Some Transition Metal Complexes of the Diacetylenic Diphosphine $Ph_2PC_2C_2PPh_2$: Synthesis and Crystal Structures[†]

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Several complexes of the acetylenic ditertiary phosphine, $Ph_2PC_2C_2PPh_2$, containing Mo, W, Fe, Ru or Au have been prepared; one C≡C triple bond in the Mo, W or Fe derivatives has been co-ordinated to $Co_2(CO)_6$ or $Pt(PPh_3)_2$ groups. Crystal structure determinations of $[\{Fe(CO)_4\}_2(\mu\text{-}PPh_2C_2C_2PPh_2)]$ **3** and $[Co_2\{\mu\text{-}\eta^2\text{-}[(OC)_5W(PPh_2)]C{\equiv}C[C_2(PPh_2)W(CO)_5]\}(CO)_6]$ **7** show that the *P*-bonded $M(CO)_n$ groups take up transoid positions; in **3**, the PCCCCP chain, which is situated about a centre of inversion, is nearly linear [P–C–C, 173.2(5); C–C–C 179.7(6) for molecule a and 174.7(5) and 177.6(6)°, respectively, for molecule b] with C≡C distances of 1.192(7) Å [1.201(6) Å, molecule b]. In **7**, co-ordination of the $Co_2(CO)_6$ group to one C≡C bond lengthens that bond by 0.13 Å, compared with the unco-ordinated C≡C bond, and induces bend-back of the substituents of 141–143(1)° (PPh_2) and 145–146(1)° (C_2PPh_2). Crystals of **3** are triclinic, space group $P\bar{1}$, $a = 11.261(1)$, $b = 12.456(2)$, $c = 13.061(2)$ Å, $\alpha = 79.23(2)$, $\beta = 75.73(1)$, $\gamma = 78.75(2)°$, $Z = 2$; 2870 data were refined to $R = 0.042$, $R' = 0.046$. Crystals of **7** are triclinic, space group $P\bar{1}$, $a = 17.940(4)$, $b = 19.695(4)$, $c = 16.449(2)$ Å, $\alpha = 111.92(1)$, $\beta = 108.83(1)$, $\gamma = 100.29(2)°$, $Z = 4$; 5942 data were refined to $R = 0.055$, $R' = 0.056$.

The acetylenic ditertiary phosphine bis(diphenylphosphino)ethyne, $C_2(PPh_2)_2$ (dppa), has been employed extensively in transition metal chemistry.[1] In particular, its reactions on cluster complexes of the iron triad have produced some unusual compounds, including cluster-bound C_2 ligands, as in $[Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{11}]$,[2] dicarbido clusters, as in $[Fe_3Ru_5(\mu_6\text{-}C)(\mu_5\text{-}C)(\mu\text{-}PPh_2)_2(CO)_{17}]$,[3] and high nuclearity clusters, such as $[Co_4Ru_5(\mu_8\text{-}C_2)(\mu\text{-}PPh_2)_2(\mu_3\text{-}SMe)_2(\mu\text{-}CO)_7(CO)_{11}]$.[4] A limited number of simple complexes is known; the C≡C triple bond is seldom involved in these derivatives, probably because of steric protection by the *P*-phenyl groups. However, prior co-ordination of the triple bond to a $W(CO)_3(S_2CNEt_2)$ group induced sufficient bending of the PPh_2 groups for them to chelate to molybdenum or to bridge a Co–Co bond;[5] an example of uncomplexed dppa bridging a Re–Re bond in $[Re_3(\mu\text{-}H)_3(\mu\text{-}dppa)(CO)_{10}]$ has also been found.[4] The crystal structure of dppa has been determined.[6]

Our success in making complexes of C_2 using dppa-derived clusters[2] suggested an extension to the four-carbon analogue, which might be obtained similarly from the corresponding butadiyne, $(Ph_2P)C{\equiv}CC{\equiv}C(PPh_2)$ (bdpp). This compound was described in 1965,[7] but there seem to be no reports of any complexes containing this ligand. We have commenced a study of suitable transition metal derivatives of bdpp, which might then be able to co-ordinate another metal moiety to the C≡C triple bond, thus affording likely precursors for mixed-metal clusters. This paper describes some complex chemistry of bdpp, including the molecular structures of a binuclear iron complex, and of a related ditungsten complex containing a $Co_2(CO)_6$ unit attached to one of the C≡C triple bonds.

Results and Discussion

The ligand bdpp was readily prepared by the method described in the literature,[7] in which the di-Grignard reagent from buta-1,3-diyne reacts with chlorodiphenylphosphine (25%); better yields (33%) were obtained from 1,4-dilithiobuta-1,3-diyne. The compound forms white crystals which slowly turn brown in air at ambient temperatures; solutions darken considerably over 2 hours. We normally keep the solid ligand at −10 °C. It is soluble in toluene and polar organic solvents such as dichloromethane, but not in methanol. The compound has a simple IR spectrum, containing a ν(CC) absorption at 2072 cm^{-1}. The ^1H NMR spectrum contains multiplets centred at δ 7.45 and 7.73, while the ^{13}C NMR spectrum contains phenyl multiplets between δ 128.71 and 132.86; the *ipso* carbons resonate at δ 134.34 (d, J_{CP} 5.7 Hz). The two types of acetylenic carbons are found at δ 80.97 (d, J_{CP} 15.8 Hz) and 91.36 (dd, J_{CP} 5.2, 2.2 Hz). In the fast atom bombardment (FAB) mass spectrum, a molecular ion at *m*/*z* 418 fragments by loss of a PPh_2 group; ions at *m*/*z* 434 and 450 assigned to the mono- and di-oxygen adducts, respectively, are also prominent.

Several derivatives containing transition metals were prepared by the simple expedient of adding two equivalents of a metal complex to one equivalent of the diphosphine. There was no difficulty in isolation, standard methods being employed to crystallise and characterise the new complexes. All were identified by the usual analytical and spectroscopic techniques, and in the following discussion only those features used to confirm their identities will be highlighted. Full details are given in the Experimental section.

Complexes containing bdpp.—(a) *Molybdenum and tungsten.* The complex $[\{Mo(CO)_5\}_2(\mu\text{-}bdpp)]$ **1** was prepared by the reaction between dppb and $[Mo(CO)_5(NCMe)]$ as pale yellow crystals in 62% yield. The IR spectrum contained a ν(CO) pattern characteristic of the $M(CO)_5$ group; the ligand ν(CC) was not evident, probably being obscured by the ν(CO) peak at 2077 cm^{-1}. The FAB mass spectrum contained a molecular ion at *m*/*z* 891, which decomposed by loss of up to ten CO groups, a phenyl group and one of the metal atoms to give $[Mo(bdpp)]^+$.

The pale yellow tungsten analogue of **1** was prepared from $[W(CO)_5(thf)]$ (thf = tetrahydrofuran) in a similar manner

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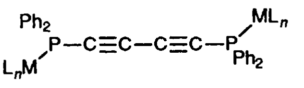
[†] *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Table 1 Selected bond lengths (Å) and angles (°) for $[\{Fe(CO)_4\}_2(\mu\text{-bdpp})]$ **3**

	Molecule a	Molecule b
Fe–P(1)	2.215(2)	2.221(1)
Fe–C(1)	1.786(7)	1.787(8)
Fe–C(2)	1.786(7)	1.783(8)
Fe–C(3)	1.789(7)	1.779(8)
Fe–C(4)	1.800(7)	1.792(7)
P(1)–Fe–C(1)	89.5(2)	89.3(2)
P(1)–Fe–C(2)	179.5(2)	178.2(2)
P(1)–Fe–C(3)	89.4(2)	91.2(2)
P(1)–Fe–C(4)	89.4(2)	86.6(2)

	Molecule a	Molecule b
P(1)–C(11)	1.764(6)	1.770(6)
C(11)–C(12)	1.192(7)	1.201(6)
C(12)–C(12′)	1.37(1)	1.36(1)
P(1)–C(Ph)	1.801(4), 1.814(4)	1.802(4), 1.810(4)
Fe–P(1)–C(11)	110.0(2)	111.4(2)
P(1)–C(11)–C(12)	173.2(5)	174.7(5)
C(11)–C(12)–C(12′)	179.7(6)	177.6(6)

Primed atom related to unprimed atom by centre of inversion.



$$L_nM(Ph_2)P{-}C{\equiv}C{-}C{\equiv}C{-}P(Ph_2)ML_n$$

	ML_n
1	$Mo(CO)_5$
2	$W(CO)_5$
3	$Fe(CO)_4$
4	$RuCl(PPh_3)(\eta\text{-}C_5H_5)$
5	AuCl

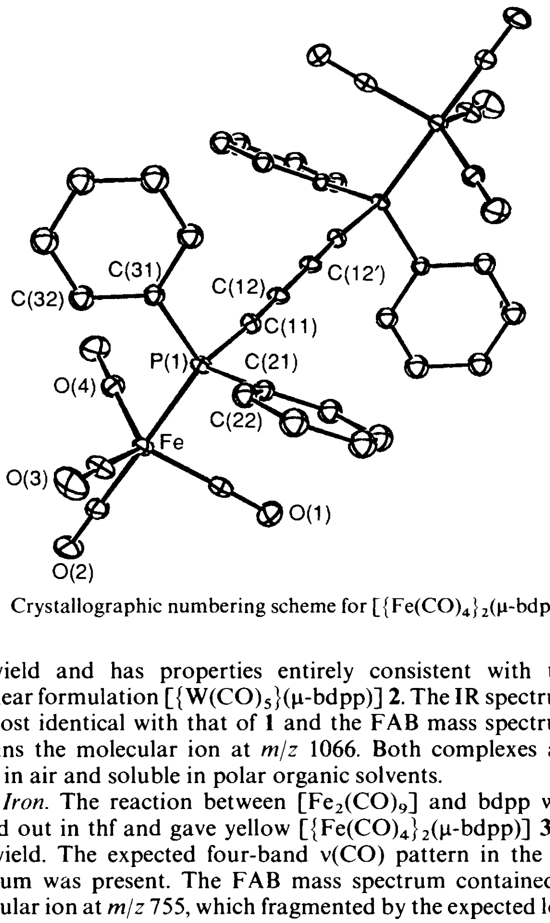


Fig. 1 Crystallographic numbering scheme for $[\{Fe(CO)_4\}_2(\mu\text{-bdpp})]$ **3**

and yield and has properties entirely consistent with the binuclear formulation $[\{W(CO)_5\}(\mu\text{-bdpp})]$ **2**. The IR spectrum is almost identical with that of **1** and the FAB mass spectrum contains the molecular ion at *m*/*z* 1066. Both complexes are stable in air and soluble in polar organic solvents.

(*b*) *Iron*. The reaction between $[Fe_2(CO)_9]$ and bdpp was carried out in thf and gave yellow $[\{Fe(CO)_4\}_2(\mu\text{-bdpp})]$ **3** in 70% yield. The expected four-band ν(CO) pattern in the IR spectrum was present. The FAB mass spectrum contained a molecular ion at *m*/*z* 755, which fragmented by the expected loss of up to eight CO groups. This complex gave well-formed crystals, which were used for an X-ray structural determination to establish the geometry of the bridging diphosphine ligand.

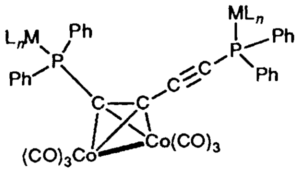
Molecular structure of $[\{Fe(CO)_4\}_2(\mu\text{-bdpp})]$ **3**. The unit cell of **3** contains two independent molecules, each disposed about a crystallographic centre of inversion, which do not differ significantly in their interatomic parameters. Fig. 1 depicts the structure of molecule b of **3**, the molecular structure and numbering scheme being identical for both molecules, and selected bond parameters are given in Table 1. There is a centre of symmetry in the molecule, which consists of the ligand bdpp containing two $Fe(CO)_4$ groups, one co-ordinated to each phosphorus atom {Fe(1)–P(1), 2.215(2), 2.221(1) Å (the two values refer to molecules a and b, respectively); *cf.* 2.244(1) Å in $[Fe(CO)_4(PPh_3)]$.[8]} The two metal groups are positioned as far apart as possible, in a mutually transoid arrangement. The geometry around the iron atoms is trigonal pyramidal, as expected from earlier studies on $[Fe(CO)_4(PPh_3)]$.[8] The P atoms occupy axial co-ordinating positions. Within the ligand, most interest centres on the diyne linkages. The P–C(sp) bond lengths are 1.764(6) Å [*cf.* 1.765(4) Å in dppa[6]], while the C_4 chain shows the expected alternation of short–long–short bonds [C(11)–C(12) 1.192(7), C(12)–C(12′) 1.37(1) Å for molecule a and 1.201(6) and 1.36(1) Å, respectively for molecule b], *i.e.*, there is only little delocalization of π-electron density along the chain. The PC_4P chain is almost but not exactly linear, with angles at the carbon atoms between 173.2(5) and 179.7(6)°.

(*c*) *Ruthenium*. We chose to prepare the bridged complex $[\{RuCl(PPh_3)(\eta\text{-}C_5H_5)\}_2(\mu\text{-bdpp})]$ **4**, as it would be used in other studies of this system. Heating a mixture of bdpp and $[RuCl(PPh_3)_2(\eta\text{-}C_5H_5)]$ in toluene readily afforded complex **4** in 53% isolated yield. It forms orange crystals, which gave a molecular ion in the FAB mass spectrum at *m*/*z* 1346. Fragmentation of this ion is complex, involving elimination of Cl, PPh_3 and intact $RuCl(PPh_3)(C_5H_5)$ groups. Only the ions $[RuCl_n(bdpp)]^+$ ($n = 0$ or 1) did not contain the C_5H_5 group.

(*d*) *Gold*. The complex $[(AuCl)_2(\mu\text{-bdpp})]$ **5** was obtained from the reaction between $[AuCl\{S(CH_2CH_2OH)_2\}]$ and dppb as white crystals. The complex was characterised by elemental microanalysis; the IR spectrum contained ν(CC) at 2102 cm^{-1}. In the FAB mass spectrum, the highest ion at *m*/*z* 848 corresponds to $[M - Cl]^+$, while the only other strong ion, at *m*/*z* 614, can be assigned to $[Au(bdpp)]^+$.

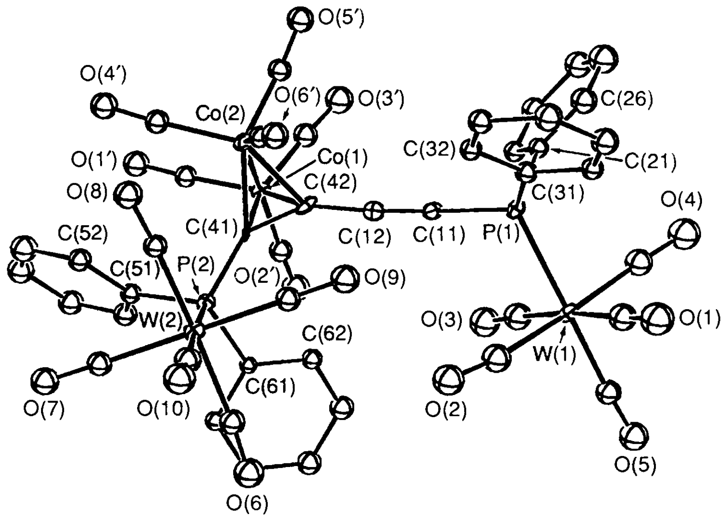
In all of the complexes **1**–**5**, two metal–ligand moieties are co-ordinated to the ligand bdpp *via* phosphorus–metal bonds. The ligand reacts preferentially by attack of the phosphorus centre on the metal system, although it must be acknowledged that in the examples chosen, with the exception perhaps of $[Fe_2(CO)_9]$, the reactivity of the metal towards *P*-donor ligands exceeds that towards alkynes. It was next of interest to establish the reactivity of the complexed ligand (in which the P atom is effectively 'protected' from further reaction) with substrates which are known to react readily with C≡C triple bonds. In the following section, we describe reactions of selected complexes with $[Co_2(CO)_8]$ and with $[Pt(\eta\text{-}C_2H_4)(PPh_3)_2]$.

Reactions of the C≡C *Bond in Complexes of bdpp*.—(*a*) *Reactions with* $[Co_2(CO)_8]$. Complexes **1**–**3** all reacted readily with $[Co_2(CO)_8]$ in thf solution at room temperature to give black crystalline complexes formulated as $[CO_2\{\mu\text{-}\eta^2\text{-}[(OC)_5M(PPh_2)]C{\equiv}C[C_2(PPh_2)M(CO)_5]\}(CO)_6]$ (M = Mo **6** or W **7**) and $[Co_2\{\mu\text{-}\eta^2\text{-}[(OC)_4Fe(PPh_2)]C{\equiv}C[C_2(PPh_2)Fe(CO)_4]\}(CO)_6]$ **8**, respectively. Again, these complexes were characterised by the usual analytical and spectroscopic techniques. Their IR spectra were essentially a superimposition of the spectra of the original complexes **1**–**3** on that of a typical $[Co_2(\mu\text{-}\eta^2\text{-alkyne})(CO)_6]$ derivative. There is thus little effect of the co-ordinated $Co_2(CO)_6$ moiety on the ν(CO) frequencies of the *P*-co-ordinated fragment. The ν(CC) bands are obscured by the ν(CO) absorptions of the $Co_2(CO)_6$ fragment. The FAB mass spectra showed the expected molecular ions, together with ions formed by loss of the CO groups. Not all of these were present, but the carbonyl-free ion was prominent in all spectra. The molecular structure of **7** was determined by an X-ray study as the first example of a complex of this type.

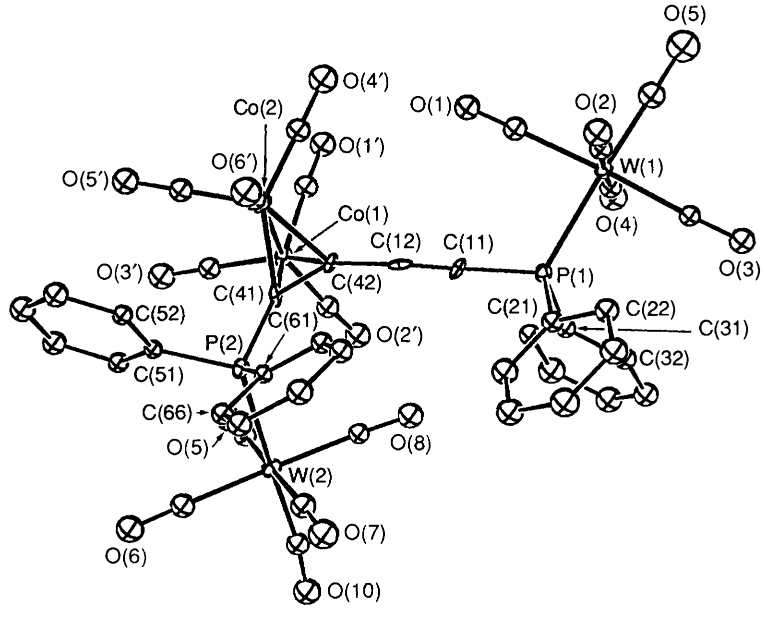


ML$_n$
6 $Mo(CO)_5$
7 $W(CO)_5$
8 $Fe(CO)_4$

Molecular structure of $[Co_2\{\mu\text{-}\eta^2\text{-}[(OC)_5W(PPh_2)]C{\equiv}C\text{-}[C_2(PPh_2)W(CO)_5]\}(CO)_6]$ **7**. The triclinic unit cell of **7** contains four molecules, two of which comprise the crystallographic asymmetric unit. The two independent molecules, a and b, differ non-trivially as can be seen from Fig. 2. Briefly, in molecule a the two $W(CO)_5$ entities lie to the same side of the molecule and further, $W(2)(CO)_5$ is orientated in the general direction of the Co(2) atom. Molecule b may be related to molecule a by two simple rotations: (*i*) about the C(12)–C(11) axis such that the two $W(CO)_5$ entities now lie on opposite sides of the PC_2C_2P backbone and (*ii*) about the C(41)–P(2) bond which now has the $W(2)(CO)_5$ group directed away from the Co(2) atom. There are no significant differences in interatomic



Molecule a



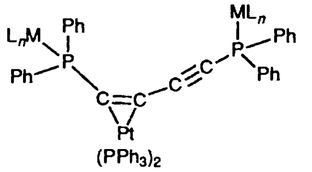
Molecule b

Fig. 2 Crystallographic numbering scheme for the independent molecules (a and b) of $[Co_2\{\mu\text{-}\eta^2\text{-}[(OC)_5W(PPh_2)]C{\equiv}C[C_2(PPh_2)W(CO)_5]\}\text{-}(CO)_6]$

Table 2 Selected bond lengths (Å) and angles (°) for $[Co_2\{\mu-\eta^2-[(OC)_5W(PPh_2)]C\equiv C[C_2(PPh_2)W(CO)_5]\}(CO)_6]$ 7

	Molecule a	Molecule b		Molecule a	Molecule b
W(1)-P(1)	2.499(5)	2.492(6)	Co(2)-C(41)	1.96(2)	1.98(2)
W(2)-P(2)	2.526(5)	2.528(4)	Co(2)-C(42)	1.94(2)	1.95(2)
W(1)-C(5)	1.97(3)	1.86(3)	P(1)-C(11)	1.72(3)	1.77(3)
W(2)-C(10)	1.96(2)	1.95(2)	C(11)-C(12)	1.23(4)	1.19(4)
Co(1)-Co(2)	2.453(4)	2.458(4)	C(12)-C(42)	1.44(3)	1.46(3)
Co(1)-C(41)	1.97(2)	1.97(2)	C(41)-C(42)	1.36(3)	1.32(4)
Co(1)-C(42)	1.93(2)	1.94(2)	P(2)-C(41)	1.79(2)	1.80(2)
W(1)-P(1)-C(11)	113.3(7)	115.5(6)	P(2)-C(41)-C(42)	141(1)	143(1)
W(2)-P(2)-C(41)	119.9(7)	117.4(7)	C(41)-C(42)-C(12)	146(1)	145(1)
P(1)-C(11)-C(12)	179(2)	177(2)	C(11)-C(12)-C(42)	175(2)	177(2)

Co-CO	1.72(3)-1.82(3) Å, av. 1.77 Å
W-CO(eq)	1.95(2)-2.04(3) Å, av. 2.00 Å
C-O(Co)	1.13(3)-1.22(4) Å, av. 1.17 Å
C-O(W)	1.10(3)-1.22(4) Å, av. 1.17 Å
P-C(Ph)	1.81(1)-1.85(1) Å, av. 1.83 Å
P-W-CO(ax)	176.4(8)-177.7(7)°, av. 176.9°
P-W-CO(eq)	86.0(9)-95.2(9)°, av. 90.6°



ML_n	
9	$Mo(CO)_5$
10	$W(CO)_5$
11	$Fe(CO)_4$

bond distances and angles describing comparable parameters in the two molecules; important geometric parameters are listed in Table 2.

As can be seen, the structure affords no surprises, with one of the $C\equiv C$ triple bonds of the original complex 2 being attached in an η^2 manner to the $Co_2(CO)_6$ fragment. Only in molecule b do the two $W(CO)_5$ moieties take up mutually transoid positions to minimise steric interactions. Each tungsten atom is octahedrally co-ordinated by five CO ligands and a P atom of the diphosphine [W-P 2.499(5), 2.526(5) Å for molecule a; 2.492(6), 2.528(4) Å for molecule b]. Individual distances and angles are similar to those found in a host of previous examples of structures of this type. The same comment can be made about the co-ordination of the alkyne to the $Co_2(CO)_6$ moiety, where the Co-Co separation [2.453(4), 2.458(4) Å] is similar to the range [2.460(1)-2.476(1) Å] found in five $[Co_2(\mu\text{-alkyne})(CO)_6]$ complexes[9] and the Co-C(alkyne) bonds range between 1.93(2) and 1.98(2) Å. The molecule offers an interesting case of adjacent co-ordinated [1.36(3), 1.32(4) Å] and unco-ordinated $C\equiv C$ triple bonds [1.23(4), 1.19(4) Å]. Comparison of the two shows the expected lengthening of the co-ordinated $C\equiv C$ bond by 0.13 Å, together with the bending back (from the Co_2 system) of the adjacent atoms C and P [C-C-C 146(1), 145(1)°, C-C-P 141(1), 143(1)°] compared with the unco-ordinated C-C-P system [174.6(17) and 178.8(15)°]. The C_2Co_2 tetragonal pyramid has C_2Co dihedral angles of 95.7 and 96.4° for molecules a and b, respectively.

(b) *Reactions with* $[Pt(\eta-C_2H_4)(PPh_3)_2]$. We have prepared the three complexes $[Pt\{\eta^2-[(OC)_5M(PPh_2)]C\equiv C[C_2(PPh_2)M(CO)_5]\}(PPh_3)_2]$ (M = Mo **9** or W **10**) and $[Pt\{\eta^2-[(OC)_4Fe(PPh_2)]C\equiv C[C_2(PPh_2)Fe(CO)_4]\}(PPh_3)_2]$ **11** by reactions between $[Pt(\eta-C_2H_4)(PPh_3)_2]$ and complexes **1**-**3** respectively. These compounds were obtained as white solids which afforded satisfactory analytical and spectroscopic data. As found for the dicobalt complexes, the ν(CO) spectra are hardly affected by the presence of the $Pt(PPh_3)_2$ group. The FAB mass spectra contain an intense ion $[Pt(PPh_3)_2]^+$ at *m/z* 719, but only the iron derivative contained ions at higher mass numbers, commencing with $[M - CO]^+$ at *m/z* 1446.

The above reactions have provided a route into novel complexes containing different transition metals attached to the P atoms and $C\equiv C$ bonds of the ligand dppb. Such complexes offer the possibility of studying co-operative effects between the two types of metal-ligand groups, and by using well-established methods, of synthesising condensed systems containing heterometallic bonds or clusters.

Experimental

General Conditions.—All reactions were carried out under nitrogen; no special precautions were taken to exclude air during work-up, since most complexes proved to be stable in air as solids, and for short times in solution. Photochemical reactions were performed using a 400 W mercury lamp (Applied Photophysics). Melting points were measured in sealed capillaries using a Gallenkamp melting point apparatus and are uncorrected. Preparative thin layer chromatography (TLC) was performed on 20 × 20 cm glass plates using a 0.5 mm thick adsorbent (60 silica gel GF_{254}, Merck). Microanalyses were performed by the Canadian Microanalytical Service, Delta, British Columbia V4G 1G7, Canada.

Instrumentation.—IR: Perkin-Elmer 1720X FT spectrometer, NaCl optics, calibrated using polystyrene absorption at 1601.4 cm^{-1}. NMR: Bruker CXP300 or ACP300 (^1H NMR at 300.13 MHz, ^{13}C NMR at 75.47 MHz) spectrometers. The internal reference was $SiMe_4$ (^1H and ^{13}C NMR). Mass spectra: FAB mass spectra were obtained on a VG ZAB 2HF instrument equipped with a FAB source. Argon was used as the exciting gas, with source pressure typically 10^{-5} kg m^{-2}; the FAB voltage was 7 kV and current 1 mA. The ion accelerating potential was 8 kV. The matrix was 3-nitrobenzyl alcohol. The complexes were made up as *ca.* 0.5 mol dm^{-3} solutions in dichloromethane; a drop was added to a drop of matrix and the mixture was applied to the FAB probe tip.

Starting Materials.—The compounds $[Fe_2(CO)_9]$,[10] $[RuCl(PPh_3)_2(\eta-C_5H_5)]$[11] and $[AuCl\{S(CH_2CH_2OH)_2\}]$[12] were prepared by literature procedures; $[Mo(CO)_6]$ (Climax Molybdenum) and $[W(CO)_6]$ (Strem) were used as received; Me_3NO was prepared by sublimation of the dihydrate (Aldrich) in vacuum. Light petroleum was a fraction of b.p. 60-80 °C.

Preparation of 1,4-*Bis*(*diphenylphosphino*)*buta*-1,3-*diyne*, $(Ph_2P)C{\equiv}CC{\equiv}C(PPh_2)$ (*bdpp*).—(i) *From* $PClPh_2$ *and* $BrMgC{\equiv}CC{\equiv}CMgBr$. This reaction was carried out as described in the original paper[7] to give bdpp in 25% yield.

(ii) *From* $LiC{\equiv}CC{\equiv}CLi$. A solution of HC_2C_2H[13] (1.3 g, 26 mmol) in Et_2O (15 cm^3) at −64 °C was added to a solution of LiBu (35 cm^3 of a 1.6 mol dm^{-3} solution in hexane, 54 mmol) at −64 °C over 15 min. After stirring for 45 min, a solution of $PClPh_2$ (13.3 g, 60 mmol) in Et_2O (30 cm^3) was added over 15 min, and the mixture warmed to room temperature over 30 min. The solution was washed with water (2 × 40 cm^3), dried over $MgSO_4$, filtered and the solvent was removed (rotary evaporator). The residue was recrystallised (CH_2Cl_2–MeOH) to give pure bdpp (6.2 g, 33%), m.p. 105 °C (lit.[7] 105 °C). IR: ν/cm^{-1}(C≡C) (Nujol) 2072. ^1H NMR: $\delta(CDCl_3)$ 7.45–7.73 (Ph). ^{13}C NMR: $\delta(CDCl_3)$ 80.97 (d, J_{CP} 15.8, P*C*C), 91.36 (dd, J_{CP} 5.2, 2.2, PC*C*), 128.71 (d, J_{CP} 8.1, $C^{3,5}$), 129.35 (s, C^4), 132.72 (d, J_{CP} 21.5, $C^{2,6}$), 134.34 (d, J_{CP} 5.7, *ipso* C). FAB MS: 450, $[M + 2O]^+$; 434, $[M + O]^+$; 418, $[M]^+$; 232, $[M - PPh_2]^+$.

Preparation of $[\{Mo(CO)_5\}_2(\mu\text{-bdpp})]$ **1**.—The compound $[Mo(CO)_6]$ (500 mg, 1.89 mmol) was dissolved in CH_2Cl_2 (30 cm^3) and MeCN (1 cm^3). Then Me_3NO (165 mg, 2.2 mmol) in MeCN (5 cm^3) and CH_2Cl_2 (30 cm^3) was added dropwise over *ca.* 20 min. After 3 h the solution was filtered through a silica plug and the volume reduced to 5 cm^3. After filtration {to remove any precipitated $[Mo(CO)_6]$} the filtrate was purified by preparative TLC (silica, 20:2.5:2.5:1 light petroleum–acetone–CH_2Cl_2–MeCN) to yield $[Mo(CO)_5(NCMe)]$ (300 mg, 59%) as a yellow oil. To a solution of $[Mo(CO)_5(NCMe)]$ (300 mg, 1.12 mmol) in CH_2Cl_2 (40 cm^3) and MeCN (5 cm^3) was added a solution of bdpp (225 mg, 0.56 mmol) in CH_2Cl_2 (30 cm^3), dropwise over 20 min. After stirring for 16 h the solvents were removed and the residue purified by preparative TLC [light petroleum–acetone (5:1)]. The major band (R_f 0.6) was crystallised (CH_2Cl_2–MeOH) to give pale yellow crystals of $[\{Mo(CO)_5\}_2(\mu\text{-bdpp})]$ **1** (310 mg, 62%), m.p. 151–152 °C (decomp.) (Found: C, 51.25; H, 2.50%; $[M + H]^+$, 891. $C_{38}H_{20}Mo_2O_{10}P_2$ requires C, 51.25; H, 2.25%; *M*, 890). IR: ν/cm^{-1}(CO)(cyclohexane) 2077w, 1994vw, 1958s. FAB MS: 891 $[M + H]^+$; 862–610, $[M - nCO]^+$ (*n* = 1–10); 533, $[M - 10CO - Ph]^+$; 514, $[Mo(bdpp)]^+$.

Preparation of $[\{W(CO)_5\}_2(\mu\text{-bdpp})]$ **2**.—The compound $[W(CO)_6]$ (250 mg, 0.71 mmol) was dissolved in thf (60 cm^3) and irradiated (400 W) for 45 min. Then bdpp (150 mg, 0.36 mmol) in thf (20 cm^3) was added dropwise (20 min) and the reaction mixture stirred for a further 15 min. After removal of the solvent the residue was recrystallised from CH_2Cl_2–MeOH to yield pale yellow crystals of $[\{W(CO)_5\}_2(\mu\text{-bdpp})]$ **2** (190 mg), m.p. 171–173 °C (decomp.). The filtrate yielded a further 38 mg (total yield = 60%) after preparative TLC [light petroleum–CH_2Cl_2 (4:1)] and recrystallisation (CH_2Cl_2–MeOH) (Found: C, 42.90; H, 2.10%; M^+, 1066. $C_{38}H_{20}O_{10}P_2W_2$ requires C, 42.80; H, 1.90%; *M*, 1066). IR: ν/cm^{-1}(CO) (hexane) 2076w, 1990vw, 1953s, 1945 (sh). ^1H NMR: $\delta(CDCl_3)$ 7.50 [s (br), Ph], 7.72 (m, Ph). ^{13}C NMR: $\delta(CDCl_3)$ 80.44 (d, J_{CP} 68.9, P*C*C), 90.87 (dd, J_{CP} 13.6, 4.4, PC*C*), 129.1 (d, J_{CP} 11.0, $C^{3,5}$), 131.0 (s, C^4), 131.4 (d, J_{CP} 14.4, $C^{2,6}$), 133.3 (d, J_{CP} 49.2, *ipso* C), 195.20 (d, J_{CP} 6.2, CO), 196.04 (d, J_{CP} 6.9, CO), 196.87 (d, J_{CP} 7.0, CO), 198.69 (d, J_{CP} 23.2, CO). FAB MS: 1066, M^+, 1038–709, $[M - nCO]^+$ (*n* = 2,4–10); 709, $[M - 10CO - Ph]^+$; 630, $[W(CO)(bdpp)]^+$; 602, $[W(bdpp)]^+$; 369, $[W(PPh_2)]^+$.

Preparation of $[\{Fe(CO)_4\}_2(\mu\text{-bdpp})]$ **3**.—The compound $[Fe_2(CO)_9]$ (500 mg, 1.37 mmol) was added to a solution of bdpp (556 mg, 1.33 mmol) in thf (100 cm^3) and the mixture was stirred for 1 h. Column chromatography [light petroleum–acetone (5:1)] eluted a yellow band, which was recrystallised from CH_2Cl_2–MeOH, yielding $[\{Fe(CO)_4\}_2(\mu\text{-bdpp})]$ **3** (700 mg, 70%), m.p. 190–191 °C (decomp.) (Found: C, 57.45; H, 2.60%, $[M + H]^+$, 755. $C_{36}H_{20}Fe_2O_8P_2$ requires C, 57.35; H, 2.65%; *M*, 754). IR: ν/cm^{-1}(CO)(cyclohexane) 2091w, 2056m, 1987m, 1958s, 1949s, 1920vw. ^{13}C NMR: $\delta(CDCl_3)$: 80.21 (d, J_{CP} 79.9, P*C*C), 91.37 (dd, J_{CP} 14.6, 4.6, PC*C*), 129.03 (d, J_{CP} 11.9, $C^{3,5}$), 131.56 (s, C^4), 131.92 (d, J_{CP} 12.8, $C^{2,6}$), 132.57 [s (high field branch of doublet obscured by $C^{2,4,6}$ peaks], *ipso* C), 212.06 (d, J_{CP} 19.0 Hz, CO). FAB MS: 755, $[M + H]^+$; 726–530, $[M - nCO]^+$ (*n* = 1–8); 474, $[Fe(bdpp)]^+$.

Preparation of $[\{RuCl(\eta\text{-}C_5H_5)(PPh_3)\}_2(\mu\text{-bdpp})]$ **4**.—The compounds $[RuCl(PPh_3)_2(\eta\text{-}C_5H_5)]$ (291 mg, 0.401 mmmol) and bdpp (84 mg, 0.200 mmol) were heated in toluene (20 cm^3) at 80 °C for 3 h. After the solvent was removed column chromatography [Florisil; light petroleum–acetone (4:1)] yielded a yellow band, which was crystallised from CH_2Cl_2–MeOH, yielding orange crystals of $[\{RuCl(PPh_3)(\eta\text{-}C_5H_5)\}_2(\mu\text{-bdpp})]$ **4** (143 mg, 53%), m.p. 202–206 °C (decomp.) (Found: C, 65.20; H, 4.30%; *M*, 1346. $C_{74}H_{40}Cl_2P_4Ru_2$ requires C, 66.00; H, 4.50%; *M*, 1346). IR: ν/cm^{-1}(C≡C) (Nujol) 2102. FAB MS: 1346, M^+; 1310, $[M - Cl]^+$; 1084, $[M - PPh_3]^+$; 1048, $[M - PPh_3 - Cl]^+$; 882, $[M - RuCl(C_5H_5)(PPh_3)]^+$; 847, $[M - Cl - RuCl(C_5H_5)(PPh_3)]^+$; 787, $[M - Cl - 2PPh_3]^+$; 620, $[RuCl(bdpp)]^+$; 613, $[Ru(PPh_2)(PPh_3)(C_5H_5)]^+$; 584, $[Ru(bdpp)]^+$; 464, $[RuCl(PPh_3)(C_5H_5)]^+$; 428, $[Ru(PPh_3)(C_5H_5)]$; 351, $[Ru(PPh_2)(C_5H_5)]^+$; 262, $[PPh_3]^+$.

Preparation of $[(AuCl)_2(\mu\text{-bdpp})]$ **5**.—Gold (300 mg, 1.52 mg atom) was dissolved in aqua regia [HCl (conc., 7.5 cm^3)–HNO_3 (conc., 2.5 cm^3)], then evaporated to dryness over a steam-bath. Concentrated HCl (10 cm^3) was added and the solution again evaporated to dryness. The residue was dissolved in water (15 cm^3), filtered and cooled in an ice-bath. After the dropwise addition of 2,2′-thiodiethanol (560 mg, 2.8 mmol), bdpp (112 mg, 0.75 mmol) in $CHCl_3$ (15 cm^3) was also added dropwise. Compound $[(AuCl)_2(\mu\text{-bdpp})]$ **5** precipitated as a white solid and was collected by filtration (275 mg, 41%), m.p. 205–207 °C (decomp.) (Found: C, 37.65; H, 2.20%; *M* − Cl, 848. $C_{28}H_{20}Au_2Cl_2P_2$ requires C, 38.10; H, 2.30%; *M*, 883). IR: ν/cm^{-1}(C≡C) (Nujol) 2102. FAB MS: $[M - Cl]^+$, 848; $[Au(bdpp)]^+$, 614.

Reactions of $[\{Mo(CO)_5\}_2(\mu\text{-bdpp})]$ **1**.—(a) *With* $[Co_2(CO)_8]$. An excess of $[Co_2(CO)_8]$ was added to a solution of $[\{Mo(CO)_5\}_2(\mu\text{-bdpp})]$ **1** (69 mg, 0.077 mmol) in diethyl ether (35 cm^3). After stirring for 7–8 h at room temperature the solvent was removed and the residue purified on a chromatotron [light petroleum–acetone (5:1)]. The major product was recrystallised from CH_2Cl_2–MeOH to yield black crystals of $[Co\{\mu\text{-}\eta^2\text{-}[(OC)_5Mo(PPh_2)]C{\equiv}C[C_2(PPh_2)Mo(CO)_5]\}(CO)_6]$ **6** (78 mg, 86%), m.p. 155–157 °C (decomp.) (Found: C, 44.85; H, 1.70%; $[M - 3CO]^+$, 1092. $C_{44}H_{20}Co_2Mo_2O_{16}P_2$ requires C, 44.95; H, 1.70%; *M*, 1176). IR: ν/cm^{-1}(CO)(cyclohexane) 2102m, 2073m, 2044m, 2031w, 1991w, 1951vs. FAB MS: 1092–728 $[M - nCO]^+$ (*n* = 3–16).

(b) *With* $[Pt(\eta\text{-}C_2H_4)(PPh_3)_2]$. Complex **1** (30 mg, 0.034 mmol) and $[Pt(\eta\text{-}C_2H_4)(PPh_3)_2]$ (30 mg, 0.040 mmol) were dissolved in CH_2Cl_2 (10 cm^3). After 10 min, the solvent was removed and the residue crystallised from CH_2Cl_2–MeOH to yield $[Pt\{\eta^2\text{-}[(OC)_5Mo(PPh_2)]C{\equiv}C[C_2(PPh_2)Mo(CO)_5]\}(PPh_3)_2]$ **9** (50 mg, 100%) as a white powder, m.p. >180 °C (decomp.) (Found: C, 54.80; H, 3.20%. $C_{74}H_{50}Mo_2O_{10}P_4Pt$ requires C, 55.20; H, 3.15%). IR: ν/cm^{-1}(CO) (cyclohexane) 2072w, 2018w, 1992w, 1951vs, 1943vs. FAB MS: 719, $[Pt(PPh_3)_2]^+$.

Reactions of $[\{W(CO)_5\}_2(\mu\text{-bdpp})]$ **2**.—(a) *With* $[Co_2(CO)_8]$. An excess of $[Co_2(CO)_8]$ was added to a solution of $[\{W(CO)_5\}_2(\mu\text{-bdpp})]$ **2** (57 mg, 0.053 mmol) in diethyl ether (30 cm^3). After stirring for 6 h at room temperature the solvent was removed and the residue purified on a chromatotron [light petroleum–acetone (5:1)]. The major product was recrystallised from CH_2Cl_2–MeOH to yield black crystals of $[Co_2\{\mu\text{-}\eta^2\text{-}$

Table 3 Fractional atomic coordinates (× 10^5 for Fe, × 10^4 for remaining atoms) for complex **3**

Atom	*x*	*y*	*z*
Fe(1a)	7 110(7)	60 864(6)	12 314(6)
Fe(1b)	30 405(7)	25 270(7)	30 334(6)
P(1a)	−517(1)	6 852(1)	2 596(1)
P(1b)	4 973(1)	2 654(1)	2 141(1)
C(1a)	2 030(6)	6 287(5)	1 661(5)
O(1a)	2 908(4)	6 422(5)	1 886(4)
C(2a)	1 704(5)	5 458(5)	139(5)
O(2a)	2 342(4)	5 073(4)	−556(4)
C(3a)	82(5)	7 193(5)	333(5)
O(3a)	−286(4)	7 901(4)	−256(4)
C(4a)	62(5)	4 831(6)	1 742(5)
O(4a)	−316(4)	4 020(4)	2 051(4)
C(11a)	−309(5)	6 021(5)	3 808(5)
C(12a)	−114(5)	5 373(5)	4 567(5)
C(22a)	−828(3)	9 129(3)	2 219(3)
C(23a)	−517(3)	10 162(3)	2 210(3)
C(24a)	420(3)	10 245(3)	2 706(3)
C(25a)	1 046(3)	9 294(3)	3 210(3)
C(26a)	736(3)	8 261(3)	3 220(3)
C(21a)	−201(3)	8 179(3)	2 724(3)
C(32a)	−2 703(3)	6 782(3)	1 977(3)
C(33a)	−3 989(3)	6 896(3)	2 122(3)
C(34a)	−4 758(3)	7 272(3)	3 039(3)
C(35a)	−4 243(3)	7 534(3)	3 811(3)
C(36a)	−2 957(3)	7 419(3)	3 666(3)
C(31a)	−2 187(3)	7 043(3)	2 749(3)
C(1b)	2 983(5)	3 777(6)	3 541(5)
O(1b)	2 939(4)	4 571(4)	3 885(4)
C(2b)	1 472(6)	2 445(5)	3 712(5)
O(2b)	481(4)	2 378(5)	4 147(4)
C(3b)	3 551(6)	1 271(6)	3 817(6)
O(3b)	3 845(5)	465(5)	4 347(5)
C(4b)	2 678(5)	2 579(5)	1 762(6)
O(4b)	2 472(4)	2 609(5)	952(4)
C(11b)	5 025(5)	3 815(4)	1 125(5)
C(12b)	4 993(5)	4 571(4)	406(4)
C(22b)	6 674(4)	1 944(2)	3 433(3)
C(23b)	7 380(4)	2 091(2)	4 122(3)
C(24b)	7 408(4)	3 153(2)	4 305(3)
C(25b)	6 730(4)	4 068(2)	3 799(3)
C(26b)	6 024(4)	3 921(2)	3 111(3)
C(21b)	5 996(4)	2 860(2)	2 927(3)
C(32b)	5 355(3)	582(3)	1 469(3)
C(33b)	6 010(3)	−232(3)	850(3)
C(34b)	7 128(3)	−64(3)	139(3)
C(35b)	7 591(3)	919(3)	47(3)
C(36b)	6 936(3)	1 733(3)	665(3)
C(31b)	5 818(3)	1 565(3)	1 376(3)

$[(OC)_5W(PPh_2)]C{\equiv}C[C_2(PPh_2)W(CO)_5]\}(CO)_6]$ **7** (52 mg, 72%), m.p. 173–174 °C (decomp.) (Found: C, 38.40; H, 1.65%: *M*, 1352. $C_{44}H_{20}Co_2O_{16}P_2W_2$ requires C, 49.10; H, 1.50%; *M*, 1352). IR: ν/cm^{-1}(CO)(cyclohexane) 2102m, 2073s, 2048m, 2031w, 1984w, 1949s, 1942vs. ^{13}C NMR: $\delta(CDCl_3)$ 74.45 (d, J_{CP} 9.5, P*C*C), 90.30 {s, PC*C*[Co_2 $(CO)_6$]}, 94.22 (d, J_{CP} 79.6, PC*C*), 106.72 {d, J_{CP} 14.1, P*C*C[$Co_2(CO)_6$]}, 128.67 (d, J_{CP} 9.7, $C^{3,5}$), 128.94 (d, J_{CP} 10.9, $C^{3',5'}$), 130.83 (d, J_{CP} 9.3, $C^{2',6'}$), 131.23, 131.41 (2 × s, $C^{4,4'}$), 132.51 (d, J_{CP} 12.2, $C^{2,6}$), 134.38 (d, J_{CP} 49.0, C^1), 137.06 (d, J_{CP} 44.8, $C^{1'}$), 196.06 (d, J_{CP} 6.1, CO), 196.46 (d, J_{CP} 6.4, CO), 196.89 (d, J_{CP} 5.9, CO), 197.73 (d, J_{CP} 6.1, CO), 198.94 (d, J_{CP} 14.1, CO), 199.24 (d, J_{CP} 14.0, CO), 200.40 (d, J_{CP} 6.1, CO). FAB MS: 1352, M^+, 1324–904, $[M - n\text{CO}]^+$ (n = 1–16); 827, $[M - 16\text{CO} - \text{Ph}]^+$.

(b) *With* $[Pt(\eta\text{-}C_2H_4)(PPh_3)_2]$. Complex **2** (30 mg, 0.028 mmol) and $[Pt(\eta\text{-}C_2H_4)(PPh_3)_2]$ (26 mg, 0.035 mmol) were dissolved in CH_2Cl_2 (10 cm^3). After 10 min, the solvent was removed and the residue recrystallised from CH_2Cl_2–MeOH to yield yellow crystals of $[Pt\{\eta^2\text{-}[(OC)_5W(PPh_2)]C{\equiv}C[C_2(PPh_2)W(CO)_5]\}(PPh_3)_2]$ **10** (45 mg, 90%), m.p. 197–198 °C (decomp.) (Found: C, 49.95; H, 2.90. $C_{74}H_{50}O_{10}P_4PtW_2$ requires C, 49.70; H, 2.80%). IR: ν/cm^{-1}(CO)(cyclohexane) 2070w, 2017vw, 1985vw, 1942 (sh), 1938vs. FAB MS: 719, $[Pt(PPh_3)_2]^+$.

Reactions of $[\{Fe(CO)_4\}_2(\mu\text{-bdpp})]$ **3**.—(a) *With* $[Co_2(CO)_8]$. An excess of $[Co_2(CO)_8]$ was added to a solution of $[\{Fe(CO)_4\}_2(\mu\text{-bppd})]$ **3** (350 mg, 0.46 mmol) in diethyl ether (60 cm^3). After stirring for 20 h at room temperature the solvent was removed and the residue purified on a chromatotron [light petroleum–acetone (10:1)]. The major product was recrystallised from CH_2Cl_2–MeOH to yield black crystals of $[Co_2\{\mu\text{-}\eta^2\text{-}[(OC)_4Fe(PPh_2)]C{\equiv}C[C_2(PPh_2)Fe(CO)_4]\}(CO)_6]$ **8** (310 mg, 64%), m.p. 143–146 °C (decomp.) (Found: C, 48.50; H, 1.90%; $[M + H]^+$ 1041. $C_{42}H_{20}Co_2Fe_2O_{14}P_2$ requires C, 48.50; H, 1.95%; *M*, 1040). IR: ν/cm^{-1}(CO)(cyclohexane) 2104m, 2057s, 2052vs, 2032w, 1982m, 1946vs, 1936 (sh), 1911vw. FAB MS: 1041, $[M + H]^+$; 1012–648, $[M - n\text{CO}]^+$ (n = 1–14); 592, $[M - 14\text{CO} - \text{Fe}]^+$; 571, $[M - 14\text{CO} - \text{Ph}]^+$.

(b) *With* $[Pt(\eta\text{-}C_2H_4)(PPh_3)_2]$. Complex **3** (10 mg, 0.013 mmol) and $[Pt(\eta\text{-}C_2H_4)(PPh_3)_2]$ (9.9 mg, 0.013 mmol) were dissolved in CH_2Cl_2 (5 cm^3). The solvent was removed and the residue crystallised from CH_2Cl_2–MeOH to yield yellow crystals of $[Pt\{\eta^2\text{-}[(OC)_4Fe(PPh_2)]C{\equiv}C[C_2(PPh_2)Fe(CO)_4]\}(PPh_3)_2]$ **11** (11 mg, 57%), m.p. 174–178 °C (decomp.) (Found: C, 57.80; H, 3.50%; $[M - \text{CO}]^+$ 1446. $C_{72}H_{50}Fe_2O_8P_4Pt$ requires C, 58.65; H, 3.40%; *M*, 1474). IR: ν/cm^{-1}(CO)(cyclohexane) 2050m, 2045 (sh), 1974m, 1951 (sh), 1942vs, 1937 (sh). FAB MS: 1446–1250, $[M - n\text{CO}]^+$ (n = 1–8); 988, $[M - 8\text{CO} - \text{PPh}_3]^+$; 932, $[M - 8\text{CO} - \text{PPh}_3 - \text{Fe}]^+$; 719, $[Pt(PPh_3)_2]^+$.

Crystallography.—Intensity data for a crystal of **3** 0.04 × 0.10 × 0.34 mm (details for **7** follow in parentheses: 0.18 × 0.26 × 0.60 mm) were measured at room temperature on an Enraf–Nonius CAD4 diffractometer with graphite-monochromatized Mo-Kα radiation λ = 0.7107 Å. The ω–2θ scan technique was employed to measure the intensities of 5372 (11 280) reflections to a maximum Bragg angle of 22.5 (21.0°) which were corrected for Lorentz and polarization effects and for absorption effects; maximum and minimum transmission factors 0.928 and 0.801, respectively (0.406 and 0.087).[14] A total of 4506 (10 310) reflections were unique (R_{merge} 0.016 and 0.045, respectively) and of these 2870 (5942) satisfied the $I \geqslant 2.5\sigma(I)$ criterion of observability and were used in the subsequent analysis.

Crystal data for **3**. $C_{36}H_{20}Fe_2O_8P_2$, $M = 754.2$, triclinic, space group $P\bar{1}$, $a = 11.261(1)$, $b = 12.456(2)$, $c = 13.061(2)$ Å, $\alpha = 79.23(2)$, $\beta = 75.73(1)$, $\gamma = 78.75(2)°$, $U = 1722.7$ Å^3, $Z = 2$, $D_c = 1.454$ g cm^{-3}, $F(000) = 764$, $\mu = 9.47$ cm^{-1}.

Crystal data for **7**·0.5CH_2Cl_2. $C_{44.5}H_{21}ClCo_2O_{16}P_2W_2$, $M = 1394.6$, triclinic, space group $P\bar{1}$, $a = 17.940(4)$, $b = 19.695(4)$, $c = 16.449(2)$ Å, $\alpha = 111.92(1)$, $\beta = 108.83(1)$, $\gamma = 100.29(2)°$, $U = 4798.4$ Å^3, $Z = 4$, $D_c = 1.930$ g cm^{-3}, $F(000) = 2620$, $\mu = 57.14$ cm^{-1}.

Solution and refinement of the structures. The structures were each solved by direct-methods[15] and refined by a full-matrix (block-matrix) least-squares procedure based on *F*.[14] For **3** non-H and non-phenyl atoms were refined with anisotropic thermal parameters and for **7** the W, Co, P, O and C atoms of the C_4 unit were refined anisotropically. Phenyl rings were modelled as hexagonal rigid groups and H atoms were included in the model of **3** in their calculated positions. After the inclusion of a weighting scheme of the form $w = k/[\sigma^2(F) + |g|F^2]$, the refinements were continued until convergence where $R = 0.042$, $k = 2.9$, $g = 0.0003$ and $R' = 0.046$ (0.055, 1.0, 0.0072 and 0.056). The analysis of variance showed no special feature in either case and

Table 4 Fractional atomic coordinates (× 10^5 for W and Co; × 10^4 for remaining atoms) for complex 7

Atom	*x*	*y*	*z*
W(1a)	1 466(1)	6 641(1)	−4 278(1)
W(2a)	1 781(1)	4 016(1)	−1 505(1)
Co(1a)	34 805(15)	73 015(15)	6 458(18)
Co(2a)	41 404(15)	63 286(16)	1 425(18)
P(1a)	2 908(3)	6 747(3)	−3 278(3)
P(2a)	2 072(3)	5 423(3)	−394(3)
O(1a)	1 367(13)	5 405(13)	−6 263(16)
O(2a)	788(12)	5 276(13)	−3 869(15)
O(3a)	1 367(13)	7 758(13)	−2 371(16)
O(4a)	2 346(14)	7 956(14)	−4 687(17)
O(5a)	−295(12)	6 624(11)	−5 445(15)
O(6a)	−108(12)	3 770(11)	−2 648(14)
O(7a)	1 320(10)	3 500(10)	−83(12)
O(8a)	3 581(10)	3 996(10)	−474(12)
O(9a)	2 263(10)	4 505(10)	−2 939(12)
O(10a)	1 309(11)	2 260(12)	−2 909(14)
O(1a′)	4 031(10)	7 539(10)	2 659(13)
O(2a′)	2 073(12)	7 902(12)	476(14)
O(3a′)	4 644(12)	8 674(12)	853(14)
O(4a′)	4 802(10)	6 087(10)	1 873(13)
O(5a′)	5 705(10)	7 426(10)	506(12)
O(6a′)	4 146(9)	4 981(10)	−1 406(12)
C(1a)	1 398(15)	5 838(16)	−5 538(20)
C(2a)	988(17)	5 791(17)	−4 059(21)
C(3a)	1 426(17)	7 404(18)	−3 066(22)
C(4a)	2 029(17)	7 483(17)	−4 488(20)
C(5a)	338(15)	6 612(14)	−5 013(18)
C(6a)	566(15)	3 880(14)	−2 253(17)
C(7a)	1 476(13)	3 705(13)	−591(16)
C(8a)	2 911(13)	4 026(12)	−862(15)
C(9a)	2 078(13)	4 317(13)	−2 400(16)
C(10a)	1 487(14)	2 921(15)	−2 412(18)
C(11a)	2 989(11)	6 636(11)	−2 269(13)
C(12a)	3 063(11)	6 565(11)	−1 540(15)
C(41a)	2 951(10)	6 167(10)	−185(11)
C(42a)	3 227(10)	6 535(11)	−642(13)
C(1a′)	3 784(13)	7 444(13)	1 848(17)
C(2a′)	2 628(14)	7 653(14)	552(17)
C(3a′)	4 191(15)	8 100(15)	789(18)
C(4a′)	4 520(13)	6 139(13)	1 175(17)
C(5a′)	5 053(13)	6 986(13)	329(16)
C(6a′)	4 163(12)	5 493(12)	−777(15)
C(21a)	3 690(8)	7 715(6)	−2 728(10)
C(22a)	3 679(8)	8 331(6)	−1 961(10)
C(23a)	4 229(8)	9 082(6)	−1 585(10)
C(24a)	4 790(8)	9 217(6)	−1 976(10)
C(25a)	4 801(8)	8 600(6)	−2 473(10)
C(26a)	4 251(8)	7 849(6)	−3 119(10)
C(31a)	3 375(8)	6 060(7)	−3 837(9)
C(32a)	3 731(8)	5 637(7)	−3 405(9)
C(33a)	4 051(8)	5 099(7)	−3 876(9)
C(34a)	4 016(8)	4 984(7)	−4 779(9)
C(35a)	3 661(8)	5 408(7)	−5 211(9)
C(36a)	3 340(8)	5 945(7)	−4 740(9)
C(51a)	2 280(8)	5 690(8)	882(8)
C(52a)	2 799(8)	5 368(8)	1 338(8)
C(53a)	3 019(8)	5 577(8)	2 315(8)
C(54a)	2 720(8)	6 108(8)	2 836(8)
C(55a)	2 201(8)	6 430(8)	2 381(8)
C(56a)	1 981(8)	6 221(8)	1 404(8)
C(61a)	1 163(6)	5 707(7)	−830(9)
C(62a)	1 147(6)	6 156(7)	−1 318(9)
C(63a)	419(6)	6 310(7)	−1 699(9)
C(64a)	−292(6)	6 017(7)	−1 593(9)
C(65a)	−275(6)	5 569(7)	−1 106(9)
C(66a)	452(6)	5 414(7)	−724(9)
W(1b)	6 651(1)	7 128(1)	8 357(1)
W(2b)	8 638(1)	11 133(1)	7 077(1)
Co(1b)	60 554(15)	90 831(17)	54 167(19)
Co(2b)	64 663(16)	80 108(16)	45 432(18)
P(1b)	7 595(3)	8 317(3)	8 528(3)
P(2b)	8 105(3)	9 766(3)	5 710(3)
O(1b)	5 578(10)	6 772(9)	6 213(12)
O(2b)	7 664(10)	6 076(10)	7 601(12)
O(3b)	7 691(9)	7 618(9)	10 586(12)
O(4b)	5 565(11)	8 111(11)	9 117(14)
O(5b)	5 511(14)	5 683(14)	8 230(16)
O(6b)	9 274(11)	11 834(10)	5 848(13)
O(7b)	10 410(12)	11 006(11)	7 989(14)
O(8b)	8 113(10)	10 480(10)	8 369(13)
O(9b)	6 937(11)	11 412(10)	6 342(12)
O(10b)	9 408(11)	12 836(11)	8 790(14)
O(1b′)	4 422(11)	8 030(10)	4 959(12)
O(2b′)	6 225(10)	10 283(11)	7 228(13)
O(3b′)	5 543(11)	9 784(11)	4 136(14)
O(4b′)	5 235(11)	6 610(11)	4 187(14)
O(5b′)	5 806(10)	8 089(10)	2 717(13)
O(6b′)	7 629(11)	7 232(11)	4 092(14)
C(1b)	5 930(14)	6 900(13)	6 971(18)
C(2b)	7 318(12)	6 480(12)	7 904(15)
C(3b)	7 324(12)	7 451(12)	9 760(15)
C(4b)	5 960(13)	7 745(13)	8 841(16)
C(5b)	5 957(16)	6 260(16)	8 283(19)
C(6b)	9 022(14)	11 575(14)	6 298(17)
C(7b)	9 735(15)	11 013(14)	7 618(18)
C(8b)	8 299(12)	10 703(12)	7 875(15)
C(9b)	7 551(14)	11 295(13)	6 616(17)
C(10b)	9 108(14)	12 173(14)	8 178(17)
C(1b′)	5 045(15)	8 434(14)	5 115(17)
C(2b′)	5 747(14)	9 503(13)	4 644(17)
C(3b′)	6 176(14)	9 836(14)	6 520(17)
C(4b′)	5 719(14)	7 197(14)	4 340(17)
C(5b′)	6 082(13)	8 050(13)	3 458(17)
C(6b′)	7 190(13)	7 556(13)	4 301(16)
C(11b)	7 301(11)	8 470(11)	7 495(14)
C(12b)	7 115(10)	8 544(10)	6 775(14)
C(41b)	7 186(10)	9 088(12)	5 542(13)
C(42b)	6 906(9)	8 682(11)	5 932(12)
C(21b)	8 697(6)	8 455(8)	8 862(10)
C(22b)	9 077(6)	8 027(8)	9 265(10)
C(23b)	9 927(6)	8 145(8)	9 514(10)
C(24b)	10 397(6)	8 691(8)	9 360(10)
C(25b)	10 016(6)	9 119(8)	8 957(10)
C(26b)	9 166(6)	9 001(8)	8 708(10)
C(31b)	7 608(8)	9 203(7)	9 463(8)
C(32b)	8 078(8)	9 396(7)	10 428(8)
C(33b)	8 049(8)	10 020(7)	11 170(8)
C(34b)	7 551(8)	10 450(7)	10 947(8)
C(35b)	7 081(8)	10 257(7)	9 982(8)
C(36b)	7 109(8)	9 633(7)	9 240(8)
C(51b)	7 828(7)	9 667(7)	4 490(7)
C(52b)	7 918(7)	9 070(7)	3 777(7)
C(53b)	7 611(7)	8 964(7)	2 828(7)
C(54b)	7 212(7)	9 455(7)	2 591(7)
C(55b)	7 121(7)	10 052(7)	3 303(7)
C(56b)	7 429(7)	10 158(7)	4 253(7)
C(61b)	8 920(6)	9 330(7)	5 888(9)
C(62b)	8 917(6)	8 798(7)	6 258(9)
C(63b)	9 579(6)	8 512(7)	6 423(9)
C(64b)	10 243(6)	8 757(7)	6 218(9)
C(65b)	10 247(6)	9 289(7)	5 848(9)
C(66b)	9 585(6)	9 576(7)	5 682(9)
Cl(1c)	2 334(5)	3 103(5)	3 977(6)
Cl(2c)	904(6)	3 621(9)	3 732(10)
C(1c)	1 850(21)	3 745(20)	4 505(25)

the maximum residual electron density peak in the final difference map was 0.70 e Å^{-3} [2.5 e Å^{-3}, near the W(2a) atom]. The scattering factors (corrected for anomalous dispersion) for neutral Fe, CO and W were from ref. 16 and those for the remaining atoms were incorporated in SHELX 76.[14] Fractional atomic coordinates are listed in Tables 3 and 4 and the crystallographic numbering schemes are shown in Figs. 1 and 2 which were drawn with ORTEP[17] at 15% probability ellipsoids.

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

Acknowledgements

We thank the Australian Research Council for financial support and Johnson Matthey Technology Centre for a generous loan of $RuCl_3.nH_2O$.

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Received 4*th October* 1991; *Paper* 1/05070B