.0(5)
Cl(4)	0	5000	5000
In the methanol molecule			
O(5)	2965(3)	4517(3)	5753(3)
C(51)	2581(4)	3759(4)	4978(4)

Molecules of solvent of crystallization were encountered in some of these species. For **1** (A = Cl) a methanol molecule is well defined and is hydrogen-bonded to the chloride anion: O(5) ··· Cl(4) 3.097(3), H(5) ··· Cl(4) 2.12 Å, O(5)–H(5) ··· Cl(4) 170.0°. The methyl group of the methanol makes good van der Waals interactions with the outer edges of the phenyl groups of the dppe ligand. In **2**·2thf the two thf solvent molecules are disordered in several orientations, but two atoms (probably the O and an adjacent C) occupy fixed sites common to all orientations. The O atom is 3.49 Å from C(13b) and 2.59 Å from H(13b) of the rhenium complex; other intermolecular contacts are normal C ··· C and C ··· H van der Waals contacts. In **2**·CD_2Cl_2 the two Cl atoms of the CD_2Cl_2 solvent molecules are related by a centre of symmetry and the C atom is disordered over two sites of half-occupancy about that centre.

Structure of $[NBu^n{}_4]_2[$*trans*-$MoCl_2(dppe)_2][BF_4]_3$ **3**. The structure of the complex cation of compound **3** is shown in Fig. 3. Atomic coordinates are in Table 7.

The crystal structure shows discrete ions of $[NBu^n{}_4]^+$, $[MoCl_2(dppe)_2]^+$ and BF_4^-, the last in two independent forms. The molybdenum complex ion has precise 222 symmetry: the Mo atom lies at the site of three mutually perpendicular, intersecting two-fold symmetry axes; the chloride atoms are on one of these axes, and each dppe ligand has a two-fold axis of symmetry passing through the central bond of the P–C–C–P linkage. This complex ion has approximately octahedral (or more precisely rectangular bipyramidal) co-ordination, with the two chloride atoms symmetrically above and below an almost planar arrangement of the four P atoms (and Mo atom). The distortions from the regular octahedral shape arise mainly from the chelating bite of the dppe ligand at the Mo (P–Mo–P 78.6°). The phenyl groups of opposite ligands are tightly bound in pairs: H(22a) of one phenyl ring is directed towards the centre of a ring of C(21b)–C(26b) of the other ligand; this contact is

Table 2 Final atom coordinates (fractional × 10^4) for *trans*-$[ReCl_2(dppe)_2]BF_4$ **1** (A = BF_4) with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Re	0	5000	0
Cl	514(1)	4602(1)	1466(2)
P(1)	−1250(1)	3917(1)	214(2)
C(1)	−1835(5)	4295(5)	687(9)
C(11)	−1340(5)	3269(5)	1378(8)
C(12)	−902(6)	2942(6)	1326(9)
C(13)	−970(7)	2415(7)	2158(11)
C(14)	−1485(8)	2243(7)	3097(11)
C(15)	−1920(6)	2560(7)	3182(9)
C(16)	−1857(6)	3069(6)	2325(9)
C(111)	−1764(5)	3336(5)	−1076(8)
C(112)	−1817(6)	2660(6)	−1242(9)
C(113)	−2184(7)	2236(6)	−2264(10)
C(114)	−2470(6)	2506(6)	−3111(9)
C(115)	−2416(6)	3184(6)	−2947(10)
C(116)	−2061(5)	3601(6)	−1934(9)
P(2)	−504(1)	5497(1)	1549(2)
C(2)	−1508(5)	4834(5)	1730(9)
C(21)	−465(5)	6360(5)	1179(9)
C(22)	52(6)	7007(6)	1732(11)
C(23)	105(7)	7678(7)	1401(13)
C(24)	−396(9)	7683(9)	496(15)
C(25)	−907(8)	7035(8)	−3(13)
C(26)	−948(6)	6386(6)	335(10)
C(211)	−211(5)	5651(6)	3135(8)
C(212)	476(6)	5793(6)	3477(8)
C(213)	716(6)	5965(7)	4673(9)
C(214)	238(7)	6004(7)	5515(9)
C(215)	−440(7)	5859(8)	5169(11)
C(216)	−670(6)	5687(8)	4004(10)
The (disordered) BF_4^- anions			
B(1)	6667	3333	3907(21)
F(11)	6667	3333	2639(10)
F(12)[a]	6584(40)	2805(26)	4501(31)
F(13)[a]	6565(43)	2571(25)	4125(33)
F(14)[a]	6375(18)	2583(27)	4292(45)
F(15)[a]	6792(22)	2763(32)	4272(53)
B(2)[b]	0	0	−533(31)
F(21)[c]	721(19)	402(41)	−1046(59)
F(22)[c]	461(70)	766(18)	−786(110)
F(23)[c]	96(114)	724(49)	−442(148)
F(24)[c]	490(28)	−54(38)	305(42)

[a] Site occupancy factor (s.o.f.) 0.25. [b] s.o.f. 0.5. [c] s.o.f. 0.17.

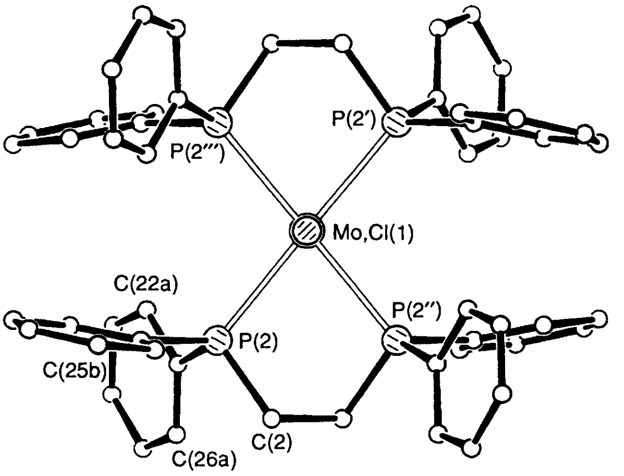

Fig. 3 View of the molybdenum complex cation in **3**

Table 3 Final atom coordinates (fractional × 10^4) for *trans*-$[\mathrm{ReCl_2(dppe)_2}]\cdot$2thf **2**·2thf with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Re	5000	5000	0
P(1)	4081(1)	3930(2)	1096(2)
C(1)	3121(4)	4235(5)	639(7)
C(11a)	4069(4)	2582(6)	903(6)
C(12a)	4251(5)	2181(7)	−221(8)
C(13a)	4238(5)	1154(7)	−384(8)
C(14a)	4049(5)	535(8)	524(8)
C(15a)	3873(5)	897(7)	1617(8)
C(16a)	3873(5)	1933(7)	1811(8)
C(11b)	3996(4)	4061(6)	2693(6)
C(12b)	3336(5)	4414(7)	3321(7)
C(13b)	3304(6)	4564(7)	4570(9)
C(14b)	3940(5)	4316(7)	5113(9)
C(15b)	4581(5)	3956(7)	4522(8)
C(16b)	4621(5)	3829(6)	3292(7)
C(2)	2984(4)	5343(6)	590(7)
P(2)	3887(1)	6090(2)	234(2)
C(21a)	3696(4)	6804(6)	−1068(6)
C(22a)	4028(5)	7728(6)	−1236(7)
C(23a)	3939(5)	8280(7)	−2274(8)
C(24a)	3511(6)	7865(8)	−3079(9)
C(25a)	3185(6)	6974(8)	−2960(9)
C(26a)	3269(5)	6437(7)	−1931(7)
C(21b)	3702(4)	7032(6)	1394(6)
C(22b)	3129(5)	7732(7)	1326(8)
C(23b)	2936(6)	8405(7)	2247(8)
C(24b)	3318(6)	8358(8)	3218(9)
C(25b)	3867(6)	7667(7)	3331(9)
C(26b)	4062(5)	6995(7)	2409(7)
Cl(3)	4390(1)	4470(2)	−1726(2)
In the disordered thf molecule			
O(71)	3384(6)	959(9)	4767(9)
C(72)	3112(9)	1697(10)	5628(13)
C(73)[a]	3453(18)	1437(27)	6726(27)
C(74)[b]	4270(11)	1103(15)	6104(16)
C(75)[b]	4181(10)	829(14)	4907(15)
C(73x)[c]	3731(14)	1829(17)	6456(20)
C(74x)[d]	3701(36)	630(50)	6539(52)
C(75x)[d]	3939(30)	332(39)	5428(44)

[a] s.o.f. 0.4. [b] s.o.f. 0.8. [c] s.o.f. 0.6. [d] s.o.f. 0.2.

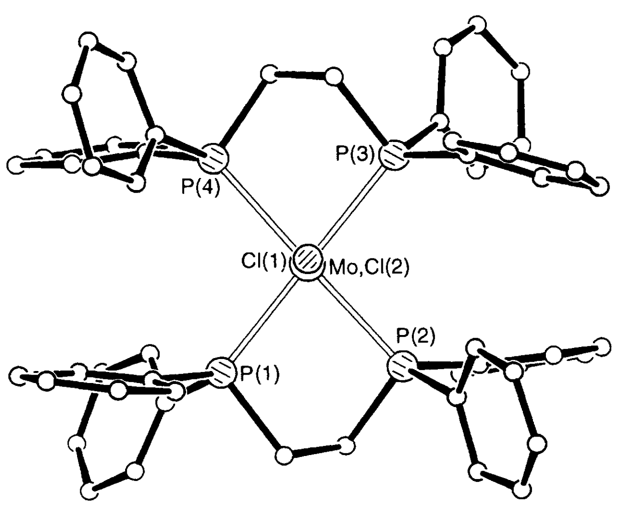

Fig. 4 View of the molybdenum complex molecule **4**[8]

Table 4 Final atom coordinates (fractional × 10^4) for *trans*-$[\mathrm{ReCl_2(dppe)_2}]\cdot\mathrm{CD_2Cl_2}$ **2**·$\mathrm{CD_2Cl_2}$ with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Re	0	0	0
Cl(1)	−2559(1)	−221(1)	751(1)
P(1)	−353(1)	−1568(1)	−897(1)
P(2)	−237(1)	−2153(1)	1599(1)
C(1)	−1082(5)	−3305(4)	268(4)
C(2)	−1481(5)	−3338(5)	1507(4)
C(3)	−1639(5)	−1109(4)	−1664(4)
C(4)	−1222(5)	−229(5)	−2839(4)
C(5)	−2233(6)	214(6)	−3371(5)
C(6)	−3654(6)	−196(6)	−2716(5)
C(7)	−4081(6)	−1069(6)	−1559(5)
C(8)	−3075(5)	−1541(5)	−1034(4)
C(9)	1114(5)	−2083(4)	−1912(4)
C(10)	2337(6)	−2306(5)	−1645(5)
C(11)	3481(6)	−2744(6)	−2335(5)
C(12)	3390(7)	−2970(6)	−3287(5)
C(13)	2143(7)	−2799(6)	−3545(4)
C(14)	1002(6)	−2361(5)	−2856(4)
C(15)	1346(5)	−3042(4)	1593(4)
C(16)	1460(6)	−4344(5)	1557(4)
C(17)	2738(7)	−4930(5)	1520(5)
C(18)	3864(6)	−4239(6)	1515(5)
C(19)	3749(6)	−2947(6)	1571(5)
C(20)	2517(5)	−2341(5)	1592(4)
C(21)	−1028(5)	−2319(4)	3147(4)
C(22)	−582(7)	−3205(6)	4032(4)
C(23)	−1162(8)	−3255(7)	5176(5)
C(24)	−2195(8)	−2437(6)	5460(5)
C(25)	−2657(6)	−1567(6)	4596(5)
C(26)	−2079(6)	−1504(5)	3443(4)
In the solvent ($\mathrm{CD_2Cl_2}$) molecule			
C(27)*	4078(15)	4824(13)	5091(12)
Cl(2)	4718(5)	6058(4)	4087(3)

* Occupancy 0.5.

repeated, by symmetry, in the three other pairs of phenyl groups. The chloride atoms are then enclosed in channels bounded by four phenyl groups.

The P–C–C–P linkages have *gauche* conformations with the C(2) atoms clearly above and below the equatorial plane. The two dppe ligands are related by a two-fold symmetry axis, therefore their P–C–C–P torsion angles have the *same* sign (and magnitude).

These arrangements are very similar to those found in the uncharged complex, *trans*-$[\mathrm{MoCl_2(dppe)_2}]\cdot\mathrm{CH_2Cl_2}$[8] **4** except that there is no precise crystallographic symmetry in that complex molecule, Fig. 4.

In the $[\mathrm{NBu^n}_4]^+$ ion in complex **3** a single two-fold symmetry axis passes through the N atom, so that there are two independent butyl chains. One chain, C(61)–C(64) is well defined, but there is site disorder in the other chain which has two possible positions, C(65)–C(67) or C(71)–C(73), with C(68) as the common methyl group to both. The N atom is also shifted from the symmetry axis when one of the C(71)–C(73) chains is occupied. The fully occupied chain C(61)–C(64) has an extended form with *trans*-conformations along its length. The other chain, in either orientation, has a much less regular shape, with a variety of *trans* and *gauche* conformations.

One of the two independent $\mathrm{BF_4}^-$ anions is well defined and lies on another site of 222 symmetry. The second anion is not only disordered in two orientations in overlapping positions, but this site is close to a two-fold symmetry axis such that only one of the pair of symmetry sites can be occupied.

Interactions between the ions are all at van der Waals distances.

Metal–Phosphorus Bond Lengths.—A general and significant decrease of the M–P bond length of about 0.1 Å results upon addition of each electron along the metal d^3, d^4 and d^5 series, corresponding to the 15-, 16- and 17-electron complex species

Table 5 Selected and averaged bond dimensions (bond lengths in Å, angles in °) with e.s.d.s in parentheses

Complex	M–P	M–Cl	P–M–P	P–M–Cl	P–C_{Ph}	P–$C_{bridging}$	M–P–C_{Ph}	M–P–$C_{bridging}$	C_{Ph}–P–C_{Ph}	C_{Ph}–P–C_{br}	Cl–M–Cl	P–C–C–P	Angle of Cl • • • Cl with normal to P_4 plane
1 (A = Cl) d^4	2.4875(4)	2.323(1)	80.43(1)	86.73(2)	1.834(2)	1.837(2)	122.2(1)	105.5(1)	103.9(1)	101.9(1)	180.0	−49.6(2)	3.9
	2.5052(4)			87.33(2)	1.827(2)	1.852(2)	116.1(1)	108.6(1)	101.5(1)	105.3(1)			
					1.822(2)		114.6(1)			104.6(1)			
					1.827(2)		124.6(1)			100.7(1)			
mean:	2.496(9)			87.0(3)	1.827(2)	1.845(7)	119.4(24)	107.1(16)		103.0(8)			
1 (A = BF_4) d^4	2.473(4)	2.316(4)	80.9(2)	85.9(2)	1.808(12)	1.834(12)	114.9(4)	105.1(4)	104.4(5)	106.2(5)	180.0	43.9(9)	4.5
	2.494(4)			87.7(2)	1.832(11)	1.862(11)	116.3(4)	108.5(4)	101.3(5)	103.8(6)			
					1.815(12)		122.4(4)			102.2(5)			
					1.829(11)		123.7(4)			100.5(5)			
mean:	2.483(11)			86.8(9)	1.822(6)	1.849(14)	119.3(22)	106.8(17)		103.1(9)			
2·2thf d^5	2.408(2)	2.435(2)	79.8(1)	85.6(1)	1.828(8)	1.847(7)	123.2(3)	107.1(2)	102.5(3)	99.5(3)	180.0	29.4(7)	8.7
	2.424(2)			81.8(1)	1.821(7)	1.876(6)	115.9(3)	110.0(3)	100.9(4)	104.0(3)			
					1.826(8)		116.4(3)			105.9(3)			
					1.838(8)		125.3(3)			97.6(3)			
mean:	2.416(8)			83.7(19)	1.828(4)	1.860(14)	120.2(24)	108.5(15)		101.7(12)			
2·CD_2Cl_2 d^5	2.421(1)	2.419(1)	80.11(3)	83.54(3)	1.832(4)	1.868(4)	114.8(1)	109.7(1)	103.5(2)	104.6(2)	180.0	−35.8(4)	7.6
	2.402(1)			85.01(3)	1.843(4)	1.846(4)	123.0(1)	106.6(1)	102.6(2)	98.7(2)			
					1.825(4)		117.4(1)			104.9(2)			
					1.841(4)		121.5(1)			101.5(2)			
mean:	2.411(9)			84.3(7)	1.835(4)	1.857(11)	119.2(19)	108.1(16)		102.6(9)			
3 d^3	2.598(1)	2.376(2)	78.62(4)	88.84(3)	1.825(6)	1.833(5)	117.1(2)	105.5(2)	105.5(2)	104.8(3)	180.0	65.7(4)	0.0
					1.829(6)		117.9(2)			104.5(3)			
mean:					1.827(2)		117.5(4)			104.9(3)			
4[8] d^4 mean:	2.495(9)	2.391(5)	80.5(2)	87.4(9)/ 92.6(8)	1.81(1)	1.84(1)	120.9(3)	104.7(6)		102.6(5)	176.9(6)	−64.7(14)	0.0

Table 6 Crystal data [λ(Mo-K$\bar{\alpha}$) = 0.710 69 Å]

	1 (A = Cl)	**1** (A = BF_4)	**2**·2thf	**2**·CD_2Cl_2	**3**
Complex formula (all are *trans*)	$[ReCl_2(dppe)_2]Cl\cdot 2MeOH$	$[ReCl_2(dppe)_2]BF_4$	$[ReCl_2(dppe)_2]\cdot 2thf$	$[ReCl_2(dppe)_2]\cdot CD_2Cl_2$	$[NBu^n{}_4]_2[MoCl_2(dppe)_2][BF_4]_3$
Elemental formula	$C_{54}H_{36}Cl_3O_2P_4Re$	$C_{52}H_{48}BCl_2F_4P_4Re$	$C_{60}H_{64}Cl_2O_2P_4Re$	$C_{53}H_{48}Cl_4D_2P_4Re$	$C_{84}H_{120}B_3Cl_2F_{12}MoN_2P_4$
M	1153.5	1140.8	1198.2	1140.9	1709.0
Crystal system	Triclinic	Trigonal	Monoclinic	Triclinic	Orthorhombic
Space group (no.)	$P\bar{1}$ (no. 2)	$P\bar{3}$ (no. 147)	$P2_1/a$ (equiv. to no. 14)	$P\bar{1}$ (no. 2)	*Fddd* (no. 70)
Cell dimensions					
a/Å	10.411(2)	20.935(1)	17.409(4)	10.058(2)	28.002(5)
b/Å	12.461(1)	20.935(1)	13.465(1)	10.495(1)	33.637(6)
c/Å	11.425(1)	11.039(1)	11.401(2)	12.940(1)	18.821(2)
α/°	71.855(7)	90	90	68.84(1)	90
β/°	112.700(11)	90	84.25(2)	70.87(1)	90
γ/°	111.059(9)	120	90	88.59(1)	90
U/Å^3	1250.1	4189.7	2659.0	1196.7	17 727.1
Z	1[a]	3[b]	2[c]	1[c,d]	8[e]
D_c/g cm^{-3}	1.532	1.36	1.496	1.58	1.281
F(000)	582	1710	1218	573	7176
μ(Mo-Kα)/cm^{-1}	27.9	24.2	25.8	30.8	3.4

[a] Rhenium cation and Cl anion lie on centres of symmetry. [b] Rhenium cation lies on a centre of symmetry; BF_4^- ions are disordered, one near a $\bar{3}$ symmetry point, the other about a three-fold symmetry axis. [c] Rhenium complex lies on a centre of symmetry. [d] Solvent molecules lie disordered about centres of symmetry. [e] The Mo atom lies on a site of 222 symmetry; N is on a two-fold symmetry axis; one BF_4^- ion is on a 222 symmetry site, the second is disordered about a two-fold symmetry axis.

trans-$[MoCl_2(dppe)_2]^+$ **3**, (d^3), *trans*-$[MoCl_2(dppe)_2]$ **4** (d^4)[8] and *trans*-$[ReCl_2(dppe)_2]^+$ **1** (d^4), and *trans*-$[ReCl_2(dppe)_2]$ **2** (d^5), respectively. The average M–P distances for these species are listed in Table 5.

An analogous decrease (0.072 Å) of the M–P average distance has been said to result from the reduction of Tc^{III} to Tc^{II} in *trans*-$[TcCl_2(dppe)_2]^{+/0}$; average Tc–P bond lengths are 2.500(1) and 2.428(1) Å, for the cation and the neutral species respectively.[9] Similar decreases are also observed for the redox pairs $[MCl_2(Me_2PCH_2CH_2PMe_2)_2]^{n+}$ (M = Cr or Mo; n = 0 or 1) and on increasing the electronic count along the series $[MCl_4(PR_3)_2]$ (M = Mo, Re, Os, Ir or Pt).[10] This observed shortening of the M–P distance upon increasing the number of available metal d electrons is consistent with increased π-electron release from filled metal d_π orbitals to empty phosphorus 3d orbitals.[10]

An alternative explanation for the shortening of the M–P bond distance as the electron complement is increased is that d_π-to-(P–C) σ^* donation occurs. This has been considered by others[10] to account for the lengthening of P–C bonds in some tertiary phosphine complexes. However, although the data obtained for our rhenium complexes tend to support such d_π–σ^* interaction, this interpretation is not valid for the molybdenum redox partners (Table 5). Here we are comparing pairs of complexes with 15/16 and 16/17 electron configurations; at the 17/18-electron level d_π–σ^* interaction may be more significant.

Orpen and Connelly[10] have noted that, on oxidation of the metal, the M–P bond length increases (as the π-back donation from M to P is diminished) and that this is accomplished by a decrease in P–C bond lengths and an increase in C–P–C angles. Although there are some quite wide ranges of values in these dimensions in Table 5, the averaged values for our series of complexes show trends towards supporting the above conclusions. Nevertheless, the role of σ donation in determining the M–P bond lengths is clearly important: it is noteworthy that the mean Re–P distances for complexes **1** [2.496(9) and 2.483(11) Å for A = Cl or BF_4, respectively] are considerably longer than that quoted, 2.438(2) Å, for the related complex *trans*-$[ReCl_2(Me_2PCH_2CH_2Me_2)_2]PF_6$ which contains a stronger σ-electron donor but weaker π-acceptor diphosphine.[11]

Metal–Chlorine Bond Lengths.—In contrast to the above-mentioned *contraction* of the M–P distance upon reduction, a

Table 7 Final atomic coordinates (fractional $\times 10^4$) for $[NBu^n{}_4]_2$-[*trans*-$MoCl_2(dppe)_2][BF_4]_3$ **3** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Mo	1250	1250	1250
Cl(1)	2098.7(7)	1250	1250
P(2)	1231.2(5)	652.5(4)	2123.9(7)
C(21a)	654(2)	522(2)	2510(3)
C(22a)	381(2)	823(2)	2810(3)
C(23a)	−49(2)	738(2)	3127(3)
C(24a)	−222(2)	355(2)	3143(4)
C(25a)	48(3)	58(2)	2847(4)
C(26a)	480(2)	134(2)	2527(3)
C(21b)	1653(2)	654(2)	2867(3)
C(22b)	1504(2)	737(2)	3548(3)
C(23b)	1837(3)	769(2)	4093(3)
C(24b)	2315(3)	718(2)	3945(4)
C(25b)	2465(3)	632(2)	3275(4)
C(26b)	2136(2)	602(2)	2734(3)
C(2)	1401(2)	218(2)	1594(3)
B(1)[a]	3774(7)	1015(5)	3552(8)
F(11)[a]	4056(11)	722(8)	3232(16)
F(12)[a]	4047(12)	1254(9)	3935(17)
F(13)[a]	3500(10)	1175(9)	3039(12)
F(14)[a]	3473(13)	793(11)	3991(18)
B(2)[b]	3725(9)	1065(7)	3655(14)
F(21)[b]	4177(6)	1180(6)	3493(11)
F(22)[b]	3488(9)	1355(7)	4015(14)
F(23)[b]	3521(8)	992(7)	3012(12)
F(24)[b]	3722(12)	730(7)	4062(13)
B(5)	6250	1250	1250
F(51)	5965(2)	1015(2)	1676(3)
N(6)	4441(3)	1250	1250
C(61)	4748(3)	1362(3)	1896(5)
C(62)	5039(3)	1748(3)	1784(5)
C(63)	5342(5)	1822(4)	2459(5)
C(64)	5628(5)	2177(4)	2381(7)
C(65)[c]	4122(4)	816(3)	1294(7)
C(66)[c]	3846(5)	641(4)	686(7)
C(67)[c]	3537(5)	296(4)	982(8)
C(68)	3091(3)	405(3)	1305(7)
C(71)[c]	4122(5)	982(4)	1697(8)
C(72)[c]	3753(7)	846(5)	1218(10)
C(73)[c]	3441(7)	500(6)	1619(10)

[a] s.o.f. 0.2. [b] s.o.f. 0.3. [c] s.o.f. 0.5.

lengthening of the M–Cl bond of *ca.* 0.11 Å occurs for the rhenium complexes, on the addition of one electron (Table 5). We also note differences, significant but of a much smaller order (*ca.* 0.016 Å), in the Re–Cl distances in our two complexes **2**; perhaps these are related to differences in packing in the crystals.

An identical increase of the M–Cl distance, by 0.105(2) Å, has been observed to result from the reduction of Tc^{III} to Tc^{II} for the related pair *trans*-$[TcCl_2(dppe)_2]^{+/0}$, with Tc–Cl bond lengths of 2.319(1) and 2.424(1) Å, for the cation and the neutral complex, respectively.[9] Similar increases in a range of metal–halide phosphine complex redox pairs have been noted.[10]

On the other hand, reduction of the molybdenum compound **3**, with a d^3 metal atom, to the corresponding neutral complex **4**, d^4, results in a much smaller increase in the metal–chlorine distance, from 2.376(2) to 2.391(5) Å (Table 5); this difference is, in fact, similar in magnitude to the 'packing' difference noted above in the rhenium complexes **2**. The corresponding increase for the redox pair $[MoCl_2(Me_2PCH_2CH_2PMe_2)_2]^{n+}$ (n = 0 or 1) is rather larger, from 2.404(2) to 2.439(1) Å.[10]

A shortening of the M–P distance with a concomitant elongation of the M–Cl bond is observed for the conversion of *trans*-$[ReCl_2(dppe)_2]^+$ **1** (d^4) into *trans*-$[ReCl_2(dppe)_2]$ **2** (d^5). Moreover, addition of a further electron leads to a Re–Cl bond cleavage (see below), as is also detected upon reduction of *trans*-$[MoCl_2(dppe)_2]$ **4** (d^4), which has more labile M–Cl bonds than the isoelectronic complex **1** (see below).

Although for the isoelectronic complexes $[ReCl_2(dppe)_2]^+$ **1** and $[MoCl_2(dppe)_2]$ **4** the average M–P distances are very similar, a considerably shorter M–Cl bond length is observed for **1** than for **4**. This conceivably results from the higher net atomic charge at the Re compared to the Mo atom, which would favour both σ- and π-electron release from the ligands to the metal, but disfavours the π-back bonding from the metal to the phosphine ligands. The two types of effect would cancel in the case of the phosphine ligands, but be additive in the case of the chloride ligands.

Cyclic Voltammetry Cleavage of M–Cl *Bonds.*—Cyclic voltammetry in a thf electrolyte at room temperature shows that the 16-electron cation *trans*-$[ReCl_2(dppe)_2]^+$ **1** undergoes a diffusion-controlled, reversible, one-electron reduction to give the stable, 17-electron, uncharged complex **2**, as noted by others,[12] with ${}^{I}E_{\frac{1}{2}}{}^{red} = -0.15$ V *versus* the saturated calomel electrode (SCE). A second, partially reversible, one-electron reduction occurs at ${}^{II}E_{\frac{1}{2}}{}^{red} = -1.29$ V. The redox process which occurs at the latter potential is Re–Cl bond cleavage to generate the known 16-electron species $[ReCl(dppe)_2]$.[13] As expected in view of this, ramp-clamp voltammetry at the second cathodic potential in presence of Bu^tNC generates the known[14] complex *trans*-$[ReCl(CNBu^t)(dppe)_2]$.

Under similar conditions to those used for the reduction of complex **1**, the uncharged, 16-electron dichlorides *trans*-$[MCl_2(dppe)_2]$ **4** (M = Mo or W) undergo partially reversible, one-electron reductions at substantially more negative potentials than that of **1** [$E_{\frac{1}{2}}{}^{red} = -1.68$ (Mo) and -1.73 V (W) *versus* SCE].[15]

The 17-electron anions produced by these reductions are unstable and the M–Cl bond is cleaved at room temperature to give the $MCl(dppe)_2$ species, which is known[15] to add a variety of substrates such as isocyanides, N_2, CO, H_2 or solvents such as thf.

The cathodically induced cleavage of the metal–chloride bonds in these compounds upon addition of an electron is in accord with the crystallographic data and the π-molecular orbital interpretation discussed above.

The difference of net charge of one unit between the isoelectronic, 16-electron complexes of Re^{III} (**1**) and Mo^{II} (**3**) places the lowest unoccupied molecular orbital (LUMO) of **1** about 1.5 eV (*ca.* 2.4×10^{-19} J) lower in energy than that of **3**. The higher effective positive charge on the Re atom in **1** is also consistent with its low-spin configuration compared to the high-spin configuration of Mo in **3**.

Experimental

All materials were handled using standard Schlenk techniques under dinitrogen or argon. Solvents were rigorously dried and distilled under dry dinitrogen prior to use. Infrared spectra were recorded on Perkin Elmer 577 or 683 spectrometers, NMR spectra on a JEOL FX90Q or Varian 300 spectrometers and EPR spectra on a Bruker ER-300SH spectrometer fitted with an ESR-9 crystal and interfaced to an ESP 1600 computer.

The electrochemical experiments were carried out either on a HI-TEK DT 2101 potentiostat/galvanostat with a HI-TEK PPRI waveform generator, or on an EG & G PAR 173 potentiostat/galvanostat with an EG & G PARC 175 universal programmer. Cyclic voltammetry was undertaken in 0.2 mol dm^{-3} $[NBu^n_4][BF_4]$–thf, in a two-compartment three-electrode cell, at a platinum-wire working electrode, probed by a Luggin capillary connected to a silver-wire pseudo-reference electrode; a platinum or tungsten auxiliary electrode was employed.

The ramp-clamp voltammograms were recorded using a clamp of 17 s duration at the cathodic wave of the complex under study. Controlled-potential electrolyses were carried out in a three-electrode H-type cell with a platinum-gauze or a mercury-pool working electrode (for anodic or cathodic processes, respectively), and with a platinum-gauze counter electrode, in compartments separated by a glass frit. The potentials are quoted relative to the SCE by using the ferrocene–ferrocenium couple as an internal reference.

Microanalyses were by Mr. C. J. Macdonald of the AFRC Nitrogen Fixation Laboratory or by Mr. L. Vieira of the Complexo 1.

Complexes **1** (A = Cl)[2] and **4**[4] were prepared by literature methods, whereas **1** (A = BF_4) was obtained by replacement of the anion of **1** (A = Cl), in CH_2Cl_2, in the presence of a four-fold molar excess of $[Et_2OH][BF_4]$ followed by concentration of the solution and addition of Et_2O.

Complex **2** is frequently obtained, although in low yields, as a side-product of various reactions of *trans*-$[ReCl(N_2)(dppe)_2]$ with different substrates, in particular nitriles. The crystalline materials which were structurally analysed were obtained by recrystallization of such samples from CH_2Cl_2–Et_2O mixtures.

Complex **3** was produced by anodic controlled-potential electrolysis of *trans*-$[MoCl_2(dppe)_2]$ in 0.2 mol dm^{-3} $[NBu^n_4][BF_4]$–thf, and was isolated upon concentration and addition of methanol.

Crystal Structure Determinations.—*trans*-$[ReCl_2(dppe)_2]Cl{\cdot}2MeOH$ **1** (A = Cl). Crystals of this complex are beautiful yellow prisms which deteriorate slowly in air. Samples were mounted on glass fibres, in air, and coated in epoxy resin; the crystal used for diffractometer measurements was 0.35 × 0.35 × 0.40 mm. Preliminary photographic examination showed the crystals to diffract well.

Accurate cell parameters were calculated from the settings of 25 reflections (θ *ca.* 14.5°) centred on an Enraf-Nonius CAD4 diffractometer with monochromated Mo-Kα radiation. Intensities of 4891 unique reflections within the range θ 1–26° were recorded and of these only three had intensities less than $2\sigma_I$. Intensities of 29 medium-strong reflections (with θ in the range 1–15°, and of widely varying indices) and their Friedal pairs were measured over a range of ψ positions, for the calculation of a semiempirical absorption correction. From the monitoring of three reflections at intervals throughout the data collection, no deterioration of this crystal was observed.

During processing of the intensity data, corrections were made for Lorentz polarization effects, for absorption (by semiempirical ψ-scan methods) and to eliminate negative net intensities (by Bayesian statistical methods). The data were entered into the SHELX system[16] for structure determination and refinement.

Table 8 Crystallographic experimental details: data collection and structure refinement

	1 (A = Cl)	**1** (A = BF_4)	**2**·2thf	**2**·CD_2Cl_2	**3**
Crystal shape, colour	Yellow prisms (deteriorate slowly in air)	Pale yellow needles	Yellow, trigonal prisms	Yellow prisms	Red, reformed octahedrons
Crystal size (mm)	0.35 × 0.35 × 0.40	0.10 × 0.10 × 0.70	0.12 × 0.14 × 0.19	0.22 × 0.18 × 0.18	*ca.* 0.30 × 0.45 × 0.50
Crystal mounting	On glass fibre, coated in epoxy resin	In capillary, sealed under dinitrogen	In capillary	In capillary, sealed under argon	On glass fibre, coated with epoxy resin
On diffractomer, range of θ/°	2.5–26	1.5–25	1.4–20	2.0–25	1.5–25
No. of unique reflections	4891	6045	2471	4202	3896
Diffraction intensities corrected for:					
Lorentz polarization effects	Yes	Yes	Yes	Yes	Yes
deterioration, with total decrease in monitored intensities *	No	No	No	No	Yes, 7.7%
absorption, with minimum, maximum transmission factors	Yes, 0.78, 0.97	Yes, 0.86, 1.00	Yes, 0.92, 0.98	No	Yes, 0.98, 1.00
to eliminate negative intensities	Yes	No	Yes	No	Yes
No. of reflections used in refinement having $I > n\sigma_I$	4884 (omitting 7 low-angle reflections)	3440	2471	4069	3536
n	0	1.5	0	1	2
Treatment of H atoms in the refinement process	In dppe ligands, included in idealized positions. In MeOH, located and refined with geometrical restraints	In idealized positions, with common U_{iso}	In dppe ligands, included in idealized positions	In dppe ligands, located in difference maps; held fixed with common U_{iso} = 0.075 Å^2	In dppe ligands, included in idealized positions
Final R	0.016	0.051	0.046	0.032	0.081
Final R'	0.017	0.075	0.039	0.040	0.079
Weighting scheme, w	σ_F^{-2}	$(\sigma_F^2 + 0.004\,06F^2)^{-1}$	σ_F^{-2}	σ_F^{-2}	1
Atoms refined anisotropically	Re, P, Cl, C, O (solvent)	All non-hydrogen atoms except those in disordered BF_4^- ions	Re, P, Cl, O (solvent)	All non-H atoms	All non-H atoms except those in disordered BF_4^- ions

From density calculations, it was estimated that there would be one rhenium complex ion per unit cell. The E statistics suggested that the structure is centrosymmetric and therefore that the space group is $P\bar{1}$. A Patterson map confirmed that the Re atom lies on a centre of symmetry (*e.g.* at the origin), and showed peaks corresponding to interatomic vectors from the Re atom to two phosphorus atoms, one co-ordinated Cl atom and a separate Cl^- ion (at another centre of symmetry 0, $\frac{1}{2}$, $\frac{1}{2}$). An electron-density Fourier map, phased by these five atoms, showed most of the remaining non-hydrogen atoms of the structure. A succeeding Fourier difference map located the missing atoms of the complex and the atoms of a solvent methanol molecule.

Refinement of the atomic parameters, by full-matrix least-squares methods, was rapid, and many hydrogen atoms were clear in difference maps. Coordinates for the H atoms in the dppe ligands were calculated for idealized positions and these atoms were set to 'ride' on the C atoms to which they were bonded. The H atoms of the methanol molecules were taken from a difference map and their parameters were allowed to refine but with some geometrical restraints. All the non-hydrogen atoms were allowed anisotropic thermal parameters.

At convergence, R = 0.016 and R' = 0.017[16] for 4884 reflections (*i.e.* all but seven low-θ reflections which were omitted with extinction problems), weighted $w = \sigma_F^{-2}$. In a final difference map the highest peak was *ca.* 0.44 e Å^{-3} in the vicinity of the methanol molecule.

Scattering factors for neutral atoms were taken from ref. 17. Computer programs have been noted above and in Table 4 of ref. 18 and were run on the VAX 11/750 machine at AFRC-IHR, Littlehampton (Glasshouse Crops Research Institute).

The experimental procedures used in the analysis of the other complexes were very similar although some were undertaken in different laboratories by different workers. Crystal data for the five samples are in Table 6. Diffraction intensities for all crystals were measured on Enraf-Nonius CAD4 diffractometers at *ca.* 293 K, and further details of the data measurements and structure refinements are in Table 8.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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