Organo–Platinum–Iron Complexes derived from Allenes. Crystal Structures of $[(OC)_3Fe(\mu\text{-dppm})\{\mu\text{-}C(O)CH_2C(=CH_2)\}Pt(PPh_3)]$, $[(OC)_3Fe(\mu\text{-dppm})\{\mu\text{-}C(=CH_2)CH_2\}Pt(PPh_3)]$, and $[(OC)_2Fe(\mu\text{-dppm})\{\eta^4\text{-}(CH_2)(CMe_2)CPt(PPh_3)\}]$ [†]

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Treatment of $[(OC)_3Fe(\mu\text{-dppm})(\mu\text{-}CO)Pt(PPh_3)]$ (**1**) (dppm = $Ph_2PCH_2PPh_2$) with allene at 20 °C in dichloromethane gave $[(OC)_3Fe(\mu\text{-dppm})\{\mu\text{-}C(O)CH_2C(=CH_2)\}Pt(PPh_3)]$ (**3**) in moderate yield. Its structure was established by *X*-ray crystallography; the crystals are orthorhombic, space group *Pbca* with a = 2 481.5(3), b = 1 906.2(2), c = 1 838.7(3) pm, and Z = 8; R 0.0315 for 4 401 observed reflections. The allene ligand has inserted into the Pt–C bond of the bridging carbonyl of (**1**) to give a dimetallacyclopentanone ring with an exocyclic methylene group. Treatment of complex (**1**) with allene at 80 °C gave $[(OC)_3Fe(\mu\text{-dppm})\{\mu\text{-}C(=CH_2)CH_2\}Pt(PPh_3)]$ (**5**) in moderate yield. The structure of (**5**) was also established by *X*-ray crystallography; the crystals are monoclinic, space group $P2_1/n$, with a = 1 195.1(2), b = 2 258.5(3), c = 1 673.9(4) pm, β = 108.15(2)°, and Z = 4; R 0.0286 for 4 835 observed reflections. The allene ligand is bridging the Fe–Pt bond to give a dimetallacyclobutane ring with an exocyclic methylene group. When complex (**3**) or (**5**) was heated at 80 °C the complex $[(OC)_2Fe(\mu\text{-dppm})\{\eta^4\text{-}(CH_2)_2CPt(PPh_3)\}]$ (**6**) was formed in high yield. Analogues of (**6**) were prepared by treatment of (**1**) with the substituted allenes $PhCH=C=CH_2$ and $Me_2C=C=CH_2$, *viz.* $[(OC)_2Fe(\mu\text{-dppm})\{\eta^4\text{-}(CH_2)(CHPh)CPt(PPh_3)\}]$ (**7**) and $[(OC)_2Fe(\mu\text{-dppm})\{\eta^4\text{-}(CH_2)(CMe_2)CPt(PPh_3)\}]$ (**8**). The structure of (**8**) was established by *X*-ray crystallography; the crystals are monoclinic, space group $P2_1/c$, with a = 1 098.4(3), b = 1 889.8(6), c = 2 216.3(5) pm, β = 103.52(2)°, and Z = 4; R 0.0311 for 5 080 observed reflections. It is most informatively viewed as a phosphine-substituted platinatrimethylenemethane complex in which the $(CH_2)(CMe_2)CPt(PPh_3)$(dppm-*P*) moiety is η^4-co-ordinated to Fe. Protonation of (**5**) with $HBF_4\cdot OEt_2$ gave the μ-propenyl cation $[(OC)_3Fe(\mu\text{-dppm})\{\mu\text{-}C(Me)=CH_2\}Pt(PPh_3)][BF_4]$ exclusively. Some similar chemistry with the diphosphine $(Ph_2P)_2C=CH_2$ is also described.

In a recent publication[1] we described the preparation of the electron-rich heterobimetallic complex $[(OC)_3Fe(\mu\text{-dppm})(\mu\text{-}CO)Pt(PPh_3)]$ (**1**) (dppm = $Ph_2PCH_2PPh_2$) and its subsequent reactions with alkynes to give complexes containing dimetallacyclopentenone rings. We expected that (**1**) might also be reactive towards allenes, however, the nature of the products was difficult to predict because of the possibility of isomerisation of co-ordinated allene to co-ordinated alkyne. Several bimetallic complexes containing co-ordinated allenes have been prepared previously and structurally characterised: $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4(\mu\text{-}CH_2=C=CH_2)]$,[2] $[Mn_2(\eta^5\text{-}C_5H_5)_2(CO)_3(\mu\text{-}CH_2=C=CH_2)]$,[3] and $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CH_2=C=CH_2)]$[4] were all shown to have 'V-shaped' allene ligands symmetrically bridging the two metal centres and allene was considered to form one olefin–metal bond to each metal. The allene complex $[Rh_2(acac)(CO)_2(\mu\text{-}CH_2=C=CH_2)]$ (acac = acetylacetonate) was also shown to have a bridging allene ligand[5] but in this case there was no metal–metal bond.

In this paper we describe the reactions of the iron–platinum complex (**1**) and its analogue with $Ph_2PC(=CH_2)PPh_2$ (vdpp) (**2**) with allenes to give new organoplatinum–iron complexes. Aspects of this work have appeared as a preliminary communication.[6]

Results and Discussion

Treatment of a dichloromethane solution of $[(OC)_3Fe(\mu\text{-dppm})(\mu\text{-}CO)Pt(PPh_3)]$ (**1**) with allene at *ca.* 20 °C gave, after several days, the complex $[(OC)_3Fe(\mu\text{-dppm})\{\mu\text{-}C(O)CH_2C(=CH_2)\}Pt(PPh_3)]$ (**3**) in 35% isolated yield. The vdpp analogue $[(OC)_3Fe(\mu\text{-vdpp})\{\mu\text{-}C(O)CH_2C(=CH_2)\}Pt(PPh_3)]$ (**4**) was similarly prepared from $[(OC)_3Fe(\mu\text{-vdpp})(\mu\text{-}CO)Pt(PPh_3)]$ (**2**) in 27% yield. Complexes (**3**) and (**4**) were characterised by elemental analysis and i.r. spectroscopy (Table 1), and by $^{31}P\text{-}\{^1H\}$ (Table 2) and ^1H (Table 3) n.m.r. spectroscopy; preparative details are given in the Experimental section. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectra of (**3**) and (**4**) were similar and each consisted of three resonances, a low-field resonance with satellites due to a small coupling to ^{195}Pt [J(PtP) 60—66 Hz] assigned to the phosphorus atom bonded to iron and two higher-field resonances also with ^{195}Pt satellites [J(PtP) *ca.* 3 000 and *ca.* 1 900 Hz] assigned to the phosphorus atoms bonded to platinum. The large values of $J(P_AP_B)$ across the dppm or vdpp ligands of 102 and 162 Hz respectively made possible the individual assignments of each of the phosphorus atoms on platinum, *i.e.* P_A and P_B. The ^1H n.m.r. spectra both showed similar resonances which were assigned to the protons of the co-ordinated allene ligands, *viz.* two mutually coupled resonances, each of relative intensity one, at *ca.* 5.2 and *ca.* 4.3 p.p.m. [J(HH) 1.5 Hz] assigned to the vinylic protons ($C=CH_2$), and a resonance at *ca.* 3.6 p.p.m., of relative intensity two, assigned to the methylene protons on the carbon atom adjacent to the C=O. The i.r. spectra were similar in the carbonyl region

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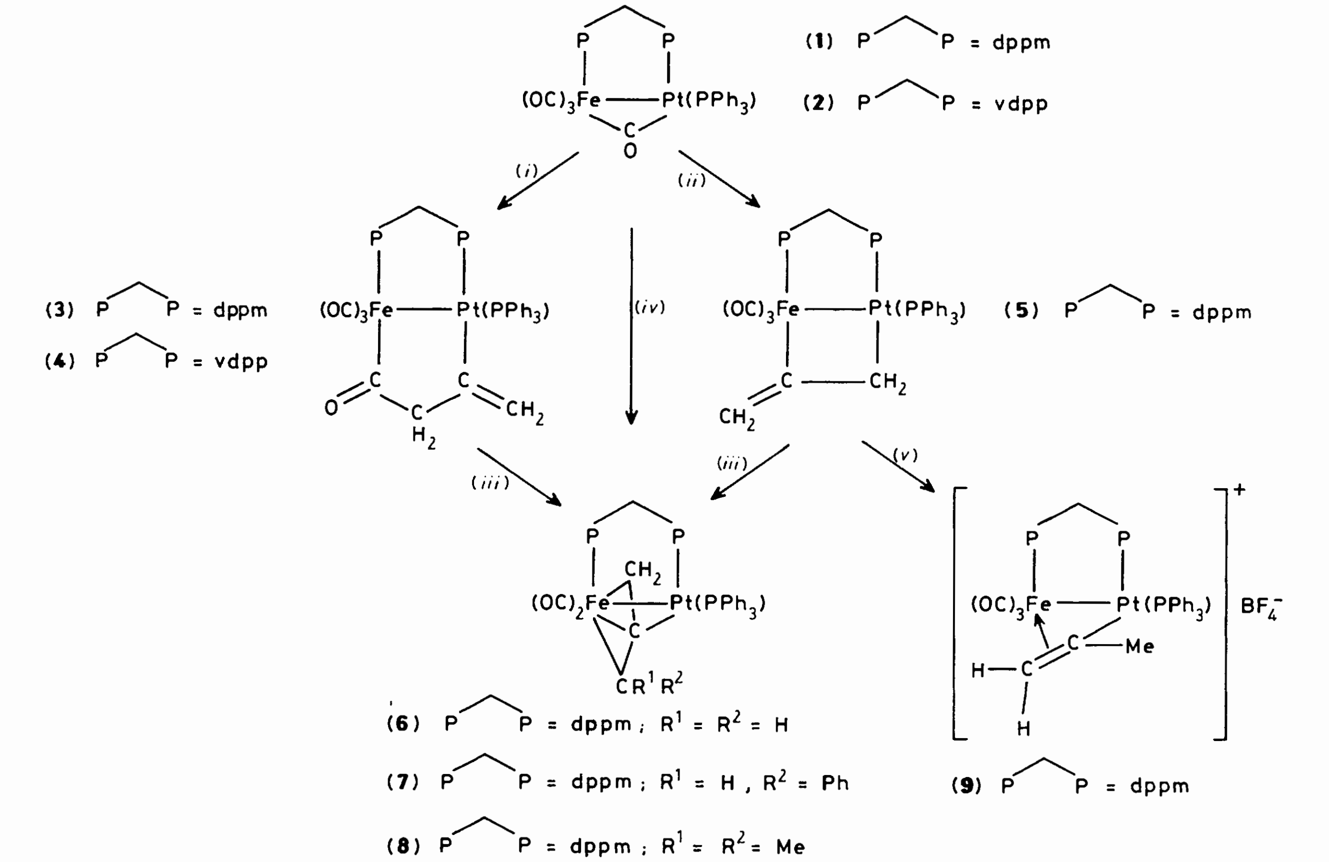
[†] μ-Bis(diphenylphosphino)methane-2,2,2-tricarbonyl-μ-[1′-oxobut-3′-ene-1′,3′-diyl-*C*$^{1'}$(Fe)*C*$^{3'}$(Pt)]-1-triphenylphosphineplatinumiron-(*Pt–Fe*), μ-bis(diphenylphosphino)methane-2,2,2-tricarbonyl-μ-[prop-2′-ene-1′,2′-diyl-*C*$^{1'}$(Pt)*C*$^{2'}$(Fe)]-1-triphenylphosphineplatinumiron-(*Pt–Fe*), and μ-bis(diphenylphosphino)methane-2,2-dicarbonyl-μ-[3′-methylbut-2′-en-1,2′-diyl-*C*$^{1'3'}$(Fe)*C*$^{2'}$(Fe,Pt)]-1-triphenylphosphineplatinumiron(*Pt–Fe*).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.



Scheme. (*i*) $CH_2=C=CH_2$, CH_2Cl_2, 20 °C; (*ii*) $CH_2=C=CH_2$, benzene, 80 °C; (*iii*) benzene, 80 °C; (*iv*) $PhCH=C=CH_2$, benzene, 80 °C, or $Me_2C=C=CH_2$, CH_2Cl_2, 40 °C; (*v*) $HBF_4 \cdot OEt_2$

Table 1. Infra-red[a] and analytical[b] data

Complex	$\nu(C\equiv O)/cm^{-1}$	Analyses (%) C	H
(3)·0.5CH_2Cl_2	1 986s, 1 918s, 1 844s, 1 622s	55.45 (55.25)	3.9 (3.8)
(4)	1 985s, 1 920s, 1 885s, 1 616s	57.6 (57.7)	4.05 (3.9)
(5)·C_6H_6	1 972s, 1 912s, 1 884s	59.7 (60.05)	4.15 (4.3)
(6)	1 948s, 1 888s	58.1 (58.0)	4.3 (4.15)
(7)	1 950s, 1 890s	60.0 (60.65)	4.2 (4.25)
(8)	1 940s, 1 885s	58.5 (58.8)	4.4 (4.45)

[a] As solutions in dichloromethane; s = strong. [b] Calculated values in parentheses.

and both showed three bands assigned to terminal carbonyl ligands and a very low-energy band at *ca.* 1 620 cm^{-1}, suggesting the presence of a ketonic type carbonyl. These data did not unambiguously define the structures of complexes (**3**) or (**4**) and so an *X*-ray diffraction study was undertaken on a crystal of (**3**).

Crystal Structure of $[(OC)_3Fe(\mu\text{-dppm})\{\mu\text{-}C(O)CH_2C(=CH_2)\}Pt(PPh_3)]$ (**3**).—The allene complex (**3**) was crystallised from dichloromethane–diethyl ether (1:3) solution. The structure is shown in Figure 1 and selected intramolecular distances and angles are in Table 4. The iron and platinum moieties are linked by a single dppm bridge to give a five-membered $\overline{FePCPPt}$ ring. The Fe–Pt distance of 267.3(4) pm indicates a metal–metal bond and is close to those found in the related complexes $[(OC)_3Fe(\mu\text{-dppm})(\mu\text{-}CO)Pt(PPh_3)]$, 257.9(4) pm, and $[(OC)_2Fe(\mu\text{-dppm})\{\mu\text{-}C(O)C_2H_2\}Pt(PPh_3)]$, 259.7(4) pm.[1,6] The allene ligand has inserted into the bridging carbonyl Pt–C bond of (**1**) to give a dimetallacyclopentanone ring containing an exocyclic methylene group. The organic ligand is therefore a simple one-electron donor to each metal atom. The Fe–C(4) distance, 201.1(10) pm, and Pt–C(6) distance, 206.7(9) pm, are similar. The C(6)–C(7) distance, 134.8(12) pm, is close to that found for the C=C double bond in the bridging vinylidene complex $[Ru_2(\eta^5\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CO)(\mu\text{-}C=CH_2)]$, 132.6(11) pm,[7] and is typical of the separation for an uncomplexed C=C double bond such as in ethylene, 133.7(3) pm.[8] The C(4)–C(5) and C(5)–C(6) distances, 150.3(12) and 146.4(11) pm, respectively, are typical of sp^2–sp^3 hybridised C–C bonds while the C(4)–O(4) distance of 122.9(9) pm is similar to that of the analogous bond in the dimetallacyclopentenone $[(OC)_2Fe(\mu\text{-dppm})\{\mu\text{-}C(O)C_2H_2\}Pt(PPh_3)]$, 121.3(10) pm.[1] The geometry of the metallacyclic ring in (**3**) shows that the Pt, Fe, C(4), and C(5) atoms are approximately in a plane, with C(6), bearing the exocyclic methylene group, out of that plane, *i.e.* the five-membered ring is in an envelope conformation. The structure of (**3**) makes an interesting comparison with that of the dimetallacyclopentenone complex $[(OC)_2Fe(\mu\text{-dppm})\{\mu\text{-}C(O)C_2H_2\}Pt(PPh_3)]$ formed from acetylene.[1] In this complex the co-ordinated acetylene is able to make a π interaction with the iron centre which has lost a terminal carbonyl ligand. Although related, the complexes derived from acetylenes and allenes are structurally quite different.

Table 2. $^{31}P-\{^1H\}$ N.m.r. data (δ)

Complex	
(3)	56.2 [dd, P_A, $J(P_AP_B)$ 102, $J(P_AP_C)$ 10, $J(PtP_A)$ 66]
	26.0 [dd, P_C, $J(P_AP_C)$ 10, $J(P_BP_C)$ 9, $J(PtP_C)$ 3 210]
	17.9 [dd, P_B, $J(P_AP_B)$ 102, $J(P_BP_C)$ 9, $J(PtP_B)$ 1 880]
(4)	64.5 [dd, P_A, $J(P_AP_B)$ 162, $J(P_AP_C)$ 10, $J(PtP_A)$ 60]
	27.3 [dd, P_B, $J(P_AP_B)$ 162, $J(P_BP_C)$ 8, $J(PtP_B)$ 1 928]
	26.3 [dd, P_C, $J(P_AP_C)$ 10, $J(P_BP_C)$ 8, $J(PtP_C)$ 3 060]
(5)	76.7 [d, P_A, $J(P_AP_B)$ 127, $J(PtP_A)$ 86]
	30.4 [d, P_B, $J(P_AP_B)$ 127, $J(PtP_B)$ 2 076]
	28.2 [s, P_C, $J(PtP_C)$ 3 384]
(6)	49.1 [dd, P_A, $J(P_AP_B)$ 57, $J(P_AP_C)$ 37, $J(PtP_A)$ 209]
	46.6 [dd, P_C, $J(P_AP_C)$ 37, $J(P_BP_C)$ 5, $J(PtP_C)$ 2 964]
	3.2 [dd, P_B, $J(P_AP_B)$ 57, $J(P_BP_C)$ 5, $J(PtP_B)$ 2 600]
(7)	47.8 [dd, P_A, $J(P_AP_B)$ 55, $J(P_AP_C)$ 35, $J(PtP_A)$ 220]
	37.7 [d, P_C, $J(P_AP_C)$ 35, $J(PtP_C)$ 3 020]
	2.2 [d, P_B, $J(P_AP_B)$ 55, $J(PtP_B)$ 2 605]
(8)	46.6 [dd, P_A, $J(P_AP_B)$ 58, $J(P_AP_C)$ 35, $J(PtP_A)$ 225]
	36.2 [d, P_C, $J(P_AP_C)$ 35, $J(PtP_C)$ 2 990]
	0.9 [d, P_B, $J(P_AP_B)$ 58, $J(PtP_B)$ 2 665]

Recorded at 162 MHz in CH_2Cl_2 solution, at 20 °C. Positive shifts to high frequency of external 85% H_3PO_4. Coupling constants in Hz. P_A and P_B refer to the dppm or vdpp phosphorus atoms bonded to iron and platinum, respectively, P_C to the triphenylphosphine phosphorus atom. The multiplicity, *i.e.* d or dd, refers to the P–P coupling.

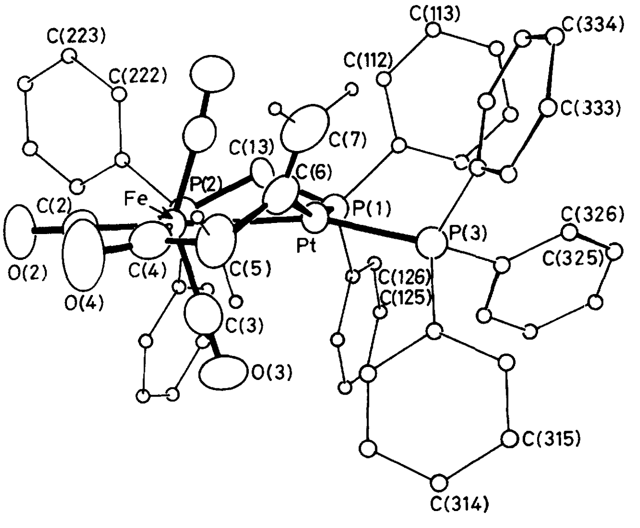


Figure 1. Molecular structure of $[(OC)_3Fe(\mu\text{-dppm})\{\mu\text{-}C(O)CH_2C(=CH_2)\}Pt(PPh_3)]$ (3) showing the principal atomic numbering

$^{31}P-\{^1H\}$ N.m.r. studies of the reaction between (1) and allene indicated an intermediate complex in the formation of (3). This intermediate appeared to contain a monodentate dppm ligand co-ordinated to iron, similar to that observed in the reaction between (1) and alkynes.[1] Presumably, the allene and alkyne reactions proceed by similar mechanisms, possibly involving an intermediate with the organic ligand η^2-bonded to platinum.

Table 3. Selected ^1H n.m.r. data[a] (δ)

Complex	
(3)	5.23 [ddd, 1 H, $C=CH_2$, $J(P_BH)$ 16, $J(P_CH)$ 4, $J(HH)$ 1.5, $J(PtH)$ 72]
	4.33 [dd, 1 H, $C=CH_2$, $J(P_BH)$ 9, $J(HH)$ 1.5, $J(PtH)$ 37]
	3.68 [d, 2 H, $C(O)CH_2$, $J(P_BH)$ 6, $J(PtH)$ 41]
	3.55 [dd, 2 H, PCH_2P, $J(P_AH)$ 10, $J(P_BH)$ 10, $J(PtH)$ 26]
(4)	5.43 [dd, 1 H, $P_2C=CH_2$, $J(PH)$ 27 and 14]
	5.42 [dd, 1 H, $P_2C=CH_2$, $J(PH)$ 25 and 15]
	5.21 [ddd, 1 H, $C=CH_2$, $J(PH)$ 20 and 4, $J(HH)$ 1.5, $J(PtH)$ 74]
	4.31 [dd, 1 H, $C=CH_2$, $J(PH)$ 9, $J(HH)$ 1.5, $J(PtH)$ 36]
	3.59 [d, 2 H, CH_2, $J(PH)$ 6, $J(PtH)$ 42]
(5)	5.52 [d, 1 H, $C=CH_2$, $J(P_AH)$ 4]
	5.11 [s, 1 H, $C=CH_2$]
	3.33 [m, 2 H, PCH_2P, $J(PtH)$ 30]
	1.93 [br, 2 H, $PtCH_2$, $J(PtH)$ 64]
(6)[b]	5.12 [AB, 1 H, PCH_2P, $J(HH)$ 15, $J(PtH)$ 70]
	3.97 [AB, 1 H, PCH_2P, $J(HH)$ 15]
	3.71 [s, 1 H, CH_2, $J(PtH)$ 53]
	3.25 [s, 1 H, CH_2, $J(PtH)$ 53]
	3.02 [d, 1 H, CH_2, $J(PH)$ 7, $J(PtH)$ 127]
	2.90 [d, 1 H, CH_2, $J(PH)$ 6, $J(PtH)$ 116]
(6)[c]	4.72 (br, 2 H, PCH_2P)
	3.95 [s, 2 H, CH_2, $J(PtH)$ 55]
	3.30 [d, 2 H, CH_2, $J(PH)$ 7, $J(PtH)$ 123]
(7)	5.95 [d, 1 H, CHPh, $J(PH)$ 58]
	5.19 [AB, 1 H, PCH_2P, $J(HH)$ 15, $J(PtH)$ 65]
	4.00 [AB, 1 H, PCH_2P, $J(HH)$ 15]
	3.65 [d, 1 H, CH_2, $J(PH)$, 7, $J(PtH)$ 121]
	3.38 [br, 1 H, CH_2, $J(PtH)$ 58]
(8)	5.22 [AB, 1 H, PCH_2P, $J(HH)$ 15, $J(PtH)$ 66]
	3.93 [AB, 1 H, PCH_2P, $J(HH)$ 15, $J(PtH)$ 5]
	3.09 [dd, 1 H, CH_2, $J(P_BH)$, 7, $J(P_CH)$ 1, $J(PtH)$ 58]
	3.00 [dd, 1 H, CH_2, $J(P_AH)$ 9, $J(P_BH)$ 5, $J(PtH)$ 118]
	1.85 (s, 3 H, CH_3)
	1.42 (s, 3 H, CH_3)

[a] Recorded in $CDCl_3$ solution at 20 °C and 400 MHz, unless stated otherwise. Chemical shifts (δ) in p.p.m. (±0.01 p.p.m.) relative to $SiMe_4$, coupling constants (J) in Hz (±0.3 Hz); $^{31}P-\{^1H\}$ coupling constants are quoted only when resolved and are specifically assigned (*i.e.* to P_A, P_B, or P_C) only when confirmed by double-irradiation experiments, P_A and P_B referring to the dppm or vdpp phosphorus atoms bonded to iron and platinum, respectively, P_C to the triphenylphosphine phosphorus atom. [b] Recorded at −20 °C. [c] Recorded in $C_6D_5CD_3$ solution at 100 °C.

When (1) was heated in benzene to 80 °C with allene bubbling through the solution the complex $[(OC)_3Fe(\mu\text{-dppm})\{\mu\text{-}C(=CH_2)CH_2\}Pt(PPh_3)]$ (5) was obtained in 57% yield. Attempts to prepare the vdpp analogue from (2) failed, only decomposition products being formed. Complex (5) was characterised by elemental analysis, and i.r., $^{31}P-\{^1H\}$ and ^1H n.m.r. spectroscopy (see Tables for details). The $^{31}P-\{^1H\}$ n.m.r. spectrum was similar to those of complexes (1) and (3), suggesting that the metal–phosphine backbone was unchanged. The ^1H n.m.r. spectrum showed resonances assigned to a co-ordinated allene ligand, *viz.* two resonances, each of relative intensity one, at 5.52 and 5.11 p.p.m. assigned to the vinylic protons ($C=CH_2$) and a resonance, of relative area two, at 3.33 p.p.m. assigned to the methylene (CH_2) protons. The i.r. spectrum showed three bands assigned to terminal carbonyl ligands. These data did not unambiguously define a structure for (5) and so a single-crystal *X*-ray diffraction study was undertaken.

Crystal Structure of $[(OC)_3Fe(\mu\text{-dppm})\{\mu\text{-}C(=CH_2)CH_2\}Pt(PPh_3)]$ (5).—The allene complex (5) was crystallised from chlorobenzene–methylcyclohexane (1 : 3) solution. The structure is shown in Figure 2 and selected intramolecular distances and angles are in Table 5. The iron and platinum moieties are linked by a single dppm bridge to give a five-membered $\overline{\text{FePCPPt}}$ ring with an Fe–Pt distance of 263.4(4) pm. This indicates a metal–metal bond and is similar to that found in (3). The allene ligand has displaced the bridging carbonyl in (1) and is now bridging the Fe–Pt bond to give a dimetallacyclobutane ring containing an exocyclic methylene group. The metallacyclic ring is almost planar. The Fe–C(5) distance of 208.8(7) pm and the Pt–C(4)

Table 4. Selected distances (pm) and angles (°) between interatomic vectors for $[(OC)_3Fe(\mu\text{-dppm})\{\mu\text{-}C(O)CH_2C(=CH_2)\}Pt(PPh_3)]$ (**3**)

Fe–Pt	267.3(4)	P(1)–Pt	232.4(4)
P(3)–Pt	228.9(4)	C(1)–Pt	265.5(9)
C(3)–Pt	274.7(10)	C(6)–Pt	206.7(9)
P(2)–Fe	224.4(4)	C(1)–Fe	175.8(10)
C(2)–Fe	174.4(10)	C(3)–Fe	175.2(10)
C(4)–Fe	201.1(10)	C(13)–P(1)	184.5(8)
C(13)–P(2)	183.4(8)	O(1)–C(1)	117.4(9)
O(2)–C(2)	116.7(9)	O(3)–C(3)	118.2(9)
O(4)–C(4)	122.9(9)	C(5)–C(4)	150.3(12)
C(6)–C(5)	146.4(11)	C(7)–C(6)	134.8(12)
P(1)–Pt–Fe	92.6	P(3)–Pt–Fe	160.4
P(3)–Pt–P(1)	101.9(2)	C(6)–Pt–Fe	81.0(3)
C(6)–Pt–P(1)	163.2(2)	C(6)–Pt–P(3)	88.4(3)
P(2)–Fe–Pt	96.1(2)	C(1)–Fe–Pt	70.2(3)
C(1)–Fe–P(2)	90.8(3)	C(2)–Fe–Pt	176.2(2)
C(2)–Fe–P(2)	87.7(3)	C(2)–Fe–C(1)	109.5(4)
C(3)–Fe–Pt	73.4(3)	C(3)–Fe–P(2)	97.4(3)
C(3)–Fe–C(1)	143.3(3)	C(3)–Fe–C(2)	106.5(4)
C(4)–Fe–Pt	90.2(3)	C(4)–Fe–P(2)	173.3(2)
C(4)–Fe–C(1)	93.2(4)	C(4)–Fe–C(2)	86.0(4)
C(4)–Fe–C(3)	82.4(4)	C(13)–P(1)–Pt	111.0(3)
C(13)–P(2)–Pt	111.7(3)	P(2)–C(13)–P(1)	110.3(4)
Fe–C(1)–Pt	71.3(3)	O(1)–C(1)–Pt	113.5(6)
O(1)–C(1)–Fe	174.1(6)	O(2)–C(2)–Fe	178.3(7)
Fe–C(3)–Pt	68.9(3)	O(3)–C(3)–Pt	112.3(6)
O(3)–C(3)–Fe	177.0(6)	O(4)–C(4)–Fe	124.3(7)
C(5)–C(4)–Fe	118.6(6)	C(5)–C(4)–O(4)	117.0(8)
C(6)–C(5)–C(4)	111.7(7)	C(5)–C(6)–Pt	119.1(6)
C(7)–C(6)–Pt	121.4(7)	C(7)–C(6)–C(5)	118.3(8)

Table 5. Selected distances (pm) and angles (°) between interatomic vectors for $[(OC)_3Fe(\mu\text{-dppm})\{\mu\text{-}C(=CH_2)CH_2\}Pt(PPh_3)]$ (**5**)

Fe–Pt	263.4(4)	P(1)–Pt	232.6(3)
P(3)–Pt	232.8(3)	C(1)–Pt	270.8(9)
C(2)–Pt	273.7(9)	C(4)–Pt	209.3(8)
P(2)–Fe	224.3(3)	C(1)–Fe	182.0(8)
C(2)–Fe	180.6(8)	C(3)–Fe	178.5(8)
C(5)–Fe	208.8(7)	C(13)–P(1)	187.0(8)
C(13)–P(2)	184.8(6)	O(1)–C(1)	118.5(9)
O(2)–C(2)	115.4(9)	O(3)–C(3)	115.4(9)
C(5)–C(4)	145.0(11)	C(6)–C(5)	135.0(9)
P(1)–Pt–Fe	92.6	P(3)–Pt–Fe	162.9
P(3)–Pt–P(1)	104.1	C(4)–Pt–Fe	73.7(3)
C(4)–Pt–P(1)	166.1(2)	C(4)–Pt–P(3)	89.7(3)
P(2)–Fe–Pt	100.9	C(1)–Fe–Pt	72.3(3)
C(1)–Fe–P(2)	93.7(3)	C(2)–Fe–Pt	73.5(3)
C(2)–Fe–P(2)	92.4(3)	C(2)–Fe–C(1)	145.8(3)
C(3)–Fe–Pt	164.0(2)	C(3)–Fe–C(2)	102.5(4)
C(5)–Fe–Pt	72.9(3)	C(5)–Fe–P(2)	170.9(2)
C(5)–Fe–C(1)	78.2(3)	C(5)–Fe–C(2)	92.1(3)
C(5)–Fe–C(3)	92.0(3)	C(13)–P(1)–Pt	113.5(2)
C(13)–P(2)–Fe	110.4(3)	O(1)–C(1)–Fe	178.9(4)
O(2)–C(2)–Pt	177.2(5)	O(3)–C(3)–Fe	176.9(6)
C(5)–C(4)–Pt	105.1(6)	C(4)–C(5)–Fe	106.8(5)
C(6)–C(5)–Fe	129.2(7)	C(6)–C(5)–C(4)	123.9(7)

distance of 209.3(8) pm are nearly the same. These distances, along with the pairs of almost equal angles, Fe–Pt–C(4) 73.7(3) and Pt–Fe–C(5) 72.9(3)°, and Pt–C(4)–C(5) 105.1(6) and Fe–C(5)–C(4) 106.8(5)°, illustrate the very symmetrial bridging of the allene ligand across the Fe–Pt bond. The C(5)–C(6) distance of 135.0(9) pm is similar to that found for the analogous moiety in (**3**), 134.8(12) pm. The C(4)–C(5) distance of 145.0(11) pm is typical of an sp^2–sp^3 hybridised C–C bond, again similar to that found in (**3**), 146.4(11) pm. Structure (**5**) can be viewed as a substituted μ-ethylene complex. Such a complex has been proposed as a possible intermediate in the borane reduction of the μ-ketene complex $[Ru_2(\eta^5\text{-}C_5Me_5)_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(O)\text{-}CH_2\}]$[9] to give, ultimately, μ-ethylidene and terminal ethylene complexes. Presumably, the exocyclic double bond in (**5**) stabilises the μ-olefin type structure and makes such rearrangements less favourable.

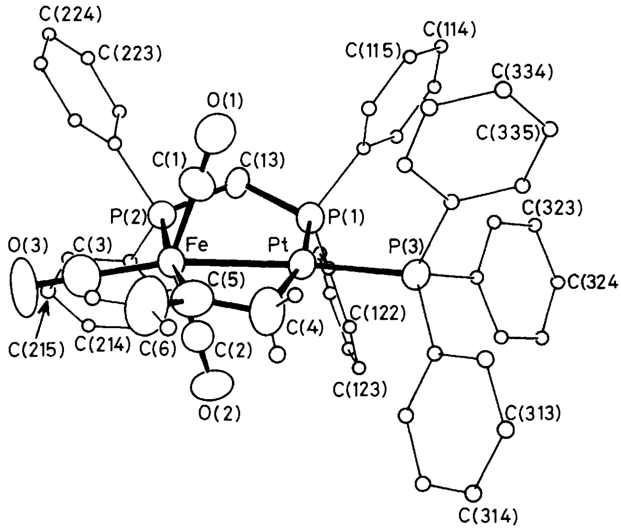


Figure 2. Molecular structure of $[(OC)_3Fe(\mu\text{-dppm})\{\mu\text{-}C(=CH_2)CH_2\}\text{-}Pt(PPh_3)]$ (**5**) showing the principal atomic numbering

It is interesting to compare the allene bonding in complex (**5**) with that found in (**3**). In (**3**) the allene inserts into the Pt–C bond of (**1**) under mild conditions to give a structure with the exocyclic methylene group of the organic ligand adjacent to platinum. In (**5**) however, the exocyclic methylene group is found to be adjacent to iron. These results suggest different mechanisms for the formation of (**3**) and (**5**) from (**1**). We attempted the conversion (**3**) ⟶ (**5**) by heating a benzene solution of (**3**), however no (**5**) was observed and a near-quantitative transformation occurred to give the new compound $[(OC)_2Fe(\mu\text{-dppm})\{\eta^4\text{-}(CH_2)_2CPt(PPh_3)\}]$ (**6**). The latter was also formed, again quantitatively, by heating (**5**) in benzene. Analogues of (**6**) with 3-phenyl-1,2-propadiene and 3-methyl-1,2-butadiene, *viz*. $[(OC)_2Fe(\mu\text{-dppm})\{\eta^4\text{-}(CH_2)\text{-}(CHPh)CPt(PPh_3)\}]$ (**7**) and $[(OC)_2Fe(\mu\text{-dppm})\{\eta^4\text{-}(CH_2)\text{-}(CMe_2)CPt(PPh_3)\}]$ (**8**), were also prepared by treating (**1**) directly with the appropriate allene (see Experimental section for details). Complexes (**6**)—(**8**) were characterised by elemental analysis, and i.r., $^{31}P\text{-}\{^1H\}$ and ^1H n.m.r. spectroscopy (see Tables for details). The $^{31}P\text{-}\{^1H\}$ n.m.r. were very similar suggesting analogous structures for these complexes. Additionally, they were of the same form as those of complexes (**1**), (**3**), and (**5**) implying a retention of the metal–phosphine backbone. A two-dimensional COSY $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of (**6**) established that $J(PtP_A) = -209$, $J(PtP_B) = +2\,600$, and $J(PtP_C) = +2\,964$ Hz (one-bond Pt–P couplings are always positive). These results are similar to those previously found for (**1**).[1] Additionally, the study established that $J(P_AP_B)$ was of a different sign to $J(P_AP_C)$ and $J(P_BP_C)$. The i.r. spectra of complexes (**6**)—(**8**) all showed two bands in the carbonyl region assigned to terminal carbonyl ligands. The discussion of the ^1H n.m.r. behaviour of these complexes is best deferred until after the *X*-ray crystal structure of (**8**) is discussed.

Crystal Structure of $[(OC)_2Fe(\mu\text{-dppm})\{\eta^4\text{-}(CH_2)(CMe_2)\text{-}CPt(PPh_3)\}]$ (**8**).—Crystals of (**8**) were grown by slow

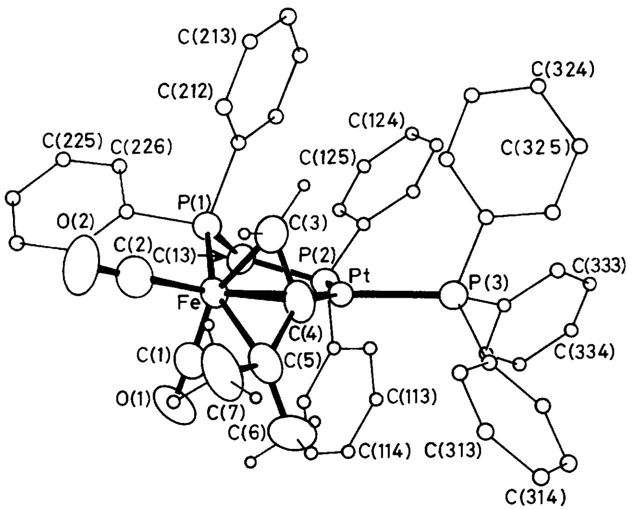


Figure 3. Molecular structure of $[(OC)_2Fe(\mu\text{-dppm})\{\eta^4\text{-}CH_2)(CMe_2)\text{-}CPt(PPh_3)\}]$ (**8**) showing the principal atomic numbering

evaporation of a dichloromethane–n-hexane (1:3) solution. The structure is shown in Figure 3 and selected intramolecular distances and angles are in Table 6. The iron and platinum moieties are linked by a single dppm bridge to give a five-membered $\overline{FePCPPt}$ ring with an Fe–Pt distance of 261.8(4) pm, indicating a metal–metal bond. The dimethylallene ligand is bridging the Fe–Pt bond and is σ-co-ordinated to Pt and η^3-co-ordinated to Fe. The molecule is most informatively viewed as a phosphine-substituted platinatrimethylenemethane complex in which the $(CH_2)(CMe_2)CPt(PPh_3)(dppm\text{-}P)$ moiety is η^4-co-ordinated to Fe. Comparison of the bonding parameters of (**8**) with those of $[Fe(CO)_3\{C(CH_2)_3\}]$ itself show a close agreement, allowing for the effect of the longer Fe–Pt distance in (**8**) with respect to an Fe–C distance. Thus, in (**8**) the C(3)–C(4) and C(4)–C(5) distances are 142.1(9) and 142.6(9) pm respectively while in $[Fe(CO)_3\{C(CH_2)_3\}]$ the C–C bond lengths are 143.7 pm.[10] In the latter the Fe–C(outer) distance of 212.3(5) pm is greater than the Fe–C(central) distance of 193.8(5) pm. These bond lengths are similar to the analogous lengths in (**8**), *viz.* the Fe–C(5) and Fe–C(3) distances of 221.1(8) and 214.4(8) pm are longer than the Fe–C(4) distance of 197.1(7) pm. The $\overline{FePCPPt}$ five-membered ring warrants further comment. It is severely distorted, with the phosphorus atom P(1) lying well below the plane made by Pt–C(4)–Fe. This contrasts with the structures of (**3**) and (**5**) in which the dppm bridging ligand lies nearly in the plane made by the metals and the organic ligand. The structure of (**8**), therefore, illustrates the great flexibility of the dppm bridge in accommodating unusual bonding arrangements which cause steric constraints.

Table 6. Selected distances (pm) and angles (°) between interatomic vectors for $[(OC)_2Fe(\mu\text{-dppm})\{\eta^4\text{-}(CH_2)(CMe_2)CPt(PPh_3)\}]$ (**8**)

Fe–Pt	261.8(4)	P(1)–Pt	227.4(3)
P(3)–Pt	226.4(3)	C(4)–Pt	204.1(7)
P(2)–Fe	218.9(4)	C(1)–Fe	175.6(9)
C(2)–Fe	176.6(9)	C(3)–Fe	214.4(8)
C(4)–Fe	197.1(7)	C(5)–Fe	221.1(8)
C(13)–P(1)	185.2(7)	C(13)–P(2)	185.3(7)
O(1)–C(1)	116.4(8)	O(2)–C(2)	116.0(8)
C(4)–C(3)	142.1(9)	C(5)–C(4)	142.6(9)
C(6)–C(5)	152.3(11)	C(7)–C(5)	151.8(11)
P(3)–Pt–Fe	150.5	C(4)–Pt–Fe	48.1(1)
C(4)–Pt–P(3)	102.5(2)	C(1)–Fe–Pt	97.1(3)
C(2)–Fe–Pt	163.6(2)	C(2)–Fe–C(1)	98.6(4)
C(3)–Fe–Pt	73.3(2)	C(3)–Fe–C(1)	158.3(2)
C(3)–Fe–C(2)	90.3(3)	C(4)–Fe–Pt	50.4(3)
C(4)–Fe–C(1)	119.0(4)	C(4)–Fe–C(2)	116.8(3)
C(4)–Fe–C(3)	40.1(2)	C(5)–Fe–Pt	76.5(3)
C(5)–Fe–C(1)	90.2(3)	C(5)–Fe–C(2)	98.9(3)
C(5)–Fe–C(3)	68.8(3)	C(5)–Fe–C(4)	39.4(2)
C(13)–P(1)–Pt	105.3(3)	C(13)–P(2)–Fe	113.3(3)
P(2)–C(13)–P(1)	110.0(4)	O(1)–C(1)–Fe	177.3(5)
O(2)–C(2)–Fe	178.3(5)	C(4)–C(3)–Fe	63.4(4)
Fe–C(4)–Pt	81.5(3)	C(3)–C(4)–Pt	110.7(5)
C(3)–C(4)–Fe	76.5(4)	C(5)–C(4)–Pt	119.3(5)
C(5)–C(4)–Fe	79.5(4)	C(5)–C(4)–C(3)	119.5(6)
C(4)–C(5)–Fe	61.2(4)	C(6)–C(5)–Fe	117.4(5)
C(6)–C(5)–C(4)	119.2(7)	C(7)–C(5)–Fe	113.8(5)
C(7)–C(5)–C(4)	123.5(7)	C(7)–C(5)–C(6)	112.0(6)

The ^1H n.m.r. spectrum of complex (**6**) is temperature dependent. At low temperature (−20 °C) all of the protons of the allene ligand are non-equivalent and the methylene protons of the dppm ligand are also non-equivalent. These observations can be explained by assuming that the low-temperature spectrum reflects the solid-state structure and that the solid-state structure of (**6**) is analogous to that determined for (**8**) [this is reasonable as the $^{31}P\text{-}\{^1H\}$ n.m.r. and i.r. parameters for (**6**) and (**8**) are similar]. Thus, the distorted diphosphine backbone effectively leads to the inequivalence of the allene protons at low temperature. At high temperature, the ^1H n.m.r. spectrum of (**6**) shows only two types of allene proton and the dppm methylene protons are now equivalent. This can be explained by envisaging a rapid flipping of the $\overline{FePCPPt}$ ring, *i.e.* there will be a plane of symmetry through Pt, C(4), and Fe at an intermediate stage which makes the two allene protons *cis* to platinum equivalent and the two allene protons *trans* to platinum equivalent. Obviously such ring flipping has no effect on the ^1H n.m.r. spectra of complexes (**7**) and (**8**) due to the substituents on the allene ligands. These spectra, therefore, are similar to that of (**6**) at −20 °C except that one or two of the resonances due to the allene protons are absent.

Protonation of (**5**) with $HBF_4{\cdot}OEt_2$ in dichloromethane gave the previously described μ-propenyl complex $[(OC)_3Fe(\mu\text{-dppm})\{\mu\text{-}C(Me){=}CH_2\}Pt(PPh_3)][BF_4]$ (**9**). The complex was characterised by comparison of its $^{31}P\text{-}\{^1H\}$ and ^1H n.m.r. and i.r. spectra with those of an authentic sample.[1] This result links the allene systems with the acetylene systems previously reported, *viz.* protonation of the propyne complex $[(OC)_2Fe(\mu\text{-dppm})\{\mu\text{-}C(O)C(Me)CH\}Pt(PPh_3)]$ also gave (**9**), exclusively.[1] Interestingly, protonation of the μ-allene complex $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4(\mu\text{-}CH_2{=}C{=}CH_2)]$ has been reported to give the μ-alkenyl cation[11] $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4\{\mu\text{-}CH{=}C(H)Me\}]^+$ and not $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4\{\mu\text{-}C(Me){=}CH_2\}]^+$ which must be formed initially. Possibly, isomerisation to give the thermodynamically most favoured product can account for the results in both the Fe–Pt and Mo_2 systems.

Experimental

General methods were as previously described in recent papers from this laboratory.[12] The complexes $[(OC)_3Fe(\mu\text{-dppm})(\mu\text{-}CO)Pt(PPh_3)]$ and $[(OC)_3Fe(\mu\text{-vdpp})(\mu\text{-}CO)Pt(PPh_3)]$ were prepared by previously described methods.[1]

Preparations.—$[(OC)_3Fe(\mu\text{-dppm})\{\mu\text{-}C(O)CH_2C({=}CH_2)\}\text{-}Pt(PPh_3)]$ (**3**). A solution of $[(OC)_3Fe(\mu\text{-dppm})(\mu\text{-}CO)Pt(PPh_3)]$ (**1**) (0.30 g, 0.30 mmol) in dichloromethane (3 cm^3) was saturated with allene. The mixture was set aside at *ca.* 20 °C for 5 d, after which time a yellow solid had precipitated. Addition of an excess of diethyl ether and refrigeration (−5 °C) overnight

Table 7. Crystallographic data *

Compound	**(3)**	**(5)**	**(8)**
Crystal data			
Formula	$C_{50}H_{41}FeO_4P_3Pt$	$C_{49}H_{41}FeO_3P_3Pt$	$C_{50}H_{45}FeO_2P_3Pt$
M	1 049.22	1 021.71	1 021.76
System	Orthorhombic	Monoclinic	Monoclinic
a/pm	2 481.5(3)	1 195.1(2)	1 098.4(3)
b/pm	1 906.2(2)	2 258.5(3)	1 889.8(6)
c/pm	1 838.7(3)	1 673.9(4)	2 216.3(5)
α/°			
β/°		108.15(2)	103.52(2)
γ/°			
U/nm³	8.698	4.483	4.729
Z	8	4	4
Space group	*Pbca*	$P2_1/n$	$P2_1/c$
D_c/g cm⁻³	1.602	1.513	1.435
μ/cm⁻¹	33.35	34.26	34.33
F(000)	4 144	2 012	2 024
Data collection			
Scan width (° + α-doublet splitting)	1.8	2.0	2.0
Total data	6 448	5 958	6 234
Unique data	5 455	5 406	5 701
No. observed [$I > 2\sigma(I)$]	4 401	4 835	5 080
Refinement			
g	0.0002	0.0003	0.0003
R	0.0315	0.0286	0.0311
R'	0.0302	0.0295	0.0316
No. of parameters	456	451	432

* Details common to all three structures. Scan speed 2.0—29.3° min⁻¹; 2θ (min., max.) 4.0, 45.0°.

Table 8. Atom co-ordinates (× 10⁴) for compound (**3**)

Atom	*x*	*y*	*z*
Pt	3 415.0(1)	3 519.0(1)	1 405.4(1)
Fe	4 297.9(4)	2 852.1(5)	1 869.7(5)
P(1)	3 560(1)	3 183(1)	206(1)
P(2)	4 535(1)	2 416(1)	782(1)
P(3)	2 772(1)	4 371(1)	1 277(1)
C(111)	2 920(1)	2 915(2)	−191(2)
C(112)	2 672(1)	2 320(2)	96(2)
C(113)	2 156(1)	2 132(2)	−133(2)
C(114)	1 888(1)	2 539(2)	−649(2)
C(115)	2 136(1)	3 135(2)	−937(2)
C(116)	2 652(1)	3 323(2)	−708(2)
C(121)	3 906(2)	3 708(2)	−478(2)
C(122)	4 240(2)	4 254(2)	−250(2)
C(123)	4 548(2)	4 622(2)	−757(2)
C(124)	4 522(2)	4 444(2)	−1 492(2)
C(125)	4 188(2)	3 898(2)	−1 720(2)
C(126)	3 880(2)	3 529(2)	−1 213(2)
C(13)	3 959(2)	2 368(3)	160(4)
C(211)	5 070(1)	2 882(2)	289(2)
C(212)	5 427(1)	3 292(2)	691(2)
C(213)	5 831(1)	3 670(2)	338(2)
C(214)	5 877(1)	3 638(2)	−417(2)
C(215)	5 520(1)	3 228(2)	−820(2)
C(216)	5 116(1)	2 850(2)	−467(2)
C(221)	4 785(2)	1 509(2)	796(3)
C(222)	4 440(2)	974(2)	1 025(3)
C(223)	4 634(2)	291(2)	1 101(3)
C(224)	5 173(2)	143(2)	948(3)
C(225)	5 518(2)	677(2)	719(3)
C(226)	5 323(2)	1 360(2)	643(3)
C(311)	2 987(2)	5 190(2)	1 713(2)
C(312)	3 503(2)	5 224(2)	2 011(2)
C(313)	3 698(2)	5 858(2)	2 284(2)
C(314)	3 376(2)	6 458(2)	2 259(2)
C(315)	2 860(2)	6 424(2)	1 960(2)
C(316)	2 665(2)	5 790(2)	1 687(2)
C(321)	2 592(2)	4 729(2)	381(2)
C(322)	3 016(2)	4 960(2)	−55(2)
C(323)	2 911(2)	5 241(2)	−741(2)
C(324)	2 382(2)	5 292(2)	−991(2)
C(325)	1 957(2)	5 061(2)	−555(2)
C(326)	2 062(2)	4 780(2)	131(2)
C(331)	2 110(2)	4 135(2)	1 634(3)
C(332)	1 850(2)	4 497(2)	2 192(3)
C(333)	1 341(2)	4 283(2)	2 425(3)
C(334)	1 093(2)	3 707(2)	2 100(3)
C(335)	1 352(2)	3 345(2)	1 542(3)
C(336)	1 861(2)	3 559(2)	1 308(3)
C(1)	3 740(3)	2 284(4)	1 908(4)
O(1)	3 399(2)	1 858(3)	1 917(3)
C(2)	4 862(3)	2 433(4)	2 231(4)
O(2)	5 246(2)	2 154(3)	2 456(3)
C(3)	4 488(3)	3 724(4)	1 708(4)
O(3)	4 619(2)	4 315(3)	1 632(3)
C(4)	4 174(3)	3 219(4)	2 881(4)
O(4)	4 487(3)	3 135(4)	3 392(2)
C(5)	3 684(3)	3 663(4)	3 022(4)

gave the desired product as pale yellow microcrystals. Yield 0.11 g, 35%. The vdpp analogoue [$(OC)_3$Fe(μ-vdpp){μ-C(O)CH_2C(=CH_2)}Pt(PPh_3)] (**4**) was prepared in a similar manner from [$(OC)_3$Fe(μ-vdpp)(μ-CO)Pt(PPh_3)] (**2**), in 27% yield.

[$(OC)_3$Fe(μ-dppm){μ-C(=CH_2)CH_2}Pt(PPh_3)] (**5**). A solution of [$(OC)_3$Fe(μ-dppm)(μ-CO)Pt(PPh_3)] (0.31 g, 0.31 mmol) in benzene (20 cm³) was refluxed for 10 min, with allene slowly bubbling through the solution. The resultant solution

Table 9. Atom co-ordinates (× 10^4) for compound (**5**)

Atom	*x*	*y*	*z*
Pt	−370.5(2)	1 346.2(1)	2 246.1(1)
Fe	1 497(1)	1 987.5(3)	2 428.2(4)
P(1)	−1 428(1)	1 800(1)	1 007(1)
P(2)	882(1)	2 528(1)	1 270(1)
P(3)	−1 619(1)	625(1)	2 398(1)
C(111)	−2 087(3)	1 294(2)	123(2)
C(112)	−3 154(3)	1 403(2)	−498(2)
C(113)	−3 615(3)	1 008(2)	−1 137(2)
C(114)	−3 009(3)	505(2)	−1 154(2)
C(115)	−1 943(3)	396(2)	−533(2)
C(116)	−1 481(3)	791(2)	106(2)
C(121)	−2 567(3)	2 335(1)	1 075(2)
C(122)	−2 855(3)	2 332(1)	1 821(2)
C(123)	−3 626(3)	2 738(1)	1 955(2)
C(124)	−4 109(3)	3 147(1)	1 344(2)
C(125)	−3 821(3)	3 151(1)	598(2)
C(126)	−3 050(3)	2 745(1)	463(2)
C(13)	−488(4)	2 236(2)	535(3)
C(211)	631(4)	3 332(1)	1 386(3)
C(212)	−433(4)	3 517(1)	1 474(3)
C(213)	−617(4)	4 094(1)	1 575(3)
C(214)	264(4)	4 485(1)	1 587(3)
C(215)	1 328(4)	4 299(1)	1 498(3)
C(216)	1 511(4)	3 723(1)	1 398(3)
C(221)	1 776(3)	2 545(2)	555(2)
C(222)	1 300(3)	2 783(2)	−242(2)
C(223)	1 936(3)	2 770(2)	−813(2)
C(224)	3 047(3)	2 518(2)	−588(2)
C(225)	3 523(3)	2 280(2)	209(2)
C(226)	2 888(3)	2 293(2)	780(2)
C(311)	−1 514(3)	482(1)	3 497(2)
C(312)	−1 563(3)	−62(1)	3 814(2)
C(313)	−1 587(3)	−132(1)	4 636(2)
C(314)	−1 561(3)	341(1)	5 142(2)
C(315)	−1 512(3)	885(1)	4 825(2)
C(316)	−1 488(3)	955(1)	4 003(2)
C(321)	−3 223(2)	716(2)	1 917(2)
C(322)	−3 719(2)	613(2)	1 058(2)
C(323)	−4 920(2)	702(2)	669(2)
C(324)	−5 626(2)	893(2)	1 139(2)
C(325)	−5 129(2)	996(2)	1 998(2)
C(326)	−3 928(2)	907(2)	2 387(2)
C(331)	−1 348(3)	−115(1)	2 000(3)
C(332)	−218(3)	−235(1)	1 972(3)
C(333)	32(3)	−765(1)	1 701(3)
C(334)	−849(3)	−1 176(1)	1 457(3)
C(335)	−1 980(3)	−1 056(1)	1 485(3)
C(336)	−2 229(3)	−526(1)	1 756(3)
C(1)	1 660(5)	1 356(3)	1 849(3)
O(1)	1 754(4)	949(2)	1 461(3)
C(2)	575(5)	2 359(3)	2 929(3)
O(2)	26(4)	2 609(2)	3 269(3)
C(3)	2 875(6)	2 343(3)	2 840(4)
O(3)	3 769(4)	2 564(3)	3 142(3)
C(4)	883(6)	1 089(4)	3 367(4)
C(5)	1 960(5)	1 377(3)	3 379(3)
C(6)	3 040(6)	1 227(4)	3 882(5)

Table 10. Atom co-ordinates (× 10^4) for compound (**8**)

Atom	*x*	*y*	*z*
Pt	2 305.0(2)	2 211.2(1)	952.4(1)
Fe	13 844.4(7)	971.0(4)	1 130.0(4)
P(1)	570(1)	2 902(1)	833(1)
P(2)	175(1)	1 607(1)	1 575(1)
P(3)	3 960(1)	2 916(1)	929(1)
C(111)	−170(3)	3 165(2)	35(1)
C(112)	−450(3)	3 869(2)	−132(1)
C(113)	−937(3)	4 046(2)	−753(1)
C(114)	−1 144(3)	3 519(2)	−1 206(1)
C(115)	−864(3)	2 815(2)	−1 039(1)
C(116)	−377(3)	2 639(2)	−418(1)
C(121)	497(3)	3 714(2)	1 269(2)
C(122)	1 608(3)	4 004(2)	1 618(2)
C(123)	1 570(3)	4 582(2)	2 005(2)
C(124)	421(3)	4 871(2)	2 042(2)
C(125)	−690(3)	4 582(2)	1 692(2)
C(126)	−652(3)	4 003(2)	1 306(2)
C(13)	−609(5)	2 344(3)	1 083(2)
C(211)	850(3)	1 987(2)	2 347(1)
C(212)	1 628(3)	1 542(2)	2 772(1)
C(213)	2 222(3)	1 795(2)	3 358(1)
C(214)	2 040(3)	2 494(2)	3 519(1)
C(215)	1 262(3)	2 939(2)	3 095(1)
C(216)	668(3)	2 686(2)	2 509(1)
C(221)	−1 292(3)	1 194(2)	1 695(2)
C(222)	−1 732(3)	567(2)	1 388(2)
C(223)	−2 874(3)	283(2)	1 443(2)
C(224)	−3 575(3)	625(2)	1 805(2)
C(225)	−3 135(3)	1 252(2)	2 112(2)
C(226)	−1 994(3)	1 536(2)	2 057(2)
C(311)	5 023(3)	2 595(2)	457(2)
C(312)	5 436(3)	1 897(2)	548(2)
C(313)	6 211(3)	1 615(2)	191(2)
C(314)	6 572(3)	2 032(2)	−256(2)
C(315)	6 158(3)	2 731(2)	−347(2)
C(316)	5 383(3)	3 012(2)	10(2)
C(321)	5 000(3)	3 028(2)	1 700(1)
C(322)	4 496(3)	2 939(2)	2 218(1)
C(323)	5 230(3)	3 071(2)	2 811(1)
C(324)	6 468(3)	3 293(2)	2 887(1)
C(325)	6 972(3)	3 382(2)	2 370(1)
C(326)	6 238(3)	3 250(2)	1 776(1)
C(331)	3 660(3)	3 824(2)	636(2)
C(332)	4 298(3)	4 414(2)	929(2)
C(333)	4 053(3)	5 083(2)	661(2)
C(334)	3 171(3)	5 160(2)	99(2)
C(335)	2 534(3)	4 570(2)	−194(2)
C(336)	2 778(3)	3 901(2)	74(2)
C(1)	279(6)	920(3)	416(3)
O(1)	−428(4)	863(2)	−62(2)
C(2)	1 158(5)	122(3)	1 419(3)
O(2)	1 042(5)	−437(3)	1 613(3)
C(3)	3 185(5)	1 040(3)	1 761(3)
C(4)	3 121(5)	1 240(3)	1 136(3)
C(5)	2 900(5)	713(3)	662(3)
C(6)	2 723(6)	940(4)	−12(3)
C(7)	3 373(6)	−42(4)	767(4)

was cooled to *ca.* 20 °C, filtered, and concentrated under reduced pressure to give the desired product as pale yellow microcrystals. Yield 0.18 g, 57%.

$[(OC)_2Fe(\mu\text{-dppm})\{\eta^4\text{-}(CH_2)_2CPt(PPh_3)\}]$ (**6**). A solution of $[(OC)_3Fe(\mu\text{-dppm})\{\mu\text{-}C({=}CH_2)CH_2\}Pt(PPh_3)]$ (**5**) (0.1 g, 0.1 mmol) in benzene (20 cm^3) was refluxed for 2 h. The mixture was then cooled to *ca.* 20 °C and the solvent removed under reduced pressure. The residue was extracted into hot n-hexane (100 cm^3) and the solution concentrated under reduced pressure, to give the desired product as yellow microcrystals. Yield 0.07 g, 72%.

$[(OC)_2Fe(\mu\text{-dppm})\{\eta^4\text{-}(CH_2)(CHPh)CPt(PPh_3)\}]$ (**7**). A solution of $[(OC)_3Fe(\mu\text{-dppm})(\mu\text{-CO})Pt(PPh_3)]$ (0.30 g, 0.30 mmol) and 3-phenyl-1,2-propadiene (0.06 g, 0.05 mmol) in benzene (20 cm^3) was refluxed for 1 h. The solution was cooled to *ca.* 20 °C and the solvent removed under reduced pressure. The residue was extracted into hot n-hexane (100 cm^3) and the solution concentrated under reduced pressure, to give the desired product as yellow microcrystals. Yield 0.18 g, 56%.

$[(OC)_2Fe(\mu\text{-dppm})\{\eta^4\text{-}(CH_2)(CMe_2)CPt(PPh_3)\}]$ (**8**). A solution of $[(OC)_3Fe(\mu\text{-dppm})(\mu\text{-CO})Pt(PPh_3)]$ (0.40 g, 0.40 mmol) and 3-methyl-1,2-butadiene (0.14 g, 2 mmol) in dichloromethane (20 cm^3) was refluxed for 48 h. The solution was cooled to *ca.* 20 °C and the solvent removed under reduced pressure. The residue was extracted into hot n-hexane (130 cm^3) and the solution concentrated under reduced pressure to give the desired product as yellow microcrystals. Yield 0.27 g, 66%.

X-*Ray Crystallography*.—All crystallographic measurements were made on a Nicolet P3/F diffractometer operating in the ω–2θ scan mode using graphite-monochromatised Mo-K_α radiation (λ = 71.069 pm) following a standard procedure described in detail elsewhere.[13] All three data sets were corrected for absorption empirically once their structures had been determined,[14] and the three structures were solved *via* standard heavy-atom methods and refined by full-matrix least squares using the SHELX program system.[15] The refinement was essentially the same for all three complexes with all non-hydrogen atoms being assigned anisotropic thermal parameters and the phenyl groups treated as rigid bodies with idealised hexagonal symmetry (C–C 139.5 pm). In each case the methylene and phenyl hydrogen atoms were included in calculated positions (C–H 108 pm) and an overall isotropic thermal parameter was assigned for each group. The hydrogen atoms on the allene groups were located experimentally for all three complexes although for compound (**8**) these were not refined. The weighting scheme $w = [\sigma^2(F_o) + g(F_o)^2]^{-1}$ was used for all three compounds in which the parameter g was included in refinement in order to obtain satisfactory agreement analyses. All relevant crystal data, data collection and structure refinement parameters are listed in Table 7, whilst non-hydrogen atomic co-ordinates for compounds (**3**), (**5**), and (**8**) are given in Tables 8, 9, and 10 respectively.

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

Acknowledgements

We thank the S.E.R.C. for support and Johnson Matthey Ltd. for the generous loan of platinum metal salts.

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Received 22*nd June* 1987; *Paper* 7/1105