Some chemistry of Re₂(μ-H)(μ-C₂Ph)(CO)₈: X-ray structures of Re₂(μ-H)(μ-C₂Ph)(CO)₆(PMe₃)₂, Re₂{ μ-Au(PPh₃)}(μ-C₂Ph)(CO)₈, Re₂(μ-X)(μ-dppm)(μ-C₂Ph)(CO)₆ [X = H, Br and Au(PPh₃)] and Re₂(μ-Br)₂(μ-dppm)(CO)₆

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Abstract

Reactions of Re₂(μ-H)(μ-C₂Ph)(CO)₇(NCMe) (2) with 1,8-diazabicyclo[5.4.0]undec-1-ene (dbu), CN^{t}Bu or PMe₃ have given Re₂(μ-H)(μ-C₂Ph)(CO)₈₋$_n$(L)$_n$ [L = dbu, n = 1; L = CN^{t}Bu (4) or PMe₃, n = 2]; with dppm, Re₂(μ-H)(μ-dppm)(μ-C₂Ph)(CO)₆ (6) was obtained. Halogenation of 6 has given Re₂(μ-X)(μ-dppm)(μ-C₂Ph)(CO)₆ [X = I, Br (8)] and Re₂(μ-Br)₂(μ-dppm)(CO)₆ (9). Cluster AuRe₂(μ-C₂Ph)(CO)₈(PPh₃) (10) was obtained as a minor product from a reaction between 2 and Na[Co(CO)₄]/AuCl(PPh₃). Replacement of the H in 6 by Au(PPh₃) was achieved by reaction with AuMe(PPh₃) to give AuRe₂(μ-dppm)(μ-C₂Ph)(CO)₆(PPh₃) (11); in contrast, treatment of 6 with LiMe, followed by addition of AuCl(PPh₃) or [{Au(PPh₃)}₃O][BF₄], gave Re₂(μ-H){ μ-(PPh₂)₂CH[Au(PPh₃)]}(μ-C₂Ph)(CO)₆ (12), in which the μ-dppm ligand has been metallated. With {Rh(μ-Cl)(cod)}₂, the product contains an Re₂Rh cluster capped by the CH(PPh₂)₂ ligand. The X-ray structures of 4, 6 and 8–11 are reported.

Keywords: Rhenium; Gold; Carbonyl; Crystal structure; Phosphine; Alkynyl

1. Introduction

The chemistry of rhenium carbonyl with alkynes has attracted attention since 1981, when Mays et al. [1] studied the reaction between Re₂(CO)₁₀ and diphenylacetylene. Several binuclear complexes containing coupled alkyne ligands were formed: these have been characterised in the intervening period by X-ray crystallography as Re₂(μ-2η¹,η⁴-C₄Ph₄)(CO)₇ [2], Re₂(μ-2η¹,η⁴-C₄Ph₄)(CO)₅(η²-C₂Ph₂) [3] and Re₂(μ-2η¹,2η³-C₆Ph₆)(CO)₄(η²-C₂Ph₂) [3]. Related chemistry has been extensively developed by Adams [4], who has elegantly demonstrated the consequences of the insertion of alkynes into the Re–Re bond.

Oxidative addition of terminal alkynes to metal–metal bonded rhenium carbonyls often affords hydrido–alkynyl complexes such as Re₂(μ-H)(μ-η¹ : η²-C₂Ph)(CO)₈ (1). This type of compound has been obtained as one of several products formed by photolysis of Re₂(CO)₁₀ in the presence of the alkyne [5]. A cleaner synthesis of Re₂(μ-H)(μ-C₂Ph)(CO)₈ has been developed by Brown and coworker [6], who treated Re₂(μ-H)(μ-CH=CHMe)(CO)₈ directly with HC₂Ph. Of more synthetic utility was the acetonitrile derivative Re₂(CO)₈(NCMe)₂, which reacts with 1-alkynes to give Re₂(μ-H)(μ-η¹,η²-C≡CR)(CO)₇(NCMe) [R = Ph (2), α-estradiol] in 50–60% yield [7]. These derivatives are presumed to be formed by ready substitution of MeCN for a CO ligand *cis* to the bridging acetylide ligand in an undetected octacarbonyl intermediate. Analogous complexes have also been obtained from 1 directly in facile thermal reactions [6]. Disubstituted complexes were assigned the *trans* geometry on the basis of their IR spectra. Complexes containing chelating bis-tertiary phosphines, such as dppm or dmpm (LL), have been

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obtained in photolytic reactions of $Re_2(\mu\text{-LL})(CO)_8$ with 1-alkynes [8].

This paper describes some reactions of $Re_2(\mu\text{-H})(\mu\text{-}C_2Ph)(CO)_7(NCMe)$ (2) with several sterically undemanding nucleophiles, such as CN^tBu and PMe_3, which might be expected to occupy *trans* coordination sites across the Re–Re bond, and with the bidentate tertiary phosphine $CH_2(PPh_2)_2$ (dppm). Further reactions of the dppm complex have provided a series of complexes wherein the electron donor power of the other bridging groups is systematically varied from $(H + C_2Ph)$ through $[Au(PPh_3) + C_2Ph]$, $(Br + C_2Ph)$ and $(Br + Br)$. Structural studies of the title complexes have allowed the structural effects of these changes to be gauged. We have previously communicated some of this chemistry; deprotonation of the μ-dppm ligand and subsequent attachment of gold or rhodium fragments gave compounds containing the $[CH(PPh_2)_2]^-$ ligand [9].

2. Results and discussion

2.1. Reactions of $Re_2(\mu\text{-H})(\mu\text{-}\eta^1 : \eta^2\text{-}C_2Ph)(CO)_7(NCMe)$ with nucleophiles (Scheme 1)

The complex $Re_2(\mu\text{-H})(\mu\text{-}C_2Ph)(CO)_7(dbu)$ (3) was obtained in 70% yield from the direct reaction between 2 and dbu, after being initially identified as the only isolated product from a reaction between 2 and {Ir(μ-Cl)(cod)}$_2$ in the presence of 1,8-diazabicyclo[5.4.0]undec-1-ene (dbu). It forms slightly air-sensitive crystals, where were identified by FAB mass spectrometry (M^+ at m/z 822) and from its IR $\nu(CO)$ spectrum, which was similar to that of 2. There are not many complexes

of this sterically demanding nitrogen heterocycle known, although some rhodium derivatives have recently been described [10].

Complex 1 is reported to react with PMe_3 at the coordinated alkynyl ligand to give the dipolar addition product $Re_2(\mu\text{-H})(\mu\text{-L})(CO)_8$ [L = $C(PMe_3)=CPh$ or $C=CPh(PMe_3)$] [6]. In contrast, 2 reacts with PMe_3 by substitution of the MeCN and one CO ligand to give $Re_2(\mu\text{-H})(\mu\text{-}\eta^1,\eta^2\text{-}C_2Ph)(CO)_6(PMe_3)_2$ (4), which has been fully characterised by X-ray crystallography (see below). The IR $\nu(CO)$ spectrum of 4 is similar to those reported for other disubstituted complexes $Re_2(\mu\text{-H})(\mu\text{-}\eta^1,\eta^2\text{-}C_2Ph)(CO)_6L_2$ (L = py, PR_3, NH_2Pr) [6]. The related reaction with ^tBuNC gave $Re_2(\mu\text{-H})(\mu\text{-}\eta^1,\eta^2\text{-}C_2Ph)(CO)_6(CN^tBu)_2$ (5). The IR spectrum of this complex contains $\nu(CN)$ at 2181 cm^{-1} and a four-band $\nu(CO)$ pattern between 2031 and 1933 cm^{-1}. In the ^1H NMR spectrum, the metal-bonded and ^tBu protons are found as singlets at δ −12.71 and 1.40 respectively; the ^{13}C NMR spectrum contains resonances at δ 30.24 (CMe_3), 89.24 and 100.48 (C_2Ph), phenyl resonances between δ 127.5 and 131.8 and three CO singlets between δ 186 and 191. Similarly, addition of dppm afforded an 80% yield of pale yellow $Re_2(\mu\text{-H})(\mu\text{-dppm})(\mu\text{-}\eta^1,\eta^2\text{-}C_2Ph)(CO)_6$ (6), a complex which has already been prepared by Brown and coworkers [8]; the crystal structure of this complex has also been determined.

2.2. Reactions of $Re_2(\mu\text{-H})(\mu\text{-dppm})(\mu\text{-}\eta^1,\eta^2\text{-}C_2Ph)(CO)_6$ with halogens (Scheme 2)

The reaction between 6 and iodine afforded a mixture of products, from which bright yellow $Re_2(\mu\text{-I})(\mu\text{-dppm})(\mu\text{-}C_2Ph)(CO)_6$ (7) was isolated in 44%

Scheme 1.

(7) X = I
(8) X = Br
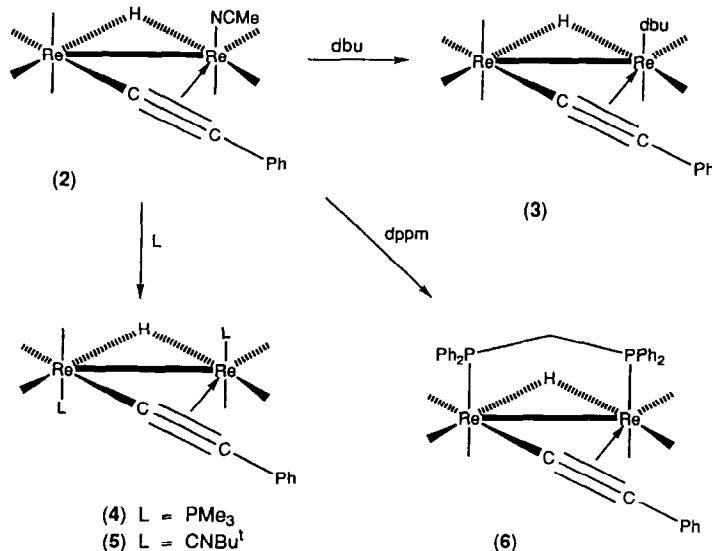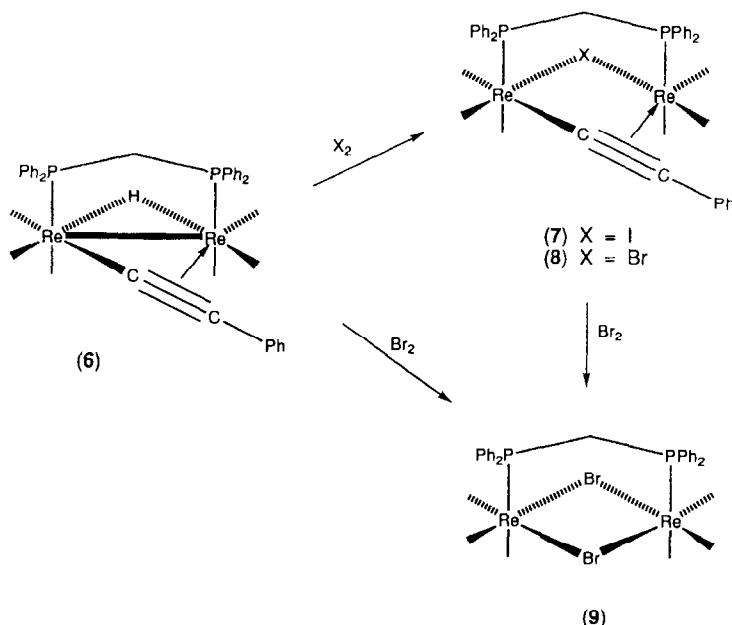
Scheme 2.

yield. This complex contains a $\nu(CO)$ spectrum very similar to that of **6**, while the ^1H and ^{13}C NMR spectra contained peaks assigned to the CH_2 and Ph groups, and to the CO groups (at δ 187.54, 188.01 and 188.84) in the latter. The ^{31}P NMR spectrum contained a single resonance at δ −13.24. These data indicate that the
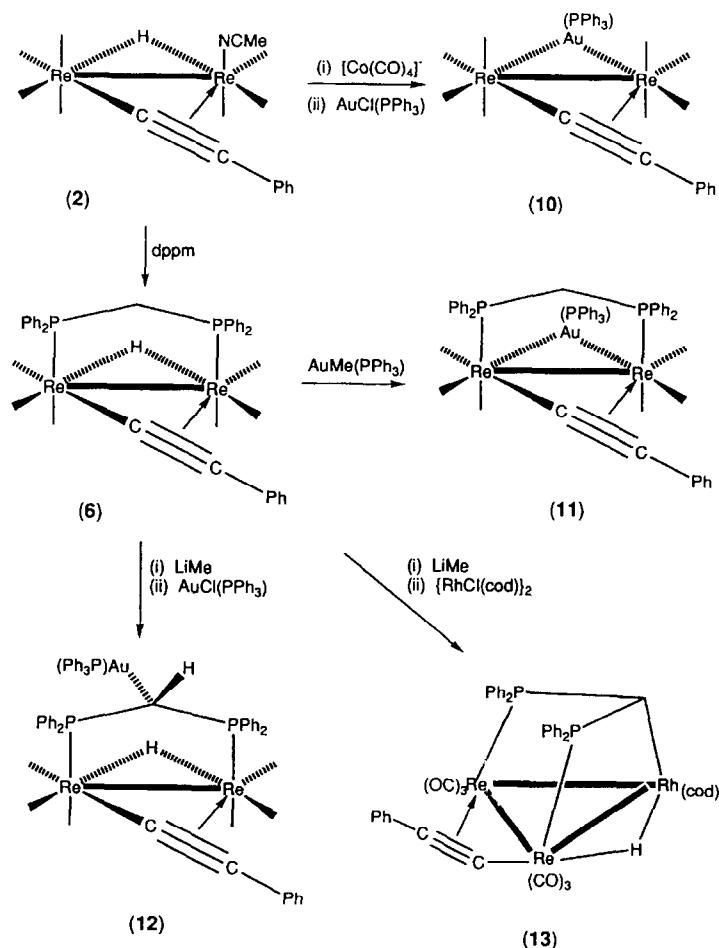
Scheme 3.

Table 1
Selected bond lengths (Å) and angles (deg) for some Re$_2$ complexes

	Re$_2$(μ-H)(μ-C$_2$Ph)(CO)$_8$ (1)	Re$_2$(μ-H)(μ-C$_2$Ph)(CO)$_7$(NCMe) (2)	Re$_2${μ-Au(PPh$_3$)}(μ-C$_2$Ph)(CO)$_8$ (10)	Re$_2$(μ-H)(μ-C$_2$Ph)(CO)$_6$(PMe$_3$)$_2$ (4)
Reference	[13]	[7]	This work	This work
Bond lengths				
Re(1)–Re(2)	3.089(1)	3.0788(4)	3.179(2)	3.156(1), 3.143(1)
Re(1)–C(1)	2.102(8)	2.095(7)	2.11(2)	2.10(2), 2.03(2)
Re(2)–C(1)	2.362(8)	2.307(7)	2.29(2)	2.31(2), 2.35(2)
Re(2)–C(2)	2.473(9)	2.446(7)	2.40(2)	2.45(2), 2.47(2)
C(1)–C(2)	1.23(1)	1.216(9)	1.18(3)	1.20(3), 1.29(2)
Re(1)–X		1.9(1) (H)	2.744(1) (Au)	1.7(–), 2.0(–) (H)
Re(2)–X		1.6(1) (H)	2.844(2) (Au)	1.8(–), 2.0(–) (H)
Re(1)–P(1)		2.151(5) (N)		2.461(6), 2.460(6)
Re(2)–P(2)				2.459(6), 2.454(6)
Re(1)–C(11)		1.907(7)	1.99(2)	1.95(2), 1.82(2)
Re(1)–C(12)		1.913(8)	1.91(2)	1.90(2), 1.92(3)
Re(1)–C(13)		1.897(7)	1.98(2)	1.95(2), 1.90(2)
Re(1)–C(14)			2.03(2)	
Re(2)–C(21)		1.966(8)	1.92(2)	1.87(2), 1.89(3)
Re(2)–C(22)		1.881(9)	1.91(2)	1.93(2), 1.91(2)
Re(2)–C(23)		1.995(8)	2.02(2)	1.97(2), 1.95(2)
P(1)–C(0)				
P(2)–C(0)				
Bond angles				
Re(1)–X–Re(2)		120.4(57) (H)	69.31(3) (Au)	129(–), 107(–) (H)
Re(1)–C(1)–C(2)	167.7(4)	170.1(6)	173(1)	172(2), 171(2)
C(1)–C(2)–C(101)	163.8(8)	160.3(7)	163(2)	157(2), 164(2)
Re(1)–Re(2)–C(22)			153.0(5)	156.0(5), 155.1(7)
Re(2)–Re(1)–C(12)			138.2(6)	147.4(7), 147.6(7)
P(1)–Re(1)–C(13)		177.1(3) (N)		170.9(5), 171.9(6)
P(2)–Re(2)–C(23)				173.9(6), 171.7(6)
Re(2)–Re(1)–P(1)				92.7(1), 91.9(1)
Re(1)–Re(2)–P(2)				90.5(1), 91.0(1)
Re(1)–P(1)–C(0)				
Re(2)–P(2)–C(0)				
P(1)–C(0)–P(2)				

complex is fluxional, probably by the well-established windshield-wiper mechanism, whereby the alkynyl group oscillates between the two rhenium atoms [6,8].

The corresponding reaction between 6 and one equivalent of bromine afforded green Re$_2$(μ-Br)(μ-dppm)(μ-C$_2$Ph)(CO)$_6$ (8) (33%). The ^{1}H and ^{13}C NMR spectra of 8 resembled those of 7. The dibromo complex Re$_2$(μ-Br)$_2$(μ-dppm)(CO)$_6$ (9) was formed (24%) when an excess of bromine was used; it is related to the corresponding chloro–dppe complex described recently [11]. The fate of the phenylethynyl group was not determined; it is likely that initial formation of BrC$_2$Ph is followed by further reaction of halogen with the C≡C triple bond. The molecular structures of both 8 and 9 have been confirmed by single-crystal X-ray studies.

2.3. Preparation of gold and rhodium derivatives of Re$_2$(μ-H)(μ-η^1,η^2-C$_2$Ph)(CO)$_6$(L)$_2$(L = PPh$_3$ or L$_2$ = μ-dppm) (Scheme 3)

Replacement of H in 1 by the isolobal Au(PPh$_3$) group was found in a minor product, AuRe$_2$(μ-C$_2$Ph)(CO)$_8$(PPh$_3$) (10), from the reaction between 2 and Na[Co(CO)$_4$] followed by addition of AuCl(PPh$_3$). Seemingly, the metal carbonyl anion acts as a base rather than displacing MeCN in this reaction. The source of the eighth CO ligand was not identified. Complex 10 was identified by FAB mass spectrometry (M$^+$ at m/z 1129) and from its IR ν(CO) spectrum which, whilst like that of 1, is shifted to lower energy by ca. 30 cm^{-1}. This suggests that the AuRe$_2$ core is more electron-rich

Re₂(μ-H)(μ-dppm)(μ-C₂Ph)(CO)₆ (6)	AuRe₂(μ-dppm)(μ-C₂Ph)(CO)₆(PPh₃) (11)	Re₂(μ-Br)(μ-dppm)(μ-C₂Ph)(CO)₆ (8)	Re₂(μ-Br)₂(μ-dppm)(CO)₆ (9)
This work	This work	This work	This work
3.095(2)	3.2260(8)	3.744(2)	3.920(1), 3.929(1)
2.06(1)	2.07(1)	2.30(2)	
2.36(1)	2.331(8)	2.49(2)	
2.50(1)	2.400(9)	2.51(2)	
1.24(2)	1.23(2)	0.79(3)	
1.9 (H)	2.7473(9) (Au)	2.657(3) (Br)	2.650(1), 2.655(2) [Br(1)]
			2.645(1), 2.638(1) [Br(2)]
1.8 (H)	2.8119(9) (Au)	2.687(3) (Br)	2.643(1), 2.6434(9) [Br(1)]
			2.646(1), 2.629(2) [Br(2)]
2.440(3)	2.445(2)	2.462(7)	2.466(2), 2.467(2)
2.461(3)	2.465(2)	2.479(7)	2.480(2), 2.472(2)
1.91(1)	1.96(1)	1.92(3)	1.884(8), 1.897(8)
1.90(2)	1.87(1)	1.64(3)	1.89(1), 1.881(9)
1.92(2)		1.85(3)	1.927(9), 1.96(1)
1.93(1)	1.915(1)	1.82(2)	1.935(9), 1.888(9)
1.88(1)	1.92(1)	1.82(3)	1.880(8), 1.871(7)
1.94(2)	1.951(7)	1.97(3)	1.944(8), 1.94(1)
1.83(1)	1.83(1)	1.82(3)	1.833(7), 1.835(8)
1.83(1)	1.830(8)	1.86(2)	1.831(8), 1.837(8)
113(−) (H)	70.93(2) (Au)	88.9(1) (Br)	95.57(4), 95.73(3) [Br(1)]
			95.60(4), 96.49(3) [Br(2)]
167.8(9)	171.9(7)	175(3)	
165(1)	151.4(8)	170(3)	
156.3(4)	153.3(3)	141.3(8)	
149.5(4)	141.2(4)	127.8(9)	
178.3(5)	175.3(4)	177(1)	
178.8(5)	176.6(3)	173.9(8)	
89.48(9)	87.95(6)	83.3(2)	80.93(6), 81.15(5)
89.58(9)	88.18(6)	82.9(2)	81.87(5), 81.51(5)
113.3(4)	113.0(3)	114.8(8)	116.1(3), 115.1(3)
111.2(4)	111.7(2)	116.3(8)	115.8(2), 117.0(3)
113.6(6)	113.5(4)	118(1)	120.5(4), 120.7(4)

than the Re₂H moiety, resulting in a greater degree of back-bonding into the CO ligands. Final confirmation of the molecular structure was achieved by a single-crystal X-ray study.

The metal-bound hydrogen in 6 was slowly eliminated as methane when it was treated with AuMe(PPh₃); after four days in refluxing CH₂Cl₂ or THF, green crystals of AuRe₂(μ-dppm)(μ-C₂Ph)(CO)₆(PPh₃) (11) were isolated in low yield. The IR ν(CO) spectrum contained five bands in the terminal region, in profile similar to those of the other hexacarbonyl complexes described above. As found for 10, the ν(CO) bands show a shift of 20–30 cm⁻¹ to lower energy compared with those of 6. In the FAB mass spectrum, a molecular ion was found at m/z 1485, the major fragmentation being by loss of CO groups. The structure of this complex, as the expected product formed by replace-

ment of the μ-H ligand in 6 by the isolobal Au(PPh₃) group, was confirmed by an X-ray study (below).

Treatment of 6 with strong bases, such as LiMe, resulted in rapid darkening of the solution. Addition of AuCl(PPh₃) or [{Au(PPh₃)}₃O][BF₄] gave the pale yellow crystalline complex Re₂(μ-H){μ-(PPh₂)₂CH[Au(PPh₃)]}(μ-C₂Ph)(CO)₆ (12) in 45 and 95% yields respectively. The ν(CO) spectrum of 12 had a pattern similar to those of the other compounds discussed above. In the ¹H NMR spectrum, a high-field resonance at δ −9.91 showed that the metal-bound H atom had not been replaced, while only one CH resonance at δ 4.15 suggested that one of the dppm methylene hydrogens had been replaced by the Au(PPh₃) group. This was confirmed by an X-ray crystal structure, which has been reported elsewhere [9].

A related reaction occurred when {Rh(μ-Cl)(cod)}₂

was used in place of the gold reagent to give the mixed rhenium–rhodium cluster $Re_2Rh(\mu-H)\{\mu_3-(PPh_2)_2-CH\}(\mu-C_2Ph)(CO)_6(cod)$ (13). The Re_2Rh core is capped by the five-electron donor ligand $[(PPh_2)_2CH]^-$, while the alkyne remains bridging the Re–Re vector. Solution spectra are consistent with a fluxional process involving rapid σ–π exchange of the phenylethynyl ligand also found in complexes 1, 2, 6 and related species. The CH proton (at δ 3.45) shows coupling to two equivalent ^{31}P nuclei, while the metal-bound H ligand gives rise to a doublet at δ -19.43. Coupled only to the ^{103}Rh nucleus, this proton apparently oscillates between the Re–Rh vectors in response to the motion of the alkynyl ligand.

As has also been reported by Ruiz et al. [12], metallation of μ-dppm ligands in manganese and rhenium complexes appears to be a characteristic reaction, which has been used to make a range of metallated derivatives containing both the $[CH(PPh_2)_2]^-$ and $[C(PPh_2)_2]^{2-}$ ligands.

3. Molecular structures

In the course of this work, the molecular structures of complexes 4, 6 and 8–13 were determined; those of 12 and 13 have been described elsewhere [9]. Other related structures in the literature include those of $Re_2(\mu$-

Fig. 1. Plot of molecule 1 of $Re_2(\mu-H)(\mu-C_2Ph)(CO)_6(PMe_3)_2$ (4) showing the atom numbering scheme. In this and subsequent figures non-hydrogen atoms are shown with 20% thermal envelopes; hydrogen atoms have arbitrary radii of 0.1 Å.

$H)(\mu-C_2Ph)(CO)_{8-n}(L)_n$ [$n = 0$ (1) [13]; L = MeCN, $n = 1$ (2) [7], 2 [13]].

3.1. $Re_2(\mu-H)(\mu-C_2Ph)(CO)_6(PMe_3)_2$ (4)

A plot of a molecule of 4 is shown in Fig. 1 and selected bond parameters are collected in Table 1. The two PMe_3 ligands occupy transoid positions across the Re–Re bond and are cis to the phenylethynyl ligand. Addition of the PMe_3 ligands results in lengthening of the Re–Re bond from 3.089(1) to 3.156(1), 3.143(1) Å (values for two independent molecules given). The Re–P bonds [2.461(6), 2.460(6) and 2.459(6), 2.454(6) Å] are trans to rhenium–carbonyl bonds which are longer [1.95(2), 1.90(2) and 1.97(2), 1.95(2) Å] than the other Re–CO bonds (av. 1.91, 1.89 Å). The phenylethynyl group is σ-bonded to Re(1) [2.10(2), 2.03(2) Å] and π-bonded to Re(2) [Re(2)–C(1,2) 2.31, 2.45(2) and 2.35, 2.47(2) Å], values which are similar to those found for the unsubstituted complex. Although the precision is not high, Re–CO(12) bonds trans to the σ-bonded carbon on Re(1) [1.95(2), 1.82(2) Å] appear to be longer than those trans to the π-bonded C_2 unit [Re(2)–C(21) 1.87(2), 1.89(2) Å]. The bridging H atom was located but not refined in the determination [Re(1,2)–H 1.7, 2.0 and 1.8, 2.0 Å].

3.2. $AuRe_2(\mu-C_2Ph)(CO)_8(PPh_3)$ (10)

A molecule of 10 is shown in Fig. 2. Replacement of H in 1 by the $Au(PPh_3)$ group has resulted in a lengthening of the Re(1)–Re(2) separation by 0.092 Å. The Au–Re bonds [2.744, 2.844(1) Å] are similar to those found in $AuRe_2(\mu-PPh_2)(CO)_8(PPh_3)$ [14]. Compared with 1, the phenylethylnyl group is somewhat more tightly π-bonded to Re(2) [Re(2)–C(1,2) 2.29, 2.40(2) vs. 2.362, 2.473(9) Å in 1 [13]], although the Re(1)–C(1) distances are similar in both complexes. This is consistent with the $AuRe_2$ core being more electron-rich than the $Re_2(\mu-H)$ system, as mentioned above.

3.3. $Re_2(\mu-X)(\mu-dppm)(\mu-C_2Ph)(CO)_6$ [X = H(6), Br(8) and Au(PPh_3) (11)]

Figs. 3–5 contain plots of the three molecules, and selected bond parameters are summarised in Table 1. In 6 and 11, the Re–Re bond is retained, that in 6 being 0.016 Å longer than that found in 1, while replacement of H by $Au(PPh_3)$ in 11 results in elongation by 0.08 Å. The overall geometry of the three complexes is similar, except for the change in Re–Re separations as the bridging ligands are changed. In the case of 8, there is no formal requirement for an Re–Re bond, as each bridging ligand contributes three electrons to the complex. Consequently, the Re atoms are separated by 3.744(2) Å.
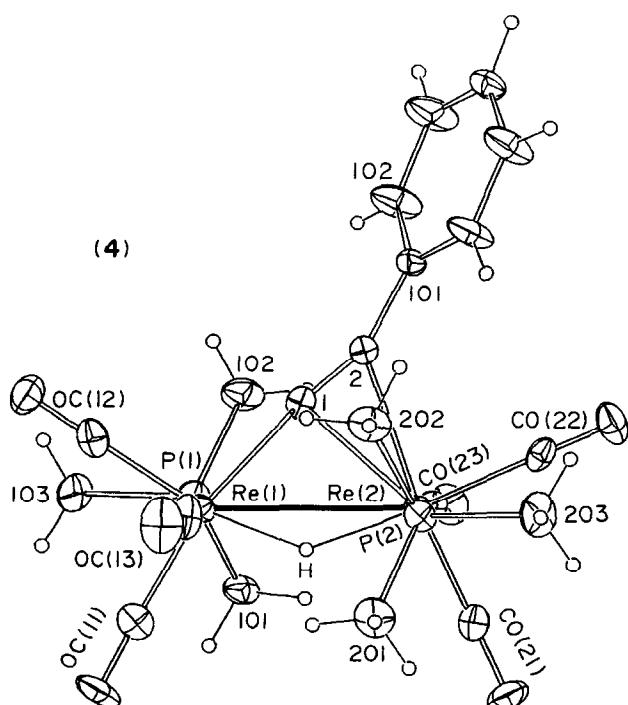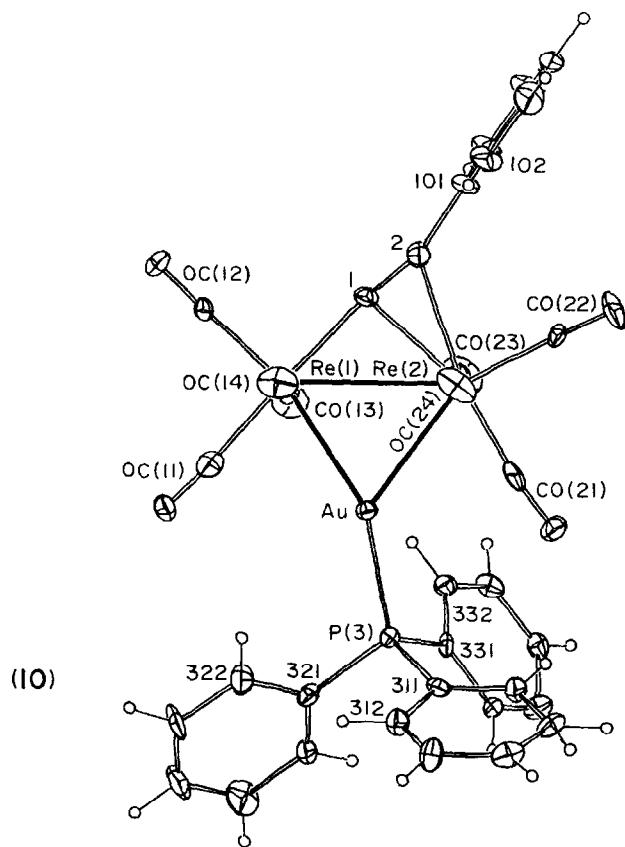
Fig. 2. Plot of a molecule of $AuRe_2(\mu-C_2Ph)(CO)_8(PPh_3)$ (10) showing the atom numbering scheme.

Fig. 4. Plot of a molecule of $Re_2(\mu-Br)(\mu-dppm)(\mu-C_2Ph)(CO)_6$ (8) showing the atom numbering scheme.

C(1,2) 2.36, 2.50(1) Å in 6; 2.331, 2.400(9) Å in 11], while in 8 the degree of uncertainty in the positions of C(1,2) renders any comparison fruitless.

Compared with 1 and 10, addition of dppm results in little change to the Re–Re separations in the μ-hydrido complex [3.095(2) vs. 3.089(1) Å in 1], while in the gold derivatives a lengthening from 3.179(2) Å (in 10) to 3.2260(8) Å (in 11) is found. The Au–Re(1) separations in 10 and 11 are similar, while the Au–Re(2) distances are 2.844(2) and 2.8119(9) Å respectively.

The μ-dppm ligand occupies coordination positions *cis* to the phenylethynyl group on each Re atom, necessarily on the same side of the Re–Re bond. The Re–P separations are between 2.44 and 2.48 Å in all three complexes. The phenylethynyl ligand is again found more tightly π-bonded to Re(2) in 11 than in 6 [Re(2)–

Fig. 3. Plot of a molecule of $Re_2(\mu-H)(\mu-dppm)(\mu-C_2Ph)(CO)_6$ (6) showing the atom numbering scheme.

Fig. 5. Plot of a molecule of $AuRe_2(\mu-dppm)(\mu-C_2Ph)(CO)_6(PPh_3)$ (11) showing the atom numbering scheme.
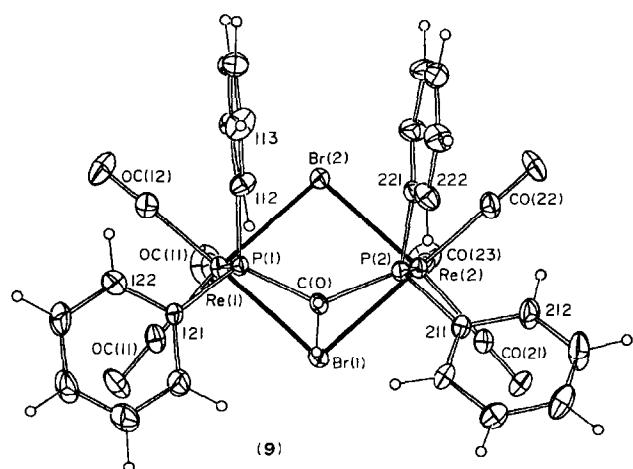
Fig. 6. Plot of molecule 1 of Re₂(μ-Br)₂(μ-dppm)(CO)₆ (9) showing the atom numbering scheme.

Other parameters are comparable with those found in the other dppm complexes. The opening of the Re(1)–X–Re(2) angle follows the increasing Re · · · Re separations: for X = Au, 69.31(3) (10), 70.93(2) (11); Br, 88.9(1) (8); 95.57–96.49(3)° (9). However, for X = H, where the H atom is necessarily close to the Re–Re axis, the angle is much larger: 129(−), 107(−)° (4).

3.4. Re₂(μ-Br)₂(μ-dppm)(CO)₆ (9)

A plot of a molecule of 9 is given in Fig. 6, with relevant bond distances and angles in Table 1. In 9 the two Re(CO)₃ units are held together by two Br atoms and the μ-dppm ligand. Comparing the structure of 9 with that of the closely related complex Re₂(μ-Cl)₂(μ-dppe)(CO)₆ [11], the Re · · · Re separations appear to be determined by the size of the halogen atoms: the smaller Cl atoms results in a value of 3.681(1) Å compared with 3.920, 3.929(1) Å for 9 (values for two independent molecules given). The marked asymmetry in the Re–Cl distances is not found in 9. In both complexes the Re atoms have approximate octahedral coordination.

The manner in which the increasing Re(1)–Re(2) separation is accommodated by the μ-dppm ligand is of interest. In complexes 6 and 8, 9 and 11, where the Re–Re separations increase from 3.095(2) Å (in 6) to 3.920(1) Å (in 9), the Re–P and P–C distances remain essentially constant [Re–P 2.44–2.48, P–C 1.83–1.84 Å]. However, consideration of the Re₂PCP intra-ring angles shows that those at Re decrease from 89° (in 6) to 81° (in 9). In contrast, those at the P atoms and at C(0) increase [at P: from ca. 113° in 6 and 11 to ca. 115.5° in 8 and 115.6, 116.4° in 9; at C: from 113.5° in 6 and 11 to 118° in 8 and 120.6° in 9]. Thus, changes in electronic requirements, and hence separations, of the metal atoms are accommodated by flexibility in the remainder of the ring.

4. Conclusions

We have shown that ready substitution of CO and MeCN by dppm occurs in complex 2. In 4, the transoid geometry proposed for the PMe₃ ligand assigned to similar complexes by consideration of the IR evidence [6] has been confirmed by the X-ray study. The dppm ligand bridges the two Re atoms, which are bonded together when the additional bridging groups are the isolobal ligands H or Au(PPh₃). Addition of halogen to the hydrido complex results in cleavage of the Re–Re bond when H is replaced by Br or I; excess bromine reacts to replace the μ-C₂Ph ligand also by Br.

Replacement of the bridging H atom in 6 occurs on reaction with AuMe(PPh₃) to give the expected AuRe₂ cluster derivative. In contrast, treatment of 6 with a strong base, such as LiMe, followed by addition of AuCl(PPh₃) or [{Au(PPh₃)}₃O]⁺, affords an isomeric complex in which the μ-dppm ligand has been aurated. A similar reaction with {Rh(μ-Cl)(cod)}₂ affords an Re₂Rh cluster containing the capping [CH(PPh₂)₂]⁻ ligand [9]. Although we have been partly successful in our objective of making mixed-metal complexes, further work remains to be done in this area.

5. Experimental

General reaction conditions were similar to those described in an earlier paper [2]. Re₂(CO)₁₀ (Strem) was used as received. The complexes Re₂(CO)₈(NCMe)₂ [15] and Re₂(μ-H)(μ-C₂Ph)(CO)₇(NCMe) [7] were prepared according to the cited methods.

5.1. Preparation of Re₂(μ-H)(μ-C₂Ph)(CO)₇(dbu) (3)

To a solution of 2 (100 mg, 0.14 mmol) in THF (10 ml) was added dbu (21 μl, 0.14 mmol) and the mixture was stirred for 10 min. After removal of solvent, the residue was purified by preparative TLC (light petroleum/CH₂Cl₂ 10/3). The major band was recrystallised (CH₂Cl₂/hexane) to give pale yellow, slightly air-sensitive crystals of Re₂(μ-H)(μ-C₂Ph)(CO)₇(dbu) (3) (82 mg, 70%). IR (THF): ν(CO) 2098m, 2021s, 1996s, 1984(sh), 1954s, 1923m, 1906m cm⁻¹. FAB mass spectrum (m/z): 822, M⁺; 794–598, [M–nCO]⁺ (n = 1–7); 446, [M–7CO–dbu]⁺.

5.2. Preparation of Re₂(μ-H)(μ-C₂Ph)(CO)₆(L)₂

5.2.1. L = PMe₃ (4)
A solution of 2 (50 mg, 0.07 mmol) in CH₂Cl₂ (5 ml) was treated with neat PMe₃ (14.5 μl, 0.14 mmol) and allowed to stir for 10 min. Volatiles were removed under vacuum and the pale yellow residue was purified by preparative TLC (light petroleum/acetone 10/3). Only the fastest moving band (R_f 0.7) gave an isolable complex. Crystallisation of this fraction (CH₂Cl₂/

Table 2
Crystal data and refinement details for complexes **4, 6, 8, 9, 10** and **11**

Compound	Re₂(μ-H)(μ-C₂Ph)(CO)₆(PMe₃)₂ (4)	Re₂(μ-H)(μ-C₂Ph)(μ-dppm)(CO)₆·0.5CHCl₃ (6)	Re₂(μ-Br)(μ-C₂Ph)(μ-dppm)(CO)₆ (8)	Re₂(μ-Br)₂(μ-dppm)(CO)₆·0.22CH₂Cl₂ (9)	AuRe₂(μ-C₂Ph)(CO)₈(PPh₃) (10)	AuRe₂(μ-dppm)(μ-C₂Ph)(CO)₆(PPh₃) (11)
Formula	$C_{20}H_{24}O_6P_2Re_2$	$C_{39}H_{28}O_6P_2Re_2 \cdot 0.5CHCl_3$	$C_{39}H_{27}BrO_6P_2Re_2$	$C_{31}H_{22}Br_2O_6P_2Re_2 \cdot 0.22CH_2Cl_2$	$C_{34}H_{20}AuO_8PRe_2$	$C_{57}H_{42}AuO_6P_3Re_2$
MW	794.8	1086.7	1105.9	1103.4	1156.9	1485.3
Crystal system	Triclinic	Monoclinic	Orthorhombic	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$ (No. 2)	$C2/c$ (No. 15)	$P2_12_12_1$ (No. 19)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a (Å)	20.812(3)	33.19(3)	15.914(7)	19.224(10)	12.573(6)	18.927(5)
b (Å)	13.174(1)	11.154(3)	15.531(3)	15.491(4)	10.854(7)	14.091(4)
c (Å)	9.831(7)	22.205(9)	15.507(9)	12.195(3)	24.320(2)	22.642(6)
α (deg)	94.29(3)			70.80(2)		
β (deg)	100.49(3)	110.89(5)		89.44(3)	101.41(3)	122.94(2)
γ (deg)	104.25(1)			87.63(3)		
V (Å³)	2548(2)	7682(8)	3833(3)	3427(2)	3252(3)	5068(3)
Z	4	8	4	4	4	4
D_c (g cm⁻³)	2.07	1.88	1.92	2.14	2.36	1.95
$F(000)$	1488	4152	2096	2061	2128	2856
Crystal size (mm³)	0.13 × 0.064 × 0.40	0.25 × 0.43 × 0.25	0.52 × 0.37 × 0.39	0.204 × 0.520 × 0.35	0.22 × 0.18 × 0.09	0.22 × 0.85 × 0.30
A^* (min, max)	1.86, 3.49 (Gaussian)	3.76, 4.89 (analytical)	4.73, 8.27 (analytical)	5.09, 10.12 (analytical)	2.66, 8.39 (analytical)	3.84, 7.06 (analytical)
μ (cm⁻¹)	96.5	72.6	74.8	101.0	120.2	78.0
$2\theta_{max}$ (deg)	50	55	55	50	55	55
N	8946	8828	4689	10574	7442	9131
N_o	6153	5298	2908	8869	4225	7263
R	0.058	0.053	0.068	0.031	0.050	0.037
R_w	0.061	0.052	0.069	0.037	0.051	0.041

Table 3
Non-hydrogen positional and isotropic displacement parameters (4)

Atom	x	y	z	U_{eq} Å^2
Re(11)	0.13741(4)	0.94774(6)	0.74282(8)	0.0403(3)
Re(12)	0.02131(4)	0.73506(6)	0.66115(8)	0.0360(3)
C(111)	0.115(1)	1.082(2)	0.736(2)	0.059(9)
O(111)	0.0995(8)	1.161(1)	0.725(2)	0.086(8)
C(112)	0.232(1)	1.014(2)	0.797(2)	0.059(9)
O(112)	0.2885(7)	1.052(1)	0.833(2)	0.089(8)
C(113)	0.137(1)	0.962(2)	0.941(2)	0.065(9)
O(113)	0.1449(9)	0.987(1)	1.057(2)	0.104(9)
C(121)	−0.0669(9)	0.751(2)	0.618(2)	0.050(8)
O(121)	−0.1227(6)	0.761(1)	0.599(2)	0.079(7)
C(122)	−0.0166(8)	0.584(2)	0.632(2)	0.050(8)
O(122)	−0.0393(8)	0.496(1)	0.620(2)	0.076(7)
C(123)	0.0192(9)	0.727(1)	0.459(2)	0.045(8)
O(123)	0.0127(7)	0.713(1)	0.345(1)	0.067(7)
P(11)	0.1524(3)	0.9561(4)	0.5010(6)	0.048(2)
C(1101)	0.080(1)	0.969(2)	0.377(2)	0.056(9)
C(1102)	0.179(1)	0.851(2)	0.421(2)	0.07(1)
C(1103)	0.219(1)	1.073(2)	0.489(2)	0.07(1)
P(12)	0.0120(3)	0.7305(4)	0.9066(5)	0.047(2)
C(1201)	−0.017(1)	0.835(2)	0.985(2)	0.08(1)
C(1202)	0.084(1)	0.723(2)	1.035(2)	0.07(1)
C(1203)	−0.051(1)	0.613(2)	0.932(3)	0.09(1)
C(11)	0.1384(8)	0.789(1)	0.720(2)	0.038(7)
C(12)	0.1312(8)	0.695(1)	0.710(2)	0.037(7)
C(101)	0.1506(8)	0.596(1)	0.695(2)	0.043(7)
C(102)	0.191(1)	0.578(2)	0.602(2)	0.08(1)
C(103)	0.217(1)	0.492(2)	0.602(3)	0.11(2)
C(104)	0.200(1)	0.417(2)	0.689(2)	0.07(1)
C(105)	0.156(1)	0.429(2)	0.766(3)	0.10(1)
C(106)	0.133(1)	0.518(2)	0.772(3)	0.09(1)
Re(21)	0.52669(4)	0.76967(7)	0.30783(8)	0.0493(3)
Re(22)	0.36958(4)	0.74315(7)	0.25590(8)	0.0467(3)
C(211)	0.583(1)	0.902(2)	0.357(2)	0.08(1)
O(211)	0.6180(7)	0.996(1)	0.387(2)	0.088(8)
C(212)	0.600(1)	0.703(2)	0.331(2)	0.07(1)
O(212)	0.6430(9)	0.663(2)	0.337(2)	0.12(1)
C(213)	0.534(1)	0.779(2)	0.119(2)	0.08(1)
O(213)	0.5490(7)	0.782(2)	0.008(2)	0.101(9)
C(221)	0.344(1)	0.871(2)	0.272(2)	0.07(1)
O(221)	0.3266(8)	0.947(1)	0.278(2)	0.095(9)
C(222)	0.276(1)	0.667(2)	0.200(2)	0.060(9)
O(222)	0.2200(7)	0.624(1)	0.173(2)	0.098(8)
C(223)	0.3601(9)	0.728(2)	0.448(2)	0.059(9)
O(223)	0.3456(8)	0.723(2)	0.554(2)	0.10(1)
P(21)	0.5339(3)	0.7589(5)	0.5587(6)	0.054(2)
C(2101)	0.490(1)	0.635(2)	0.613(3)	0.08(1)
C(2102)	0.510(1)	0.863(2)	0.657(2)	0.06(1)
C(2103)	0.620(1)	0.777(2)	0.656(2)	0.07(1)
P(22)	0.3660(3)	0.7695(5)	0.0104(6)	0.053(2)
C(2201)	0.417(1)	0.894(2)	−0.020(2)	0.08(1)
C(2202)	0.381(1)	0.666(2)	−0.103(2)	0.08(1)
C(2203)	0.284(1)	0.777(2)	−0.077(2)	0.08(1)
C(21)	0.447(1)	0.640(2)	0.256(2)	0.059(9)
C(22)	0.3905(9)	0.568(2)	0.219(2)	0.056(9)
C(201)	0.3391(9)	0.467(2)	0.166(2)	0.055(9)
C(202)	0.343(1)	0.405(2)	0.052(2)	0.08(1)
C(203)	0.297(1)	0.312(2)	0.010(3)	0.11(1)
C(204)	0.248(1)	0.271(2)	0.075(3)	0.10(1)
C(205)	0.242(1)	0.324(2)	0.188(3)	0.10(1)
C(206)	0.289(1)	0.424(2)	0.243(3)	0.10(1)

MeOH) gave white $Re_2(\mu$-H)(μ-C_2Ph)(CO)$_6$(PMe$_3$)$_2$ (4) (10 mg, 18%). IR (CH$_2$Cl$_2$): ν(CO) 2030m, 2009s, 1980(sh), 1921(br) cm^{-1}. ^{r}H NMR: δ(CDCl$_3$) − 12.45

Table 4
Non-hydrogen positional and isotropic displacement parameters (6)

Atom	x	y	z	U_{eq} Å^2
Re(1)	0.65835(2)	0.28178(5)	0.53697(2)	0.0392(2)
Re(2)	0.57530(2)	0.37017(5)	0.55591(2)	0.0396(2)
C(11)	0.6536(4)	0.177(1)	0.4665(7)	0.049(6)
O(11)	0.6501(3)	0.113(1)	0.4237(5)	0.080(5)
C(12)	0.7194(5)	0.282(1)	0.5638(6)	0.043(5)
O(12)	0.7570(3)	0.282(1)	0.5796(5)	0.082(5)
O(13)	0.6604(4)	0.492(1)	0.4488(5)	0.097(6)
C(13)	0.6579(4)	0.415(1)	0.4822(7)	0.057(6)
C(21)	0.5228(4)	0.301(1)	0.4970(6)	0.049(5)
O(21)	0.4921(3)	0.2582(9)	0.4637(5)	0.071(5)
C(22)	0.5426(4)	0.458(1)	0.5943(6)	0.050(6)
O(22)	0.5221(3)	0.5084(9)	0.6184(5)	0.068(5)
C(23)	0.5718(4)	0.502(1)	0.4974(7)	0.056(6)
O(23)	0.5690(3)	0.581(1)	0.4629(5)	0.092(6)
P(1)	0.6596(1)	0.1080(3)	0.6044(2)	0.038(1)
C(111)	0.6742(4)	−0.029(1)	0.5751(5)	0.041(5)
C(112)	0.7172(5)	−0.042(1)	0.5783(7)	0.062(7)
C(113)	0.7314(5)	−0.145(2)	0.5590(8)	0.082(8)
C(114)	0.7032(7)	−0.238(2)	0.5349(7)	0.081(9)
C(115)	0.6622(5)	−0.229(1)	0.5297(8)	0.078(8)
C(116)	0.6481(5)	−0.126(1)	0.5509(7)	0.061(7)
C(121)	0.6955(4)	0.102(1)	0.6892(5)	0.036(5)
C(122)	0.7023(4)	−0.005(1)	0.7219(6)	0.044(5)
C(123)	0.7273(4)	−0.009(1)	0.7860(7)	0.057(6)
C(124)	0.7458(5)	0.094(2)	0.8173(7)	0.067(7)
C(125)	0.7397(5)	0.201(2)	0.7864(7)	0.071(7)
C(126)	0.7137(4)	0.206(1)	0.7212(6)	0.052(6)
C(0)	0.6068(3)	0.072(1)	0.6081(5)	0.035(4)
P(2)	0.5799(1)	0.2000(3)	0.6286(2)	0.037(1)
C(211)	0.6059(4)	0.217(1)	0.7160(5)	0.042(5)
C(212)	0.6207(5)	0.119(1)	0.7569(7)	0.055(6)
C(213)	0.6387(5)	0.136(2)	0.8214(7)	0.063(7)
C(214)	0.6422(5)	0.246(2)	0.8477(7)	0.067(7)
C(215)	0.6273(5)	0.346(1)	0.8091(7)	0.073(8)
C(216)	0.6089(5)	0.330(1)	0.7428(6)	0.052(6)
C(221)	0.5276(4)	0.140(1)	0.6219(6)	0.044(5)
C(222)	0.5038(5)	0.205(1)	0.6513(8)	0.070(7)
C(223)	0.4635(5)	0.166(2)	0.646(1)	0.09(1)
C(224)	0.4464(5)	0.062(2)	0.6131(9)	0.09(1)
C(225)	0.4696(5)	−0.003(1)	0.5864(8)	0.076(8)
C(226)	0.5107(4)	0.035(1)	0.5912(7)	0.063(7)
C(1)	0.6504(4)	0.401(1)	0.6026(6)	0.039(5)
C(2)	0.6389(4)	0.480(1)	0.6322(6)	0.044(5)
C(101)	0.6377(4)	0.579(1)	0.6764(6)	0.049(6)
C(102)	0.6674(5)	0.579(1)	0.7390(7)	0.068(7)
C(103)	0.6662(6)	0.667(2)	0.7818(8)	0.081(8)
C(104)	0.6366(7)	0.756(2)	0.763(1)	0.09(1)
C(105)	0.6078(6)	0.758(1)	0.702(1)	0.08(1)
C(106)	0.6082(5)	0.672(1)	0.6589(7)	0.058(6)
Cl(1)	1/2	0.806(2)	3/4	0.40(2)
Cl(2) *	0.477(2)	0.554(3)	0.729(2)	0.39(5)
Cl(3) *	0.5476(8)	0.675(3)	0.826(1)	0.28(2)
C *	0.517(2)	0.656(4)	0.743(2)	0.4(1)

* Site occupancy factor 0.5.

[1H, t, J(HP) = 8.3 Hz, Re–H], 1.46 [18H, d, J(HP) = 7.4 Hz, PMe$_3$], 7.26–7.51 (5H, m, Ph). FAB mass spectrum (m/z): 794, M$^+$; 776–626, [M–nCO]$^+$ (n = 1–6).

5.2.2. L = CN^{t}Bu (5)

A solution of 2 (100 mg, 0.14 mmol) and ^{t}BuNC (70 mg, 0.8 mmol) in CH$_2$Cl$_2$ (10 ml) was heated at reflux point for 2 h. The reaction products were separated by preparative TLC (light petroleum/acetone 10/3). The first band (R_f 0.7) gave white crystals of Re$_2$(μ-H)(μ-C$_2$Ph)(CO)$_6$(CN^{t}Bu)$_2$ (5) (58 mg, 51%) after crystallisation (CH$_2$Cl$_2$/MeOH). Anal. Found: C, 35.65; H, 2.99; N, 3.49. C$_{24}$H$_{24}$N$_2$O$_6$Re$_2$ Calc.: C, 35.64; H, 2.97; N, 3.46%. IR (CH$_2$Cl$_2$): ν(CN) 2181m; ν(CO) 2031m, 2019s, 1946(br), 1933(br) cm^{-1}. ^{1}H NMR: δ(CDCl$_3$) − 12.71 (1H, s, Re–H), 1.40 (18H, s, CMe_3), 7.26–7.52 (5H, m, Ph). ^{13}C NMR: δ(CDCl$_3$) 30.24 (s, CMe_3), 89.24 (s, C$_\alpha$), 100.48 (s, C$_\beta$), 127.49, 128.34, 129.39, 131.79 (4 × s, C$_2$Ph), 186.78, 188.40, 190.23 (3 × s, CO). FAB mass spectrum (m/z): 808, M$^+$; 780–640, [M–nCO]$^+$ (n = 1–6).

5.3. Preparation of Re$_2$(μ-H)(μ-dppm)(μ-C$_2$Ph)(CO)$_6$ (6)

A solution of 2 (1.5 g, 2.1 mmol) and dppm (810 mg, 2.1 mmol) in THF (20 ml) was heated at reflux point for 1 h. After removal of solvent, the pale yellow residue was recrystallised (CH$_2$Cl$_2$/hexane) to give pale yellow crystals of Re$_2$(μ-H)(μ-dppm)(μ-C$_2$Ph)(CO)$_6$ (6) (1.7 g, 80%), m.p. 205–207°C (dec.). Anal. Found: C, 45.16; H, 2.80. C$_{39}$H$_{28}$O$_6$P$_2$Re$_2$ Calc.: C, 45.57; H, 2.73%. IR (CH$_2$Cl$_2$): ν(CO) 2044s, 2016vs, 1991(sh), 1954(br), 1929(br) cm^{-1}. ^{1}H NMR: δ(CDCl$_3$) − 11.83 [1H, t, J(HP) = 10.17 Hz, Re–H], 2.58, 3.11 (2H, m, CH$_2$P), 7.16–7.40 (25H, m, Ph). ^{13}C NMR: δ(CDCl$_3$) 21.76 [t, J(CP) = 18.9 Hz, CH$_2$P], 93.48 (s, C$_\alpha$), 103.62 (s, C$_\beta$), 127.56–133.05 (m, Ph), 186.62, 189.29, 192.35 (3 × s, CO). FAB mass spectrum (m/z): 1027, M$^+$; 999–859, [M–nCO]$^+$ (n = 1–6).

5.4. Preparation of Re$_2$(μ-I)(μ-dppm)(μ-C$_2$Ph)(CO)$_6$ (7)

A mixture of 6 (100 mg, 0.10 mmol) and I$_2$ (25 mg, 0.05 mmol) was heated in refluxing THF (10 ml) for 5 h, after which time no starting material remained (TLC). After removal of solvent, preparative TLC (light petroleum/acetone 10/3) enabled the separation of Re$_2$(μ-I)(μ-dppm)(μ-C$_2$Ph)(CO)$_6$ (7) (52 mg, 44%), m.p. 258–260°C, as the fastest moving (R_f 0.6) bright yellow band. Anal. Found: C, 40.15; H, 2.36. C$_{39}$H$_{27}$IO$_6$P$_2$Re$_2$ Calc.: C, 40.63; H, 2.34%. IR (CH$_2$Cl$_2$): ν(CO) 2044s, 2028vs, 2009w, 1952s, 1945(sh), 1919(br) cm^{-1}. ^{1}H NMR: δ(CDCl$_3$) 4.50,

5.09 (2H, m, CH$_2$P), 7.00–7.63 (25H, m, Ph). ^{13}C NMR: δ(CDCl$_3$) 28.57 [t, J(CP) = 15.7 Hz, CH$_2$P], 59.54 (s, C$_\alpha$), 97.66 (s, C$_\beta$), 124.77–137.02 (m, Ph), 187.54, 188.01, 188.84 (3 × s, CO). ^{31}P NMR: δ(CDCl$_3$) − 13.24 (s, PPh$_2$). FAB mass spectrum (m/z): 1152, M$^+$; 1124–984, [M–nCO]$^+$ (n = 1–6).

Two other complexes present in orange and red–orange bands (R_f 0.55, 0.50 respectively) were not characterised.

Table 5
Non-hydrogen positional and isotropic displacement parameters (8)

Atom	x	y	z	U_{eq} Å^2
Re(1)	0.12192(7)	0.32763(8)	0.83203(7)	0.0467(4)
Re(2)	0.28332(7)	0.22626(8)	0.68873(8)	0.0491(4)
Br	0.1705(2)	0.1665(2)	0.8029(2)	0.059(1)
C(11)	0.035(2)	0.294(2)	0.911(2)	0.063(9)
O(11)	−0.022(1)	0.275(1)	0.953(1)	0.079(6)
C(12)	0.104(2)	0.431(2)	0.847(2)	0.053(8)
O(12)	0.078(1)	0.508(1)	0.867(1)	0.080(7)
C(13)	0.190(2)	0.327(2)	0.929(2)	0.066(9)
O(13)	0.246(2)	0.327(2)	0.980(2)	0.114(9)
C(21)	0.307(1)	0.113(2)	0.672(2)	0.038(6)
O(21)	0.323(1)	0.040(1)	0.659(1)	0.070(6)
C(22)	0.354(2)	0.252(2)	0.600(2)	0.048(8)
O(22)	0.402(1)	0.272(2)	0.544(1)	0.091(7)
C(23)	0.367(2)	0.229(2)	0.782(2)	0.060(8)
O(23)	0.422(1)	0.230(2)	0.832(2)	0.104(8)
P(1)	0.0340(4)	0.3205(5)	0.7016(5)	0.042(2)
C(111)	−0.081(2)	0.299(2)	0.726(2)	0.044(7)
C(112)	−0.117(2)	0.220(2)	0.717(2)	0.08(1)
C(113)	−0.200(2)	0.207(3)	0.745(2)	0.11(1)
C(114)	−0.241(2)	0.270(3)	0.777(2)	0.11(1)
C(115)	−0.208(2)	0.347(2)	0.782(2)	0.10(1)
C(116)	−0.127(2)	0.368(2)	0.757(2)	0.070(9)
C(121)	0.028(2)	0.415(2)	0.635(2)	0.058(8)
C(122)	0.077(2)	0.484(2)	0.646(2)	0.058(9)
C(123)	0.068(2)	0.560(2)	0.599(2)	0.07(1)
C(124)	0.011(2)	0.560(2)	0.532(2)	0.08(1)
C(125)	−0.032(2)	0.492(2)	0.521(2)	0.09(1)
C(126)	−0.029(2)	0.416(2)	0.564(2)	0.07(1)
C(0)	0.059(1)	0.232(2)	0.629(2)	0.041(6)
P(2)	0.1661(4)	0.2258(5)	0.5834(4)	0.040(2)
C(211)	0.168(2)	0.124(2)	0.530(2)	0.054(8)
C(212)	0.133(2)	0.048(2)	0.564(2)	0.057(8)
C(213)	0.143(2)	−0.030(2)	0.528(2)	0.08(1)
C(214)	0.192(2)	−0.043(2)	0.454(2)	0.10(1)
C(215)	0.231(2)	0.032(2)	0.426(2)	0.08(1)
C(216)	0.220(2)	0.115(2)	0.461(2)	0.067(9)
C(221)	0.161(2)	0.302(2)	0.499(2)	0.046(7)
C(222)	0.208(2)	0.374(2)	0.495(2)	0.08(1)
C(223)	0.199(2)	0.435(2)	0.434(2)	0.09(1)
C(224)	0.146(2)	0.427(2)	0.370(2)	0.09(1)
C(225)	0.099(2)	0.350(2)	0.363(2)	0.09(1)
C(226)	0.107(2)	0.291(2)	0.429(2)	0.09(1)
C(1)	0.232(1)	0.367(1)	0.744(1)	0.023(5)
C(2)	0.270(1)	0.385(2)	0.717(1)	0.033(6)
C(101)	0.348(2)	0.435(3)	0.670(3)	0.11(1)
C(102)	0.334(2)	0.517(2)	0.634(2)	0.09(1)
C(103)	0.394(3)	0.580(3)	0.609(3)	0.12(2)
C(104)	0.472(3)	0.551(3)	0.626(3)	0.13(2)
C(105)	0.502(3)	0.479(3)	0.680(3)	0.12(1)
C(106)	0.441(2)	0.421(2)	0.698(2)	0.10(1)

Table 6
Non-hydrogen positional and isotropic displacement parameters (9)

Atom	x	y	z	U_{eq} Å
Re(11)	0.72305(2)	0.40035(2)	1.01790(3)	0.0373(1)
Re(12)	0.62026(2)	0.44152(2)	0.72796(3)	0.0365(1)
Br(11)	0.74659(4)	0.38446(5)	0.81081(7)	0.0449(3)
Br(12)	0.59229(4)	0.42975(5)	0.94516(7)	0.0420(3)
C(111)	0.8185(4)	0.3767(5)	1.0540(7)	0.051(3)
O(111)	0.8778(3)	0.3620(5)	1.0748(6)	0.078(3)
C(112)	0.7090(4)	0.4113(6)	1.1665(7)	0.055(4)
O(112)	0.7014(4)	0.4145(5)	1.2580(5)	0.095(4)
C(113)	0.7074(5)	0.2711(6)	1.0778(7)	0.057(4)
O(113)	0.6958(4)	0.1939(4)	1.1165(6)	0.091(3)
C(121)	0.6496(4)	0.4386(6)	0.5770(7)	0.051(4)
O(121)	0.6668(3)	0.4363(5)	0.4913(5)	0.069(3)
C(122)	0.5303(4)	0.4802(6)	0.6679(7)	0.057(4)
O(122)	0.4749(3)	0.5062(5)	0.6310(6)	0.094(4)
C(123)	0.5945(4)	0.3146(5)	0.7722(7)	0.049(3)
O(123)	0.5775(4)	0.2413(4)	0.8041(6)	0.084(3)
P(11)	0.7364(1)	0.5666(1)	0.9298(2)	0.0359(7)
C(1111)	0.6776(4)	0.6455(5)	0.9702(6)	0.040(3)
C(1112)	0.6888(5)	0.7393(5)	0.9297(7)	0.054(4)
C(1113)	0.6458(6)	0.7996(6)	0.9610(9)	0.078(5)
C(1114)	0.5902(5)	0.7694(7)	1.0306(8)	0.070(4)
C(1115)	0.5784(5)	0.6776(7)	1.0717(8)	0.064(4)
C(1116)	0.6214(4)	0.6151(6)	1.0442(7)	0.051(4)
C(1121)	0.8212(4)	0.5980(5)	0.9656(7)	0.042(3)
C(1122)	0.8287(5)	0.6148(8)	1.0683(9)	0.078(5)
C(1123)	0.8938(6)	0.6329(9)	1.1045(9)	0.095(6)
C(1124)	0.9510(5)	0.6337(8)	1.0375(9)	0.086(5)
C(1125)	0.9439(5)	0.6160(8)	0.938(1)	0.091(6)
C(1126)	0.8804(5)	0.5983(8)	0.9007(8)	0.077(5)
C(10)	0.7344(4)	0.6119(5)	0.7707(6)	0.037(3)
P(12)	0.6574(1)	0.6000(1)	0.6904(2)	0.0364(7)
C(1211)	0.6830(4)	0.6552(5)	0.5387(6)	0.040(3)
C(1212)	0.6339(5)	0.6558(7)	0.4553(7)	0.067(4)
C(1213)	0.6466(6)	0.6972(8)	0.3398(9)	0.098(6)
C(1214)	0.7085(6)	0.7389(7)	0.3042(8)	0.084(5)
C(1215)	0.7580(5)	0.7389(6)	0.3859(8)	0.064(4)
C(1216)	0.7436(5)	0.6968(5)	0.5042(7)	0.050(3)
C(1221)	0.5929(4)	0.6846(5)	0.7084(7)	0.043(3)
C(1222)	0.6043(5)	0.7778(6)	0.6506(8)	0.062(4)
C(1223)	0.5558(5)	0.8432(6)	0.6599(9)	0.068(4)
C(1224)	0.4967(5)	0.8177(6)	0.7252(8)	0.071(4)
C(1225)	0.4840(5)	0.7267(7)	0.7802(8)	0.078(5)
C(1226)	0.5339(5)	0.6595(6)	0.7715(8)	0.063(4)
Re(21)	0.93600(2)	0.20502(2)	0.41878(3)	0.0402(1)
Re(22)	0.78608(2)	0.03053(2)	0.48266(3)	0.0377(1)
Br(21)	0.80902(5)	0.19684(5)	0.34009(7)	0.0506(3)
Br(22)	0.91784(4)	0.03145(5)	0.53774(7)	0.0457(3)
C(211)	0.9405(5)	0.3313(6)	0.3327(8)	0.057(4)
O(211)	0.9431(4)	0.4082(4)	0.2812(6)	0.077(3)
C(212)	1.0274(4)	0.2094(5)	0.4697(7)	0.051(3)
O(212)	1.0857(3)	0.2152(5)	0.4917(6)	0.078(3)
C(213)	0.9726(5)	0.1711(5)	0.2872(8)	0.058(4)
O(213)	0.9946(5)	0.1543(5)	0.2122(6)	0.102(4)
C(221)	0.6927(5)	0.0326(5)	0.4352(7)	0.055(4)
O(221)	0.6350(3)	0.0298(5)	0.4106(7)	0.092(4)
C(222)	0.7765(4)	−0.0873(5)	0.5883(7)	0.048(3)
O(222)	0.7720(4)	−0.1615(4)	0.6524(5)	0.069(3)
C(223)	0.8141(5)	−0.0172(5)	0.3596(8)	0.059(4)
O(223)	0.8305(4)	−0.0454(5)	0.2880(6)	0.100(4)
P(21)	0.8829(1)	0.2370(1)	0.5871(2)	0.0387(8)
C(2111)	0.9221(4)	0.1835(5)	0.7293(7)	0.049(3)
C(2112)	0.8908(5)	0.2009(6)	0.8269(8)	0.064(4)
C(2113)	0.9223(5)	0.1696(7)	0.9346(8)	0.072(5)

Table 6 (continued)

Atom	x	y	z	U_{eq} Å
C(2114)	0.9851(5)	0.1180(7)	0.9475(8)	0.074(5)
C(2115)	1.0137(5)	0.1000(8)	0.8553(8)	0.077(5)
C(2116)	0.9826(4)	0.1329(6)	0.7454(7)	0.058(4)
C(2121)	0.8843(4)	0.3587(5)	0.5697(7)	0.046(3)
C(2122)	0.8400(5)	0.4195(6)	0.4929(9)	0.066(4)
C(2123)	0.8424(6)	0.5121(6)	0.472(1)	0.089(5)
C(2124)	0.8910(6)	0.5449(7)	0.530(1)	0.109(7)
C(2125)	0.9334(6)	0.4848(8)	0.609(1)	0.106(7)
C(2126)	0.9323(5)	0.3907(7)	0.628(1)	0.077(5)
C(20)	0.7892(4)	0.2191(5)	0.6044(7)	0.042(3)
P(22)	0.7549(1)	0.1055(1)	0.6278(2)	0.0376(8)
C(2211)	0.6615(4)	0.1305(5)	0.6230(7)	0.044(3)
C(2212)	0.6181(5)	0.0654(6)	0.6858(8)	0.063(4)
C(2213)	0.5463(5)	0.0786(7)	0.676(1)	0.076(5)
C(2214)	0.5177(5)	0.1571(8)	0.602(1)	0.082(5)
C(2215)	0.5610(5)	0.2235(7)	0.5338(9)	0.073(5)
C(2216)	0.6325(4)	0.2094(6)	0.5443(8)	0.055(4)
C(2221)	0.7727(4)	0.0442(5)	0.7799(7)	0.043(3)
C(2222)	0.7413(5)	0.0736(6)	0.8647(8)	0.066(4)
C(2223)	0.7546(6)	0.0252(7)	0.9830(9)	0.083(5)
C(2224)	0.7972(6)	−0.0496(8)	1.0137(8)	0.089(5)
C(2225)	0.8298(5)	−0.0798(7)	0.9315(8)	0.070(4)
C(2226)	0.8173(4)	−0.0321(5)	0.8128(7)	0.047(3)
Cl(1) *	0.482(3)	0.988(3)	1.016(4)	0.21(2)
Cl(2) *	0.3903(8)	1.024(1)	0.849(1)	0.237(9)
C(0) *	0.439(2)	0.954(3)	0.947(2)	0.15(2)

* Site occupancy factor 0.438(5).

5.5. Reactions between $Re_2(\mu\text{-}H)(\mu\text{-}dppm)(\mu\text{-}C_2Ph)\text{-}(CO)_6$ and Br_2

(i) Addition of Br_2 (11 μl, 0.2 mmol) to a solution of **6** (100 mg, 0.1 mmol) in THF (10 ml) resulted in an immediate colour change to dark green. Preparative TLC (light petroleum/acetone 10/3) separated several bands, of which the major band gave green crystals (from $CH_2Cl_2/MeOH$) of $Re_2(\mu\text{-}Br)(\mu\text{-}dppm)(\mu\text{-}C_2Ph)(CO)_6$ (**8**) (37 mg, 33%), m.p. 250–253°C. Anal. Found: C, 41.67; H, 2.52. $C_{39}H_{27}BrO_6P_2Re_2 \cdot 0.5CH_2Cl_2$ Calc.: C, 41.27; H, 2.43%. IR (CH_2Cl_2): $\nu(CO)$ 2046s, 2030s, 2013m, 1952s, 1942s, 1917(br) cm^{-1}. ^{1}H NMR: $\delta(CDCl_3)$ 4.14, 4.55 (2H, 2 × m, CH_2P), 7.10–7.54 (25H, m, Ph). ^{13}C NMR: $\delta(CDCl_3)$ 23.70 [t, $J(CP) = 14.6$ Hz], CH_2P], 67.90 (s, C_α), 98.02 (s, C_β), 124.14–135.36 (m, Ph), 189.46, 190.03, 190.40 (3 × s, CO). ^{31}P NMR: $\delta(CDCl_3)$ −6.07 (s, PPh_2). FAB mass spectrum (m/z): 1105, M$^+$; 1077–937, [M−nCO]$^+$ ($n = 1$–6).

(ii) To a stirred solution of **6** (100 mg, 0.1 mmol) in THF (10 ml) was added Br_2 (25 μl, 0.49 mmol), dropwise over 10 min. After 30 min, the solution had changed from dark green to orange. Preparative TLC (light petroleum/acetone 10/3) separated white $Re_2(\mu\text{-}Br)_2(\mu\text{-}dppm)(CO)_6$ (**9**) (28 mg, 24%), m.p. > 275°C (dec.). Anal. Found: C, 34.25; H, 1.59. $C_{31}H_{22}Br_2O_6P_2Re_2$ Calc.: C, 34.32; H, 2.03%. IR (THF): $\nu(CO)$ 2048s, 2035s, 1953s, 1946s, 1918(br) cm^{-1}. ^{1}H NMR: $\delta(CDCl_3)$ 4.46 [2H, t, $J(HP) = 11.4$

Hz, CH_2P], 7.73–7.52 (20H, m, Ph). FAB mass spectrum (m/z): 1084, M$^+$; 1056–916, [M−nCO]$^+$ ($n = 1$–6).

5.6. Preparation of $AuRe_2(\mu\text{-}C_2Ph)(CO)_8(PPh_3)$ (10)

A 50 ml Schlenk flask was flushed with dry nitrogen and charged with $Co_2(CO)_8$ (24 mg, 0.07 mmol) and 3% sodium amalgam (120 mg, 0.16 g atom). Freshly distilled THF (20 ml) was added and the solution allowed to stir for 5 min. After standing, the resulting yellow solution of $Na[Co(CO)_4]$ was carefully removed by syringe and added to a stirred solution of **2** (100 mg, 0.14 mg) in THF (10 ml). After 10 min, solid $AuCl(PPh_3)$ (70 mg, 0.14 mmol) was added and the mixture was stirred briefly. The solvent was removed and the residue purified by preparative TLC (light petroleum/acetone 10/3). Several bands separated: the slowest moving (R_f 0.3) gave $AuRe_2(\mu\text{-}C_2Ph)(CO)_8$-$(PPh_3)$ (**10**) (11 mg, 7%) after crystallisation from $CHCl_3/MeOH$. IR (CH_2Cl_2): $\nu(CO)$ 2093w, 2063m, 2004s, 1970m, 1939m cm^{-1}. ^{1}H NMR: $\delta(CDCl_3)$ 7.0–7.5 (m, Ph). FAB mass spectrum (m/z): 1129–989, [M−nCO]$^+$ ($n = 1$–6).

5.7. Preparation of $AuRe_2(\mu\text{-}dppm)(\mu\text{-}C_2Ph)(CO)_6$-$(PPh_3)$ (11)

A solution of **6** (100 mg, 0.1 mmol) and $AuMe(PPh_3)$ (46 mg, 0.1 mmol) in CH_2Cl_2 (10 ml) was heated at

reflux point for four days. Over this time, the solution turned to green and metallic gold was deposited on the walls of the flask. Preparative TLC (light petroleum/ acetone 10/3) separated two bands. The top band (R_f 0.6) was recrystallised (CH_2Cl_2/hexane) to give green crystals of $AuRe_2(\mu\text{-dppm})(\mu\text{-}C_2Ph)(CO)_6(PPh_3)$ (11) (25 mg, 60% conversion), m.p. 248–253°C (dec.). Anal. Found: C, 46.16; H, 2.95. $C_{57}H_{42}AuO_6P_3Re_2$ Calc.: C, 46.08; H, 2.83%. IR (THF): ν(CO) 2018s, 1987vs, 1935m, 1914s, 1903 cm^{-1}. ^{1}H NMR: δ(CDCl$_3$) 2.53–2.63 (1H, m, CH$_2$P), 4.18–4.27 (1H, m, CH$_2$P), 6.92–7.56 (40H, m, Ph). FAB mass spectrum (m/z): 1485, M$^+$; 1457–1317, [M–nCO]$^+$ (n = 1–6). The second

Table 7
Non-hydrogen positional and isotropic displacement parameters (10)

Atom	x	y	z	U_{eq} Å^2
Re(1)	0.29054(5)	0.45344(7)	0.57343(3)	0.0357(2)
Re(2)	0.19369(5)	0.21827(7)	0.50304(3)	0.0358(2)
Au	0.22595(5)	0.45485(7)	0.45883(3)	0.0343(2)
C(11)	0.312(1)	0.625(2)	0.5486(8)	0.055(8)
O(11)	0.330(1)	0.723(1)	0.5386(6)	0.071(6)
C(12)	0.354(2)	0.494(2)	0.6492(8)	0.056(8)
O(12)	0.391(1)	0.515(1)	0.6955(6)	0.083(7)
C(13)	0.434(1)	0.407(2)	0.5577(8)	0.046(7)
O(13)	0.5149(9)	0.386(2)	0.5467(7)	0.082(7)
C(14)	0.140(1)	0.504(2)	0.5821(7)	0.046(7)
O(14)	0.060(1)	0.539(2)	0.5865(6)	0.083(7)
C(21)	0.159(1)	0.226(2)	0.4228(8)	0.051(7)
O(21)	0.139(1)	0.215(1)	0.3733(5)	0.079(6)
C(22)	0.146(1)	0.051(2)	0.4961(6)	0.040(6)
O(22)	0.118(1)	−0.047(1)	0.4896(7)	0.082(7)
C(23)	0.346(1)	0.167(2)	0.4991(9)	0.057(8)
O(23)	0.429(1)	0.135(2)	0.4954(8)	0.099(8)
C(24)	0.045(1)	0.277(2)	0.5123(9)	0.050(7)
O(24)	−0.038(1)	0.304(1)	0.5161(7)	0.084(7)
P(3)	0.2218(3)	0.5249(4)	0.3676(2)	0.033(1)
C(311)	0.091(1)	0.535(2)	0.3223(7)	0.040(6)
C(312)	0.031(1)	0.645(2)	0.3206(8)	0.054(8)
C(313)	−0.074(1)	0.654(2)	0.2905(9)	0.060(8)
C(314)	−0.121(1)	0.554(2)	0.2611(8)	0.061(8)
C(315)	−0.065(1)	0.446(2)	0.2595(7)	0.056(8)
C(316)	0.040(1)	0.436(2)	0.2914(8)	0.048(7)
C(321)	0.280(1)	0.674(2)	0.3618(7)	0.039(6)
C(322)	0.267(1)	0.766(2)	0.3999(8)	0.058(8)
C(323)	0.311(2)	0.886(2)	0.398(1)	0.08(1)
C(324)	0.366(2)	0.912(2)	0.355(1)	0.08(1)
C(325)	0.380(2)	0.823(2)	0.318(1)	0.09(1)
C(326)	0.338(1)	0.703(2)	0.3230(8)	0.054(7)
C(331)	0.302(1)	0.420(1)	0.3347(7)	0.035(6)
C(332)	0.378(1)	0.347(2)	0.3697(7)	0.041(6)
C(333)	0.439(1)	0.259(2)	0.3478(8)	0.050(7)
C(334)	0.421(1)	0.241(2)	0.2898(8)	0.045(7)
C(335)	0.347(1)	0.315(2)	0.2548(8)	0.055(8)
C(336)	0.287(1)	0.404(2)	0.2766(7)	0.036(6)
C(1)	0.257(1)	0.271(2)	0.5948(7)	0.040(6)
C(2)	0.230(1)	0.168(2)	0.6012(8)	0.050(7)
C(101)	0.212(2)	0.046(2)	0.6269(8)	0.058(8)
C(102)	0.296(2)	−0.041(2)	0.6362(9)	0.065(9)
C(103)	0.277(2)	−0.149(2)	0.658(1)	0.08(1)
C(104)	0.172(2)	−0.171(2)	0.6709(9)	0.09(1)
C(105)	0.094(2)	−0.082(2)	0.661(1)	0.08(1)
C(106)	0.112(1)	0.028(2)	0.6396(9)	0.067(9)

Table 8
Non-hydrogen positional and isotropic displacement parameters (11)

Atom	x	y	z	U_{eq} Å^2
Re(1)	0.17962(2)	0.46001(2)	0.66594(2)	0.0399(2)
Re(2)	0.30647(2)	0.29797(2)	0.67660(2)	0.0365(2)
Au	0.16388(2)	0.26988(2)	0.68328(2)	0.0431(2)
C(11)	0.0925(6)	0.4519(7)	0.6876(5)	0.064(6)
O(11)	0.0439(4)	0.4503(6)	0.7025(4)	0.092(5)
C(12)	0.1517(6)	0.5874(7)	0.6412(5)	0.063(5)
O(12)	0.1328(5)	0.6655(5)	0.6218(4)	0.101(5)
C(13)	0.1005(5)	0.4247(7)	0.5683(5)	0.057(5)
O(13)	0.0534(4)	0.4061(5)	0.5101(3)	0.083(4)
C(21)	0.3027(5)	0.1738(6)	0.7092(4)	0.051(4)
O(21)	0.3059(4)	0.0970(4)	0.7283(3)	0.069(4)
C(22)	0.3939(6)	0.2510(7)	0.6657(4)	0.057(5)
O(22)	0.4414(4)	0.2183(5)	0.6553(3)	0.083(4)
C(23)	0.2232(5)	0.2638(6)	0.5791(4)	0.050(4)
O(23)	0.1765(4)	0.2419(5)	0.5226(3)	0.073(3)
P(1)	0.2878(1)	0.5055(2)	0.7865(1)	0.041(1)
C(111)	0.2933(5)	0.6335(6)	0.7987(4)	0.045(4)
C(112)	0.3556(6)	0.6902(6)	0.8052(5)	0.051(5)
C(113)	0.3511(6)	0.7874(7)	0.8100(5)	0.066(6)
C(114)	0.2870(7)	0.8293(7)	0.8086(6)	0.083(7)
C(115)	0.2243(8)	0.7734(8)	0.8021(7)	0.097(9)
C(116)	0.2264(7)	0.6753(7)	0.7974(7)	0.083(8)
C(121)	0.2858(5)	0.4676(6)	0.8628(4)	0.044(4)
C(122)	0.3484(6)	0.4983(7)	0.9292(5)	0.065(6)
C(123)	0.3483(8)	0.4730(8)	0.9899(5)	0.086(7)
C(124)	0.2818(7)	0.4173(8)	0.9796(6)	0.081(7)
C(125)	0.2209(7)	0.3856(8)	0.9148(5)	0.076(6)
C(126)	0.2224(6)	0.4104(7)	0.8561(5)	0.061(5)
C(0)	0.3944(5)	0.4761(6)	0.8104(4)	0.044(4)
P(2)	0.4082(1)	0.3506(2)	0.7982(1)	0.039(1)
C(211)	0.5178(5)	0.3448(6)	0.8231(4)	0.045(4)
C(212)	0.5677(5)	0.4219(6)	0.8337(4)	0.053(5)
C(213)	0.6492(6)	0.4096(8)	0.8501(5)	0.066(5)
C(214)	0.6805(6)	0.3212(8)	0.8541(5)	0.073(6)
C(215)	0.6321(6)	0.2415(8)	0.8446(5)	0.068(5)
C(216)	0.5509(6)	0.2531(7)	0.8290(5)	0.060(5)
C(221)	0.4158(5)	0.2931(6)	0.8749(4)	0.044(4)
C(222)	0.4880(6)	0.3072(7)	0.9406(4)	0.062(5)
C(223)	0.4926(8)	0.2705(7)	1.0000(5)	0.080(6)
C(224)	0.4274(7)	0.2201(7)	0.9938(5)	0.077(7)
C(225)	0.3553(8)	0.2051(8)	0.9268(6)	0.081(8)
C(226)	0.3498(6)	0.2406(7)	0.8676(5)	0.057(5)
P(3)	0.0709(1)	0.1556(2)	0.6755(1)	0.048(1)
C(311)	0.0888(6)	0.1225(6)	0.7599(5)	0.058(5)
C(312)	0.0503(8)	0.1716(8)	0.7883(6)	0.085(7)
C(313)	0.0725(8)	0.1486(8)	0.8572(6)	0.096(8)
C(314)	0.1269(8)	0.0816(9)	0.8929(6)	0.095(8)
C(315)	0.1658(9)	0.032(1)	0.8668(6)	0.114(9)
C(316)	0.1465(8)	0.0545(9)	0.7999(6)	0.091(7)
C(321)	−0.0397(5)	0.1925(6)	0.6208(4)	0.049(4)
C(322)	−0.0592(6)	0.2737(7)	0.5814(5)	0.068(6)
C(323)	−0.1425(7)	0.3012(8)	0.5362(6)	0.086(6)
C(324)	−0.2057(7)	0.2471(9)	0.5312(5)	0.089(6)
C(325)	−0.1853(7)	0.167(1)	0.5694(7)	0.110(8)
C(326)	−0.1029(7)	0.1369(8)	0.6151(6)	0.085(7)
C(331)	0.0737(6)	0.0448(6)	0.6360(5)	0.056(5)
C(332)	0.1066(6)	0.0459(7)	0.5937(5)	0.063(5)
C(333)	0.1068(7)	−0.0354(8)	0.5601(5)	0.083(6)
C(334)	0.0757(8)	−0.1168(8)	0.5682(6)	0.101(8)
C(335)	0.042(1)	−0.1197(8)	0.6080(8)	0.12(1)
C(336)	0.0401(9)	−0.0391(7)	0.6413(6)	0.097(9)
C(1)	0.2768(5)	0.4585(6)	0.6492(4)	0.044(4)
C(2)	0.3337(5)	0.4453(6)	0.6392(4)	0.050(4)

Table 8 (continued)

Atom	x	y	z	U_{eq} Å^2
C(101)	0.3850(5)	0.4760(6)	0.6133(4)	0.043(4)
C(102)	0.3461(6)	0.5213(8)	0.5495(5)	0.071(5)
C(103)	0.3930(7)	0.5576(9)	0.5253(5)	0.087(6)
C(104)	0.4780(7)	0.5467(7)	0.5624(6)	0.073(7)
C(105)	0.5178(6)	0.5024(7)	0.6257(5)	0.066(6)
C(106)	0.4715(6)	0.4657(7)	0.6504(5)	0.062(5)

band (R_f 0.4) contained unreacted 6 (71 mg, 71%) (IR, spot TLC).

6. Crystallography

Unique data sets were measured at ca. 295 K within the specified $2\theta_{max}$ limits using an Enraf-Nonius CAD4 diffractometer ($2\theta/\theta$ scan mode; monochromatic Mo Kα radiation, λ 0.7107$_3$ Å); N independent reflections were obtained, N_0 with $I > 3\sigma(I)$ being considered 'observed' and used in the full-matrix least-squares refinement after application of absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were included constrained at estimated values. Conventional residuals R, R' on $|F|$ are quoted, statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$ being used. Computation used the XTAL 3.0 program system [16] implemented by Hall; neutral atom complex scattering factors were employed. Pertinent results are given in the figures and tables. Material deposited comprises thermal and hydrogen parameters, full molecular non-hydrogen geometries and structure factor amplitudes.

6.1. Abnormal features / variations in procedure

(4) Putative core hydrogen atoms were observed in difference maps but, in the context of rather weak data, would not refine meaningfully. They were included, constrained, at observed sites.

(6) Crystals for the X-ray study were obtained from chloroform/hexane; residues presumed to be chloroform solvent were observed about a two-fold axis and modelled as such, in terms of one chlorine atom located on that axis and the remainder in half-weighted sites disposed about it. Total solvent occupancy was set at 1 after trial refinement.

(8) Despite substantial size, specimens diffracted very

weakly, supporting meaningful anisotropic thermal parameter refinement for Re, Br and P only, C and O being refined with the isotropic form. Although definitive of non-hydrogen atom stoichiometry and connectivity, in the context of a non-centrosymmetric space group (refinement in the preferred hand), light (non-hydrogen) atom geometries are imprecise and should be treated circumspectly.

(9) Difference map residues were modelled in terms of dichloromethane solvent, ordered but only partially occupied with population established by refinement.

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