Methoxylation of the Re–Re Bond in $[Re_2(CO)_{10}]$ by Methanol under Ambient Conditions

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Addition of 1,1′-bis(diphenylphosphino)ferrocene (dppf) to an 'activated mixture' containing $[Re_2(CO)_{10}]$ and $Me_3NO{\cdot}2H_2O$ in thf–MeOH (2:1) in the molar ratio 1.0:1.0:2.4 at 25 °C gives $[Re_2(\mu\text{-}OMe)_2(CO)_6(\mu\text{-}dppf)]$ in 34% yield. The molecular structure was determined by X-ray diffraction analysis: monoclinic, space group $P2_1/n$, $a = 13.646(1)$, $b = 18.440(2)$, $c = 17.850(4)$ Å, $\beta = 97.69(1)$ °, final R 0.030 for 3992 observations. It contains two tricarbonylrhenium(I) moieties bridged by dppf and two methoxo ligands. The cp–Fe–cp (cp = $\eta\text{-}C_5H_5$) axis of dppf makes a projection of 53.5° onto the Re–Re axis.

The photosensitivity of metal–metal bonds in binary carbonyls and metal clusters is a subject of intense research activity.[1] Photolytic cleavage of the M–M bond in the presence of protic or halogenated solvents often leads to oxidised products.[2] These M–M bonds are however more resistive to thermal cleavage.[3] We report here a facile rupture of the Re–Re bond in $[Re_2(CO)_{10}]$ in the presence of Me_3NO and methanol. Methanolysis occurs to give a dimethoxo-bridged complex $[Re_2(\mu\text{-}OMe)_2(CO)_6(\mu\text{-}dppf)]$ [dppf = 1,1′-bis(diphenylphosphino)ferrocene] whose structure is reported. Carbonylation of metal alkoxides is an established avenue for the synthesis of alkoxo carbonyl species.[4] Alkoxylation of carbonyl complexes by alcohols, though having received relatively little attention, is of equal importance because of its ease of reaction especially when base catalysed and its potential for entry into methoxo clusters which are possible models in the study of metal-catalysed hydrogenation of CO.[5]

Results and Discussion

Oxidative decarbonylation of $[Re_2(CO)_{10}]$ by $Me_3NO{\cdot}2H_2O$ (1.0:2.4) in thf–MeOH mixture at room temperature (r.t.) followed by phosphine (dppf) addition yielded a chrome-yellow complex characterised as $[Re_2(\mu\text{-}OMe)_2(CO)_6(\mu\text{-}dppf)]$. A single-crystal X-ray diffraction study revealed its dinuclear nature with two $Re(CO)_3$ moieties bridged by a dppf and two methoxo ligands in a *syn* configuration [6] (Fig. 1). With the latter contributing four electrons to each rhenium(I) centre, no M–M bond is envisaged. However, the Re···Re non-bonding distance of 3.4042(6) Å is shorter than those in most reported dinuclear rhenium(I) complexes.[8] This at first glance is somewhat surprising in view of the many examples known in which dppf spans a large M···M distance.[9] The present structure represents one of the few cases [10] in which a sterically demanding dppf ligand can coexist with two bridging ligands of much smaller bite. To facilitate such coexistence, the cp–Fe–cp (cp = $\eta\text{-}C_5H_5$) axis of dppf is twisted by 53.5° from a parallel position with the Re···Re axis. Such tilting though largely unnoticed in the literature seems a prerequisite for dppf to span two metal centres in close proximity. In an attempt to study the electronic effects on the rhenium and phosphorus centres due to this skewing of dppf, X-ray photoelectron spectra of the sample were examined. The sharpness of the Re $4f_{\frac{7}{2}}$ and $4f_{\frac{5}{2}}$ sub-levels, with a full width at half maximum (f.w.h.m.) for each band of 1.80 eV, discounts any significant electronic disparity between the two rhenium centres. The measured binding energies (42.0 and 44.4 eV respectively) are normal for rhenium(I) carbonyl complexes.[9a] The P(2p) band though slightly broader (f.w.h.m. = 2.00 eV) is not unusual and its binding energy of 131.8 eV is in accord with those of other dppf complexes.[11,12]

A twist angle of 85.9(5)° gives an approximately eclipsed conformation of the ferrocenyl moiety (13.9° from exactly eclipsed) and allows the two phosphine groups to be disposed in the *syn* orientation, which is also a requirement for a closed $M_2(\mu\text{-}dppf)$ bridging system. The dppf molecular skeleton displays little strain, as is evident in the virtual coplanarity of the two cp planes [$\varphi = 0.9(4)°$] and the negligible displacement of the phosphorus atoms from the cp planes [0.016(16) for P(1) and 0.034(15) Å for P(2)]. In spite of the destruction of the C_{2v} symmetry of the $Re_2(\mu\text{-}OMe)_2(CO)_6$ moiety by such twisting of the dppf axis, no distortion is apparent in the $Re_2(\mu\text{-}OMe)_2$ core. In fact, though not required crystallographically, the molecule exhibits C_2 molecular symmetry as evidenced from its structural parameters. The two methoxo ligands are symmetrically disposed between the two rhenium(I) centres with the average Re–O 2.163(6) Å and Re–O–Re 103.83(23)°.

Cleavage of the M–M bond in $[Re_2(CO)_{10}]$ in refluxing methanolic KOH has been reported to generate $[ReH_2(CO)_4]^-$ which reacts further to give $[Re_2(\mu\text{-}OMe)_3(CO)_6]^-$.[13] The present use of amine oxide is found to be more facile than the above base-promoted decarbonylation. The amount of oxide used is less than the stoichiometric requirement whilst an excess of it does not enhance the yield of reaction. This may be attributed to some catalytic effect for decarbonylation by MeOH in the presence of adventitious NMe_3. The dppm ($Ph_2PCH_2PPh_2$) analogue of the present complex has been reported to be formed in prolonged photolysis of the M–M bonded $[Re_2(\mu\text{-}H)(\mu\text{-}OMe)(CO)_6(\mu\text{-}dppm)]$ in toluene–MeOH mixture.[14] The substrate was generated similarly from $[Re_2(CO)_8(\mu\text{-}dppm)]$. We have not detected any of the analogous dppf complexes in our reaction mixtures. The r.t. non-photolytic conditions we employed also discount the likelihood of homolytic cleavage of the Re–Re bond. There is no evidence of similar products when $ClCH_2CH_2OH$ or water is

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Non-SI unit employed: eV ≈ 1.60×10^{-19} J.

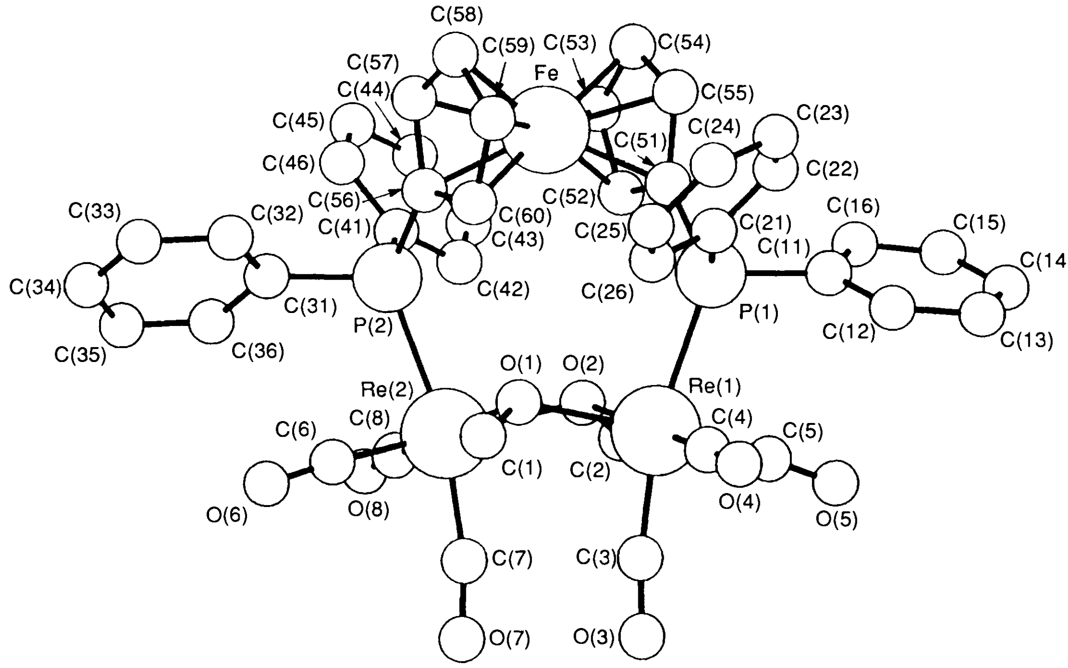

Fig. 1 A PLUTO[7] drawing of [$Re_2(\mu$-$OMe)_2(CO)_6(\mu$-dppf)] showing the atomic labelling scheme

used instead of MeOH. For EtOH, the IR spectrum indicates only a trace quantity of the bridging ethoxo complex.

The present complex yields [Re($MeCO_2$)$(CO)_3$(dppf)], the PPh_3 analogue[15] of which has been synthesised from [Re($MeCO_2$-*O*,*O*′)$(CO)_2(PPh_3)_2$],[15,16] when refluxed with $MeCO_2H$ in tetrahydrofuran (thf). No observable reaction occurs at r.t., which suggests the poor basicity of the μ-OMe groups. Bridge cleavage does not occur at r.t. in the presence of excess of CO or dppf. The isolation of the present complex provides ubiquitous support that, in spite of their vast differences in steric requirement, dppf can resemble dppm and diphosphanes R_2P–PR_2 in promoting metal co-operation in close proximity.

Experimental

General.—All reactions were performed under pure dry argon using standard Schlenk techniques. Precoated silica plates of layer thickness 0.25 mm were obtained from Merck. The general procedures and instruments used were as described in our earlier reports.[17] Core-level X-ray photoelectron spectra were obtained on a VG ESCA/SIMSLAB MK II spectrometer under similar conditions to those previously described.[9a]

Synthesis of [$Re_2(\mu$-$OMe)_2(CO)_6(\mu$-dppf)].—A solution of $Me_3NO{\cdot}2H_2O$ (0.062 g, 0.56 mmol) in thf–MeOH (1:1) (20 cm^3) was transferred to a stirred solution of [$Re_2(CO)_{10}$] (0.151 g, 0.23 mmol) in thf (10 cm^3) at r.t. The resultant yellow solution was stirred *in vacuo* for 4 h at r.t. Solid dppf (0.128 g, 0.23 mmol) was then introduced and the orange solution so formed was stirred *in vacuo* for 1 h. It was then evaporated to half its volume and stirred for 3 h. The solvent was removed and the residue redissolved in the minimum of CH_2Cl_2 and chromatographed on silica TLC plates (CH_2Cl_2–hexane 1:4). The complex [$Re_2(\mu$-$OMe)_2(CO)_6(\mu$-dppf)] was isolated from the main band and recrystallised from CH_2Cl_2–MeOH to give fine chrome-yellow crystals, m.p. 214–215 °C (decomp.), yield 0.085 g (34%) (Found: C, 43.80; H, 2.60; Fe, 4.50. $C_{42}H_{34}FeO_8P_2Re_2$ requires C, 43.60; H, 2.95; Fe, 4.85%). ν_{max}(CO) 2027s, 2011m, 2000w(sh), 1925m, 1904s and 1895(sh) cm^{-1} ($CHCl_3$); δ_H($CDCl_3$) 7.44 (m, 20 H, Ph), 4.76 [m(vbr), 4 H, cp], 4.59 (s, 6 H, MeO) and 3.63 (m, 4 H, cp); δ_P($CDCl_3$) 5.25(s). XPS Binding energy (f.w.h.m.): 708.4 (1.80) [Fe($2p_{\frac{3}{2}}$)], 131.8 (2.00) [P(2p)], 44.4 (1.8) [Re($4f_{\frac{5}{2}}$)] and 42.0 (1.80) [Re($4f_{\frac{7}{2}}$)] eV.

Reactions with water, EtOH and $ClCH_2CH_2OH$ were carried out in a similar manner except that the volume of the solution was not reduced by half during the experiment. No identifiable product was isolated except that in the case of EtOH a trace quantity of a chrome-yellow complex was isolated whose IR spectrum suggests it to be analogous to [$Re_2(\mu$-$OMe)_2(CO)_6(\mu$-dppf)].

Orange single crystals of complex [$Re_2(\mu$-$OMe)_2(CO)_6(\mu$-dppf)]$\cdot CH_2Cl_2$ were grown from CH_2Cl_2–MeOH at 5 °C. Those suitable for X-ray diffraction were mounted inside a lithium glass capillary for characterisation and intensity data collection.

Reaction of [$Re_2(\mu$-$OMe)_2(CO)_6(\mu$-dppf)] *with* $MeCO_2H$.—Ten drops of glacial acetic acid (*ca.* 0.5 cm^3) were added to a thf solution (10 cm^3) of [$Re_2(\mu$-$OMe)_2(CO)_6(\mu$-dppf)] (0.045 g, 0.039 mmol). The mixture was refluxed for 1 h, after which the solvent was removed *in vacuo*. The residue was redissolved in the minimum of CH_2Cl_2 and chromatographed on silica TLC plates. Elution by acetone–hexane (3:7) followed by recrystallisation from CH_2Cl_2–hexane yielded chrome-yellow microcrystals of [Re($MeCO_2$)$(CO)_3$(dppf)]$\cdot 0.17CH_2Cl_2$ (0.021 g, 59%), m.p. 221–222 °C (decomp.) (Found: C, 52.60; H, 3.55; Fe, 5.85; P, 7.25. $C_{39.17}H_{31.33}Cl_{0.33}FeO_5P_2Re$ requires C, 52.40; H, 3.50; Fe, 6.20; P, 6.90%). ν_{max}(CO) 2027m, 1948m, 1890m (CH_2Cl_2), (RCO_2) 1637m cm^{-1} (KBr); δ_H($CDCl_3$) 7.64 (m, 8 H, Ph), 7.38 (m, 12 H, Ph), 4.69 (m, 2 H, cp), 4.37 (m, 6 H, cp) and 1.78 (s, 3 H, CH_3CO_2); δ_P($CDCl_3$) 7.94(s). XPS Binding energy (f.w.h.m.): 721.2 (1.80) [Fe($2p_{\frac{1}{2}}$)], 131.8 (1.95) [P(2p)], 44.0 (1.8) [Re($4f_{\frac{5}{2}}$)] and 41.7 (1.80) [Re($4f_{\frac{7}{2}}$)] eV.

Crystal Structure Determination of [$Re_2(\mu$-$OMe)_2(CO)_6(\mu$-dppf)]$\cdot CH_2Cl_2$.—*Crystal data.* $C_{43}H_{36}Cl_2FeO_8P_2Re_2$, $M = 1241.86$, monoclinic, $a = 13.646(1)$, $b = 18.440(2)$, $c = 17.850(4)$ Å, $\beta = 97.69(1)^\circ$, $U = 4451.2(13)$ Å^3, $Z = 4$, $D_c = 1.853$ Mg m^{-3}, $F(000) = 2391.41$, μ(Mo-Kα) = 6.06 mm^{-1}, $\lambda = 0.709\ 30$ Å. Space group determined from the systematic absences as $P2_1/n$. Crystal dimensions 0.32 ×

Table 1 Final fractional coordinates for $[Re_2(\mu\text{-}OMe)_2(CO)_6(\mu\text{-}dppf)]\cdot CH_2Cl_2$

Atom	x	y	z
Re(1)	0.014 50(3)	0.904 39(2)	0.169 20(2)
Re(2)	0.257 57(3)	0.911 53(2)	0.145 04(2)
Fe	0.203 84(10)	1.039 34(7)	0.376 70(7)
P(1)	−0.011 65(18)	0.963 70(12)	0.292 91(13)
P(2)	0.354 02(18)	0.983 75(12)	0.250 73(13)
O(1)	0.127 3(4)	0.978 6(3)	0.142 9(3)
O(2)	0.157 3(4)	0.861 1(3)	0.214 3(3)
O(3)	−0.016 9(6)	0.825 1(4)	0.016 5(4)
O(4)	−0.173 3(6)	0.980 8(5)	0.100 6(4)
O(5)	−0.116 9(6)	0.778 5(4)	0.205 1(4)
O(6)	0.366 8(6)	0.995 9(4)	0.034 2(4)
O(7)	0.200 2(7)	0.821 6(5)	0.001 2(5)
O(8)	0.429 3(6)	0.805 2(4)	0.162 8(5)
C(1)	0.106 9(8)	1.026 9(6)	0.080 1(5)
C(2)	0.159 8(8)	0.784 4(5)	0.227 1(6)
C(3)	0.002 6(8)	0.855 4(6)	0.072 9(6)
C(4)	−0.101 5(8)	0.952 2(6)	0.127 8(5)
C(5)	−0.067 4(7)	0.827 6(6)	0.195 1(5)
C(7)	0.212 0(8)	0.854 9(6)	0.056 0(6)
C(8)	0.365 2(8)	0.846 0(6)	0.157 2(6)
C(9)	0.328 1(8)	0.965 3(6)	0.078 1(6)
C(11)	−0.101 8(7)	0.908 0(5)	0.334 7(5)
C(12)	−0.199 9(7)	0.910 3(5)	0.304 7(5)
C(13)	−0.268 2(7)	0.864 0(6)	0.332 0(6)
C(14)	−0.237 1(9)	0.815 6(6)	0.387 8(6)
C(15)	−0.139 4(9)	0.813 6(5)	0.417 8(6)
C(16)	−0.071 2(7)	0.859 4(5)	0.392 7(5)
C(21)	−0.070 6(7)	1.053 0(5)	0.283 8(5)
C(22)	−0.128 6(9)	1.077 5(6)	0.336 1(6)
C(23)	−0.171 3(10)	1.145 8(6)	0.328 8(7)
C(24)	−0.154 3(10)	1.190 5(6)	0.270 3(7)
C(25)	−0.095 9(9)	1.166 7(6)	0.218 6(7)
C(26)	−0.054 5(7)	1.097 2(5)	0.225 4(5)
C(31)	0.456 6(7)	1.031 6(5)	0.215 1(5)
C(32)	0.455 9(9)	1.105 8(5)	0.207 5(6)
C(33)	0.533 7(11)	1.138 8(7)	0.177 2(8)
C(34)	0.606 7(11)	1.099 6(9)	0.152 6(7)
C(35)	0.606 3(8)	1.026 5(9)	0.158 1(7)
C(36)	0.531 7(8)	0.991 6(6)	0.189 1(6)
C(41)	0.420 3(7)	0.929 3(5)	0.327 9(5)
C(42)	0.388 9(8)	0.860 2(5)	0.342 0(6)
C(43)	0.436 4(9)	0.821 1(6)	0.402 3(6)
C(44)	0.515 3(9)	0.850 1(7)	0.448 3(6)
C(45)	0.547 0(8)	0.918 9(6)	0.434 2(6)
C(46)	0.501 3(7)	0.958 1(6)	0.374 3(5)
C(51)	0.084 7(7)	0.973 3(4)	0.371 6(5)
C(52)	0.172 6(7)	0.931 7(4)	0.382 0(5)
C(53)	0.231 0(7)	0.953 7(5)	0.450 3(5)
C(54)	0.176 4(9)	1.008 9(5)	0.482 1(5)
C(55)	0.087 3(7)	1.021 8(5)	0.434 4(5)
C(56)	0.297 5(6)	1.055 1(4)	0.298 7(5)
C(57)	0.334 3(7)	1.089 6(5)	0.368 4(5)
C(58)	0.265 0(8)	1.140 4(5)	0.384 9(5)
C(59)	0.183 0(7)	1.139 6(5)	0.326 9(6)
C(60)	0.203 1(7)	1.085 8(4)	0.273 1(5)
C	0.318 1(21)	0.161 8(16)	0.001 6(17)
Cl(1)*	0.309 9(8)	0.247 6(6)	0.039 9(6)
Cl(2)*	0.415 0(9)	0.183 5(7)	−0.049 7(7)
Cl(3)*	0.322 0(14)	0.166 0(9)	−0.091 8(10)
Cl(4)*	0.423 7(55)	0.251 3(40)	−0.003 6(41)
Cl(5)*	0.291 5(21)	0.208 5(15)	0.073 8(16)

* Composite scattering curves for the following solvate atoms were used in the refinement: Cl(1) and Cl(2) 0.67 Cl/0.33 H, Cl(3) 0.33 Cl/0.67 H, Cl(4) 0.10 Cl/0.20 H and Cl(5) 0.23 Cl/0.47 H, making a total scattering power of 2 Cl and 2 H atoms.

Table 2 Selected bond lengths (Å), angles (°) and torsional angles (°) for $[Re_2(\mu\text{-}OMe)_2(CO)_6(\mu\text{-}dppf)]\cdot CH_2Cl_2$

Re(1)–P(1)	2.532(2)	P(1)–C(11)	1.836(9)
Re(1)–O(1)	2.158(5)	P(1)–C(21)	1.831(9)
Re(1)–O(2)	2.159(6)	P(1)–C(51)	1.800(9)
Re(1)–C(3)	1.929(11)	P(2)–C(31)	1.839(9)
Re(1)–C(4)	1.876(12)	P(2)–C(41)	1.842(9)
Re(1)–C(5)	1.899(10)	P(2)–C(56)	1.799(9)
Re(2)–P(2)	2.530(2)	O(1)–C(1)	1.429(11)
Re(2)–O(1)	2.161(5)	O(2)–C(2)	1.433(10)
Re(2)–O(2)	2.172(6)	O–C (carbonyl)	1.152(14) (mean)
Re(2)–C(7)	1.933(11)	Fe–C(51–55)	2.038(9) (mean)
Re(2)–C(8)	1.892(11)	Fe–C(56–60)	2.039(9) (mean)
Re(2)–C(6)	1.909(12)		
P(1)–Re(1)–O(1)	95.96(15)	C(7)–Re(2)–C(8)	84.8(4)
P(1)–Re(1)–O(2)	93.43(16)	C(7)–Re(2)–C(6)	84.3(4)
P(1)–Re(1)–C(3)	167.0(3)	C(8)–Re(2)–C(6)	87.4(4)
P(1)–Re(1)–C(4)	86.0(3)	Re(1)–P(1)–C(11)	107.0(3)
P(1)–Re(1)–C(5)	87.4(3)	Re(1)–P(1)–C(21)	115.0(3)
O(1)–Re(1)–O(2)	71.4(2)	Re(1)–P(1)–C(51)	123.4(3)
O(1)–Re(1)–C(3)	94.6(3)	C(11)–P(1)–C(21)	103.3(4)
O(1)–Re(1)–C(4)	101.8(3)	C(11)–P(1)–C(51)	101.4(4)
O(1)–Re(1)–C(5)	170.4(3)	C(21)–P(1)–C(51)	104.3(4)
O(2)–Re(1)–C(3)	97.1(4)	Re(2)–P(2)–C(31)	109.8(3)
O(2)–Re(1)–C(4)	173.1(3)	Re(2)–P(2)–C(41)	115.2(3)
O(2)–Re(1)–C(5)	99.5(3)	Re(2)–P(2)–C(56)	121.8(3)
C(3)–Re(1)–C(4)	84.4(4)	C(31)–P(2)–C(41)	101.5(4)
C(3)–Re(1)–C(5)	83.4(4)	C(31)–P(2)–C(56)	102.0(4)
C(4)–Re(1)–C(5)	87.3(4)	C(41)–P(2)–C(56)	104.0(4)
P(2)–Re(2)–O(1)	93.3(2)	Re(1)–O(1)–Re(2)	104.1(2)
P(2)–Re(2)–O(2)	96.1(2)	Re(1)–O(1)–C(1)	119.7(5)
P(2)–Re(2)–C(7)	167.2(3)	Re(2)–O(1)–C(1)	116.4(5)
P(2)–Re(2)–C(8)	86.1(3)	Re(1)–O(2)–Re(2)	103.6(2)
P(2)–Re(2)–C(6)	86.4(3)	Re(1)–O(2)–C(2)	115.2(5)
O(1)–Re(2)–O(2)	71.1(2)	Re(2)–O(2)–C(2)	120.7(6)
O(1)–Re(2)–C(7)	96.9(3)	Re(1)–C–O	174.7(10) (mean)
O(1)–Re(2)–C(8)	172.5(3)	Re(2)–C–O	174.4(10) (mean)
O(1)–Re(2)–C(6)	100.1(3)	O(2)–Re(2)–C(8)	101.5(3)
O(2)–Re(2)–C(7)	94.5(4)	O(2)–Re(2)–C(6)	170.9(3)

C(51)–CEN1–CEN2–C(56)	−85.9(5)
C(51)–CEN1–CEN2–C(60)	−13.9(5)
C(52)–CEN1–CEN2–C(56)	−14.0(5)
C(53)–CEN1–CEN2–C(57)	−14.6(6)
C(54)–CEN1–CEN2–C(58)	−13.2(6)
C(55)–CEN1–CEN2–C(59)	−13.8(6)

CEN1 and CEN2 are the centroids of C(51)–C(55) and C(56)–C(60), respectively.

0.27 × 0.24 mm. Cell dimensions were obtained from 25 reflections with 2θ in the range 14.59–31.33°.

Data collection and processing. Nonius diffractometer, θ–2θ mode with scan width = 2(0.6 + tan θ)°, scan speed varying from 1.03 to 8.24° min^{-1}, graphite-monochromated Mo-Kα radiation; 6091 reflections measured of which 5806 were unique. Data were collected to a maximum 2θ of 44.9°. The range of indices was h −14 to 14, k 0–19, l 0–19. After corrections for absorption effects, 3992 data were used with $I > 2.0\sigma(I)$. The minimum and maximum transmission factors were 0.711 and 1.000.

Structure analysis and refinement. The structure was solved by direct methods and MULTAN.[18] Refinement was by full-matrix least-squares calculations with all non-hydrogen atoms allowed anisotropic motion. All hydrogen atoms were fixed as isotropic ellipsoids in the final cycles of least-squares refinement. The non-hydrogen atoms were varied anisotropically. The last least squares cycle was calculated with 95 atoms, 520 parameters, and 3992 out of 5806 reflections and converged with $R_f = 0.030$, $R' = 0.032$ (for all reflections, $R = 0.061$ and $R' = 0.036$). The goodness of fit is 1.31. Weights based on counting statistics were used. The weight modifier was 0.000 100. The maximum shift/error ratio was 0.203:1. In the last difference map the deepest hole was −0.880 e $Å^{-3}$, and the highest peak 0.680 e $Å^{-3}$. The structure contains disordered CH_2Cl_2 molecules. Since there were no reasonable models for the explanation of electron-density maps around the solvate region, final refinement employed composite scattering curves for solvate atoms such that Cl(1) and Cl(2) were actually 0.67 Cl/0.33 H, Cl(3) was 0.33 Cl/0.67 H, Cl(4) was 0.10 Cl/0.20 H and Cl(5) was 0.23 Cl/0.47 H, totalling 2 Cl and 2 H atoms. The atomic scattering curves for Re, Fe, P, O, C and H were taken from ref. 19. Computations were carried out on a microVAX 3600 computer with the NRCC package.[20] Final atomic coordinates and selected bond distances and angles are listed in Tables 1 and 2.

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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