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Synthesis of metallocenes of zirconium, hafnium, manganese, iron, tin, lead and half-sandwich complexes of rhodium and iridium containing the ligands (η-$C_5R_4CR'_2PMe_2$), where R and R′ may be H or Me

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This paper is dedicated to Professor Alberto Dias on the occasion of his 60th birthday

Abstract

The dimethylphosphino substituted cyclopentadienyl precursor compounds [$M(C_5Me_4CH_2PMe_2)$], where $M = Li^+$ (**1**), Na^+ (**2**), or K^+ (**3**), and [$Li(C_5H_4CR'_2PMe_2)$], where $R'_2 = Me_2$ (**4**), or $(CH_2)_5$ (**5**), [$HC_5Me_4CH_2PMe_2H$]X, where $X^- = Cl^-$ (**6**) or PF_6^- (**7**) and [$HC_5Me_4CH_2PMe_2$] (**8**), are described. They have been used to prepare new metallocene compounds, of which representative examples are [$Fe(\eta$-$C_5R_4CR'_2PMe_2)_2$], where R = Me, R′ = H (**9**); R = H and $R'_2 = Me_2$ (**10**), or $(CH_2)_5$ (**11**), [$Fe(\eta$-$C_5H_4CMe_2PMe_3)_2]I_2$ (**12**), [$Fe\{\eta$-$C_5Me_4CH_2P(O)Me_2\}_2$] (**13**), [$Zr(\eta$-$C_5R_4CR'_2PMe_2)_2Cl_2$], where R = H, R′ = Me (**14**), or R = Me, R′ = H (**15**), [$Hf(\eta$-$C_5H_4CMe_2PMe_2)_2]Cl_2$] (**16**), [$Zr(\eta$-$C_5H_4CMe_2PMe_2)_2Me_2$] (**17**), {[$Zr(\eta$-$C_5Me_4CH_2PMe_2)_2]Cl$}{$(C_6F_5)_3$-$BClB(C_6F_5)_3$} (**18**), [$Zr\{(\eta$-$C_5Me_4CH_2PMe_2)_2Cl_2\}PtI_2$] (**19**), [$Mn(\eta$-$C_5Me_4CH_2PMe_2)_2$] (**20**), [$Mn\{(\eta$-$C_5Me_4CH_2PMe_2B(C_6F_5)_3\}_2$] (**21**), [$Pb(\eta$-$C_5H_4CMe_2PMe_2)_2$] (**23**), [$Sn(\eta$-$C_5H_4CMe_2PMe_2)_2$] (**24**), [$Pb\{\eta$-$C_5H_4CMe_2PMe_2B(C_6F_5)_3\}_2$] (**25**), [$Pb(\eta$-$C_5H_4CMe_2PMe_2)_2PtI_2$] (**26**), [$Rh(\eta$-$C_5Me_4CH_2PMe_2)(C_2H_4)$] **29**, [$M(\eta,\kappa P$-$C_5Me_4CH_2PMe_2)I_2$], where M = Rh (**30**), or Ir, (**31**).

Keywords: Functionalised metallocene compounds; Chelating cyclopentadienyl-phosphine ligands; Chelating cyclopentadienyl-phosphine complexes; Bimetallic complexes; Derivatised ferrocenes; Derivatised manganocenes

1. Introduction

Metallocenes containing tertiary phosphine ligands attached to the cyclopentadienyl rings, in the general class [η-$C_5R_4(CR'_2)_nPR''_2$], where $n = 0$, 1, 2 or 3, R = H or alkyl, R′ = H, alkyl or aryl, R″ = alkyl or aryl, have been long known. There are various methods for the synthesis of the tertiary phosphine substituted cyclopentadienyl ligand precursors [1–5].

The first metallocene to contain such a ligand was [$Ti\{\eta$-$C_5H_4(CH_2)_2PPh_2\}_2Cl_2$] [6]. It was shown that this compound could act as a chelating diphosphine ligand to a $Mo(CO)_4$ moiety to form the heterobimetallic system {[$Ti\{\eta$-$C_5H_4(CH_2)_2PPh_2\}_2Cl_2$]$Mo(CO)_4$}.

Since then many mono- and bis-η-cyclopentadienyl-tertiary phosphine compounds have been prepared [7–12,18b]. Representative examples are: the ruthenium complexes [$Ru(\eta,\kappa P$-$C_5H_4CH_2CH_2PPh_2)(L)Cl$], where L = PPh_3 and $P(OMe)_3$], and [$Ru(\eta,\kappa P$-$C_5H_4CH_2CH_2$-$PPh_2)(PPh_3)[(+)$-$NH_2C(Me)Ph]\}BF_4$ [13], the cobalt compounds [$Co(\eta,\kappa P$-$C_5H_4CH_2CH_2PPh_2)L$], where L = CO, C_2H_4 [14–17], the rhodium and iridium compounds [$M(\eta,\kappa P$-$C_5H_4CH_2CH_2PPh_2)I_2$], where M = Rh and Ir [18] and the zirconocene compounds [$Zr(\eta$-$C_5H_4CMe_2PPh_2)_2X_2$] [19], where X = Cl or Me. The compound [$Zr(\eta$-$C_5H_4CMe_2PPh_2)_2Me_2$] undergoes

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abstraction of one methide (CH_3^-) group on treatment with $[B(C_6F_5)_3]$ to form the cationic species $[Zr(\eta\text{-}C_5H_4CMe_2PPh_2)_2Me][BMe(C_6F_5)_3]$ which is stabilised by intramolecular bonding of both the PPh_2 groups to the zirconium centre [19a].

Studies by Butenschon et al. have demonstrated the capability of the phosphine group on these bifunctional ligands to selectively bind to the metal centre $[Zr(\eta\text{-}C_5H_4CR_2PAr_2)_2R'_2]$, $R' = Cl$ or Me [12,14–17]. When $R' = Me$, treatment with $[B(C_6F_5)_3]$ gives mononuclear dications with intramolecular bonding of the PAr_2 group to the metal centre, as in $[Zr(\eta\kappa P\text{-}C_5H_4CR_2PAr_2)_2][MeB(C_6F_5)_3]_2$ [19].

Many heterobimetallic compounds combining bis-η-cyclopentadienyl derivatives of Group 4 metals containing alkyl- or aryl-phosphino substituents react as diphosphine ligands with later transition metals [1,20–22,54a]. For example, treatment of $[Mo(nbd)(CO)_4]$ with the bidentate ligand $[Zr(\eta\text{-}C_5H_4PPh_2)_2Cl_2]$ results in the isolation of the heterobimetallic complex $[\{Zr(\eta\text{-}C_5H_4PPh_2)_2Cl_2\}Mo(CO)_4]$ [1,3].

Similar heterobimetallic compounds are formed by the compounds $[Ti(\eta\text{-}C_5H_4CH_2CH_2PPh_2)_2Cl_2]$ and $[Zr(\eta\text{-}C_5H_4CH_2CH_2PPh_2)_2Cl_2]$. The compound $[Zr(\eta\text{-}C_5H_4CMe_2PAr_2)_2Cl_2]$ reacts with $[MCl_2(NCPh)_2]$, where M = Pd and Pt, to give the bimetallic complexes $[\{Zr(\eta\text{-}C_5H_4CMe_2PAr_2)_2Cl_2\}MCl_2]$ (M = Pd, Pt; Ar = Ph, *p*-tolyl) [3]. The NMR data indicated a *trans*-structure [4,23–26].

The zirconocene $[Zr(\eta\text{-}C_5Me_4PMe_2)_2Cl_2]$ reacts with $[Ru(H_2)H_2(PPh_3)_3]$ to give the compounds $[ZrCl(\eta\text{-}C_5Me_4PMe_2)_2(\mu\text{-}H)(\mu\text{-}Cl)RuH(PPh_3)]$ and $[ZrCl(\eta\text{-}C_5Me_4PMe_2)_2(\mu\text{-}H)_2RuCl(PPh_3)]$ [27]. Related bimetallic compounds of Pd, Pt, Rh and Ir have been described [21,28,29].

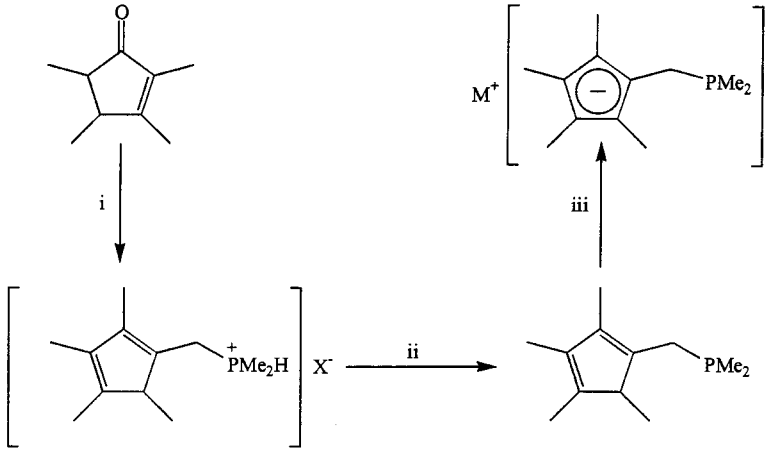
2. Results and discussion

New metallocenes containing the dimethylphosphinoalkyl-η-cyclopentadienyl ligands in the general class $(\eta\text{-}C_5R_4CR'_2PMe_2)$, where R, R′ may be H or Me, have been prepared. The ligand precursors which have been synthesised may be organised into anionic, cationic and neutral compounds. The anionic salts are $M[C_5Me_4CH_2PMe_2]$, where $M = Li^+$ (**1**), Na^+ (**2**), or K^+ (**3**); and $[Li(C_5H_4CR'_2PMe_2)]$, where $R'_2 = Me_2$ (**4**), or $(CH_2)_5$ (**5**). The cationic salts are $[HC_5Me_4CH_2PMe_2H]X$, where $X^- = Cl^-$ (**6**) or PF_6^- (**7**). The neutral compound $[HC_5Me_4CH_2PMe_2]$ (**8**), prepared by treatment of compound **7** with a methanol solution of potassium hydroxide, is a water-stable, air-sensitive, pale-yellow oil soluble in pentane, toluene, benzene, THF and diethyl ether.

The ligand syntheses are exemplified in Scheme 1 and in Section 3. The analytical and spectroscopic data which characterise the ligand precursor compounds **1**–**8**, and all the other new compounds described in this work, are given in Table 1. Compounds **1**–**5** and **8** were handled under an atmosphere of dry dinitrogen, whereas **6** and **7** are air-stable; the anionic systems are especially sensitive to oxygen and water.

A selection of the salts containing the dimethylphosphinoalkylcyclopentadienide anions were reacted with ferrous chloride to give functionalised ferrocenes in the class bis(dimethylphosphinoalkyl-η-cyclopentadienyl)-iron namely, $[Fe(\eta\text{-}C_5R_4CR'_2PMe_2)_2]$, where R = Me, R′ = H (**9**); R = H and $R'_2 = Me_2$ (**10**) or $(CH_2)_5$ (**11**). These new ferrocenes are shown in Scheme 2. Treatment of compound **10** with methyliodide gave the air-stable trimethylphosphonium derivative $[Fe(\eta\text{-}C_5H_4CMe_2PMe_3)_2]I_2$ (**12**).

Addition of ferrous chloride to a THF solution of **1** at −78 °C gave orange lozenges of $[Fe(\eta\text{-}C_5Me_4CH_2\text{-}$



Scheme 1. (i) $[Li(CH_2PMe_2)]$ in THF at −78 °C; then, HCl in Et_2O, for X = Cl **6** 90%; for $X = PF_6$ **7**, add NH_4PF_6 to **6** in H_2O, 85%. (ii) $X = PF_6$: add KOH in methanol, 45%. (iii) $M[N(SiMe_3)_2]$ in THF at −78 °C, for 12 h. M = Li **1**, 76%; M = Na **2**, 57%; M = K **3**, 79%.

Table 1
Analytical and spectroscopic data

Compound and analysis [a]	NMR data [b]
[Li($C_5Me_4CH_2PMe_2$)] (**1**)	^{1}H pyridine-d_5
White	2.93 [s, 2H, CH_2]
Very air sensitive	2.25 [s, 6H, $C_{ring}CH_3$]
	2.23 [s, 6H, $C_{ring}CH_3$]
	1.03 [s, 6H, P(CH_3)$_2$]
	^{13}C{^{1}H} pyridine-d_5
	105.15 [s, $C_{ring}CH_3$]
	104.91 [s, $C_{ring}CH_3$]
	104.80 [s, C_{ipso}]
	29.20 [d, CH_2] $J_{CP} = 7.76$
	13.37 [d, P(CH_3)$_2$] $J_{CP} = 17.2$
	10.87 [s, $C_{ring}CH_3$]
	10.37 [s, $C_{ring}CH_3$]
	^{31}P{^{1}H} pyridine-d_5
	−52 [s, $P(CH_3)_2$]
[Na($C_5Me_4CH_2PMe_2$)] (**2**)	^{1}H pyridine-d_5
White	2.71 [d, 2H, CH_2] $^2J_{HP} = 1.5$
C, 63.1 (66.0)	2.22 [s, 6H, $C_{ring}CH_3$]
H, 9.2 (9.2)	2.17 [s, 6H, $C_{ring}CH_3$]
P, 14.3 (14.2)	0.86 [d, 6H, P(CH_3)$_2$]
	$^2J_{HP} = 2.5$
Very air sensitive	^{13}C{^{1}H} pyridine-d_5
	105.58 [s, C_{ipso}]
	105.59 [s, $C_{ring}CH_3$]
	105.34 [s, $C_{ring}CH_3$] $J_{CP} = 7.5$
	131.10 [d, CH_2]
	14.40 [d, P(CH_3)$_2$] $J_{CP} = 16$
	12.40 [s, $C_{ring}CH_3$]
	11.96 [s, $C_{ring}CH_3$]
	^{31}P{^{1}H} pyridine-d_5
	−46.0 [s, $P(CH_3)_2$]
[K($C_5Me_4CH_2PMe_2$)] (**3**)	^{1}H THF-d_8
White	2.44 [d, 2H, CH_2] $^2J_{HP} = 1.5$
C, 57.9 (61.5)	1.85 [s, 6H, $C_{ring}CH_3$]
H, 8.8 (8.6)	1.84 [s, 6H, $C_{ring}CH_3$]
Very air sensitive	0.92 [d, 6H, P(CH_3)$_2$]
	$^2J_{HP} = 2.5$
	^{13}C{^{1}H} THF-d_8
	107.93 [s, C_{ipso}]
	107.13 [s, $C_{ring}CH_3$]
	106.44 [s, $C_{ring}CH_3$] $J_{CP} = 8.0$
	31.64 [d, CH_2]
	15.73 [d, P(CH_3)$_2$] $J_{CP} = 17.0$
	12.06 [s, C_{ring} CH_3]
	11.63 [s, C_{ring} CH_3]
	^{31}P{^{1}H} THF-d_8
	−45.4 [s, $P(CH_3)_2$]
[Li($C_5H_4CMe_2PMe_2$)] (**4**)	^{1}H pyridine-d_5
White	6.29 [s, 2H, $C_{ring}H$]
	6.17 [s, 2H, $C_{ring}H$]
	1.57 [d, 6H, P(CH_3)$_2$]
	$^2J_{PH} = 15$
	0.97 [s, 6H, C(CH_3)$_2$]
	^{13}C{^{1}H} pyridine-d_5
	123.74 [d, C_{ipso}] $^2J_{PC} = 5.5$
	101.62 [s, C_{ring}]
	101.54 [s, C_{ring}]
	31.49 [d, C(CH_3)$_2$] $^2J_{PC} = 9$
	25.42 [d, $C(CH_3)_2$] $^1J_{PC} = 19$
	9.53 [d, P(CH_3)$_2$] $^1J_{PC} = 22.5$
	^{31}P{^{1}H} pyridine-d_5
	−28 [s, $P(CH_3)_2$]

Table 1 (*Continued*)

Compound and analysis [a]	NMR data [b]
[Li{$C_5H_4C(CH_2)_5PMe_2$}] (**5**)	^{1}H pyridine-d_5
White powder	6.3 [s, 2H, $C_{ring}H$]
	6.03 [s, 2H, $C_{ring}H$]
	2.2-2.3 [m, 2H, ring CH_2]
	1.2-2.0 [m, 8H, ring CH_2]
	0.85 [d, 6H, P(CH_3)$_2$] $^2J_{PH} = 3.5$
	^{13}C{^{1}H} pyridine-d_5
	103.0 [s, $C_{ring}C$] (2 quaternary signals not detected)
	102.4 [s, C_{ring}C]
	33.5 [s, CH_2]
	28.5 [s, CH_2]
	22.8 [d, CH_2] $J_{PC} = 8.6$
	9.8 [d, P(CH_3)$_2$] $^1J_{PC} = 20.2$
	^{31}P {^{1}H} pyridine-d_5
	−26.6 [s, $P(CH_3)_2$]
[$HC_5Me_4CH_2PMe_2H$][Cl] (**6**)	^{1}H acetone-d_6
White solid	3.90 [t, 1H, CH_b] $^2J_{HbP} = 14.0$, $^2J_{HbHa} = 15.0$
	3.51 [t, 1H, CH_a] $^2J_{HaP} = 14.0$, $^2J_{haHb} = 15.0$
^{13}C{^{1}H}- and ^{1}H-NMR spectra were assigned using a ^{1}H–^{13}C correlation HMQC experiment	2.85 [m, 1H, $HC_{ring}CH_3$]
	2.10 [d, 3H, P(CH_3)$_2$]
	$^2J_{HP} = 14.5$
	2.06 [d, 3H, P(CH_3)$_2$]
	$^2J_{HP} = 14.5$
	1.93 [s, 3H, $C_{ring}CH_3$]
	1.83 [s, 3H, $C_{ring}CH_3$]
	1.77 [s, 3H, $C_{ring}CH_3$]
	1.08 [d, 3H, $HC_{ring}CH_3$]
	$^3J_{HH} = 8.0$
	^{13}C{^{1}H} D_2O
	143.3 [s, C_{ring}]
	134.3 [s, C_{ring}]
	127.2 [s, C_{ring}]
	127.1 [s, C_{ring}]
	49.93 [s, $HC_{ring}CH_3$]
	17.96 [d, CH_2] $J_{PC} = 51.6$
	13.10 [s, $HC_{ring}CH_3$]
	11.14 [s, CH_3C_{ring}]
	10.83 [s, CH_3C_{ring}]
	9.97 [s, CH_3C_{ring}]
	2.93 [d, P(CH_3)$_2$] $J_{PC} = 28.9$
	2.51 [d, P(CH_3)$_2$] $J_{PC} = 28.9$
	^{31}P{^{1}H} acetone-d_6
	40.38 [s, $P(CH_3)_2H$]
[$HC_5Me_4CH_2PMe_2H$][PF_6] (**7**)	^{1}H acetone-d_6
White solid	5.80 [d,1H, $HP(CH_3)_2$]
C, 42.2 (42.1)	3.69 [t, 1H, CH_b] $^2J_{HaP} = 14.0$, $^2J_{HaHb} = 15.0$
H, 6.3 (6.5)	3.35 [t, 1H, CH_a] $^2J_{HaP} = 14.0$ $^2J_{HaHb} = 15.0$
P, 18.8 (18.1)	2.86 [q, 1H, $HC_{ring}CH_3$]
	$^3J_{HH} = 7.5$
	2.00 [d, 3H, P(CH_3)$_2$]
	$^2J_{HP} = 13.5$
^{13}C{^{1}H}- and ^{1}H-NMR spectra were assigned using a ^{1}H–^{13}C correlation HMQC experiment	1.92 [s, 3H, $C_{ring}CH_3$]

Table 1 (*Continued*)

Compound and analysis [a]	NMR data [b]
	1.88 [d, 3H, P(CH_3)$_2$] $^2J_{HP}$ = 13.5 1.86 [s, 3H, C$_{ring}$CH_3] 1.80 [s, 3H, C$_{ring}$CH_3] 1.07 [d, 3H, HC$_{ring}$CH_3] $^3J_{HH}$ = 15.0 ^{13}C{^{1}H} acetone-d_6 143.2 [s, C_{ring}] 142.5 [s, C_{ring}] 134.3 [s, C_{ring}] 127.3 [s, C_{ring}] 50.7 [s, HC_{ring} –CH$_3$] 17.8 [d, CH$_2$] J_{CP} = 46.5 13.8 [s, HC$_{ring}$CH_3] 12.4 [s, C$_{ring}$CH_3] 11.8 [s, C$_{ring}$CH_3] 11.3 [s, C$_{ring}$CH_3] 3.32 [d, P(CH_3)$_2$] J_{CP} = 47.8 2.50 [d, P(CH_3)$_2$] J_{CP} = 47.8 ^{19}F acetone-d_6 −195.51 [d, PF_6] J_{FP} = 710
[HC$_5$Me$_4$CH$_2$PMe$_2$] (**8**) Pale yellow oil C, 76.3 (73.4) H, 8.3 (10.8)	^{1}H C$_6$D$_6$ 2.85 [m, 1H, HC$_{ring}$CH$_3$] 2.42 [dd, 1H, bridge CH] $^2J_{PH}$ = 10, $^4J_{H-H}$ = 3 2.31 [d, 1H, bridge CH] $^2J_{PH}$ = 10 1.79 [s, 3H. C$_{ring}$CH_3] 1.77 [s, 3H, C$_{ring}$CH_3] 1.75 [s, 3H, C$_{ring}$CH_3] 1.07 [d, 3H, HC$_{ring}$CH_3] $^3J_{HH}$ = 7.5 0.89 [d, 3H, PCH_3] $^2J_{PH}$ = 3 0.83 [d, 3H,, PCH_3] $^2J_{PH}$ = 2.5 ^{13}C{^{1}H} C$_6$D$_6$ 138.6 [s, C_{ring}] 138.2 [s, C_{ring}] 135.8 [s, C_{ring}] 134.0 [s, C_{ring}] 50.42 [s, HC_{ring}CH$_3$] 31.10 [d, CH$_2$] J_{CP} = 10.0 14.57 [d, P(CH_3)$_2$] J_{CP} = 11.0 14.50 [s, HC$_{ring}$CH_3] 14.46 [d, P(CH_3)$_2$] J_{CP} = 11.0 12.40 [s, C$_{ring}$CH_3] 11.79 [s, C$_{ring}$CH_3] 11.22 [s, C$_{ring}$CH_3] ^{31}P{^{1}H} C$_6$D$_6$ −45.9 [s, P(CH$_3$)$_2$]
[Fe(η-C$_5$Me$_4$CH$_2$PMe$_2$)$_2$] (**9**) Orange crystals C, 64.9 (64.6) H, 9.5 (9.0) P, 13.9 (13.9) Fe, 12.0 (12.0)	^{1}H C$_6$D$_6$ 2.27 [br s, 4H, CH_2] 1.74 [s, 12H, C$_{ring}$CH_3] 1.63 [s, 12H, C$_{ring}$CH_3] 0.83 [d, 12H, P(CH_3)$_2$] $^2J_{PH}$ = 3 ^{13}C{^{1}H} C$_6$D$_6$ 80.0 [d, C$_{ring}$C] J_{PC} = 10.7 79.2 [s, C$_{ring}$C] 78.1 [d, C$_{ring}$C] J_{PC} = 1.5 28.9 [d, PCH_2] $^1J_{PC}$ = 13.5 14.5 [d, P(CH_3)$_2$] $^1J_{PC}$ = 16 10.6 [d, C$_{ring}$CH_3] J_{PC} = 2.5

Table 1 (*Continued*)

Compound and analysis [a]	NMR data [b]
	9.6 [s, C$_{ring}$CH_3] ^{31}P{^{1}H} C$_6$D$_6$ −50.0 [s, P(CH$_3$)$_2$]
[Fe(η-C$_5$H$_4$CMe$_2$PMe$_2$)$_2$] (**10**) Orange crystals C, 60.80 (61.55) H, 8.15 (8.26)	^{1}H C$_6$D$_6$ 3.97 [m, 4H, C$_{ring}$$H$] 3.79 [m, 4H, C$_{ring}$$H$] 1.29 [d, 12H, P(C$H_3$)$_2$] $^2J_{PH}$ = 14.0 0.60 [d, 12H, C(CH_3)$_2$] $^3J_{PH}$ = 3.6 ^{13}C{^{1}H} C$_6$D$_6$ 96.3 [s, C_{ring}] 67.4 [s, C_{ring}] 66.4 [d, C_{ipso}] $^3J_{PC}$ = 1.7 31.3 [d, C(CH$_3$)$_2$] $^1J_{PC}$ = 15.0 25.7 [d, C(CH$_3$)$_2$] $^2J_{PC}$ = 20.0 10.2 [d, P(CH$_3$)$_2$] $^1J_{PC}$ = 20.0 ^{31}P{^{1}H} C$_6$D$_6$ −18.5 [s, P(CH$_3$)$_2$]
[Fe{η-C$_5$H$_4$C(CH$_2$)$_5$PMe$_2$}$_2$] (**11**) Orange crystals C, 65.9 (66.4) H, 8.4 (8.6) Fe, 11.7 (11.9) P, 12.7 (13.2)	^{1}H C$_6$D$_6$ 4.06 [s, 4H, C$_{ring}$$H$] 3.77 [s, 4H, C$_{ring}$$H$] 2.15–2.25 [m, 4H, ring CH_2] 1.75–2.0 [m, 10H, ring CH_2] 1.5–1.6 [m, 4H, ring CH_2] 1.2–1.35 [m, 2H, ring CH_2] 0.49 [d, 12H, P(CH_3)$_2$] $^2J_{PH}$ = 4.0 ^{13}C{^{1}H} C$_6$D$_6$ 97.5 [s, C_{ring}H] 67.1 [s, C_{ring}H] 65.5 [s, C_{ring}H] 36.4 [d, C_{ring}(CH$_2$)$_5$] J_{PC} = 21 34.3 [d, ring CH$_2$] J_{PC} = 15 27.7 [s, ring CH$_2$] 22.7 [d, ring CH$_2$] $^1J_{PC}$ = 12 9.1 [d, P(CH$_3$)$_2$] $^1J_{PC}$ = 20 ^{31}P{^{1}H} C$_6$D$_6$ −39.3 [s, PMe$_2$]
[Fe(η-C$_5$H$_4$CMe$_2$PMe$_3$)$_2$I$_2$] (**12**) Yellow–orange microcrystals C, 38.5 (39.2) H, 5.3 (5.7) MS (electrospray) m/z 547.2 [M+H−I]$^+$ m/z 421.3 [M+H−2I]$^+$	^{1}H D$_2$O 4.42 [s, 4H, C$_{ring}$$H$] 4.34 [s, 4H, C$_{ring}$$H$] 1.54 [d, 12H, C(C$H_3$)$_2$] $^2J_{PH}$ = 17.1 1.50 [d, 18H, P(CH_3)$_2$] $^2J_{PH}$ = 13.2 ^{31}P{^{1}H} D$_2$O 39.2 [s, PMe$_2$]
[Zr(η-C$_5$H$_4$CMe$_2$PMe$_2$)$_2$Cl$_2$] (**14**) White crystalline C, 42.5 (43.4) H, 6.2 (5.9) P, 10.6 (10.6) Zr, 15.5 (15.7) Cl, 23.6 (24.4) MS (EI) m/z 494/496/498	^{1}H CD$_2$Cl$_2$ 6.40 [s, 2H, C$_{ring}$$H$] 6.35 [s, 2H, C$_{ring}$$H$] 1.54 [d, 6H, P(C$H_3$)$_2$] $^2J_{PH}$ = 13.5 0.73 [d, 6H, C(CH_3)$_2$] $^3J_{PH}$ = 3.5 ^{13}C{^{1}H} CD$_2$Cl$_2$ 138.5 [C_{ring}] 113.9 [d, C_{ring}] $^3J_{PC}$ = 22 111.6 [d, C_{ring}] $^3J_{PC}$ = 18 33.4 [d, C(CH$_3$)$_2$] $^1J_{PC}$ = 16 21.9 [C(CH$_3$)$_2$]

Table 1 (*Continued*)

Compound and analysis [a]	NMR data [b]
	8.60 [d, P(CH_3)$_2$,] $^1J_{PC}$ = 21 ^{31}P{^{1}H} CD_2Cl_2 −10.8 [s, $P(CH_3)_2$]
[Zr(η-$C_5Me_4CH_2PMe_2)_2Cl_2$] (**15**) Pale yellow C, 49 8 (52.1) H, 7.30 (7.29) P, 11.1 (11.2) Zr, 17.4 (16.5) MS (FAB) *m*/*z* 547 [M−Cl+2O] 50% The analysis suggests the compound has been oxidised during storage. This explains the MS. Theoretical values for [Zr(η-$C_5Me_4CH_2P(O)Me_2)_2Cl_2$] are: C, 49.31; H, 5.47; P, 10.60; Zr, 15.60	^{1}H pyridine-d_5 2.52 [s, 2H, CH_2] 1.81 [s, 6H, $C_{ring}CH_3$] 1.65 [s, 6H, $C_{ring}CH_3$] 0.62 [s, 6H, P(CH_3)$_2$] ^{13}C{^{1}H} pyridine-d_5
	125.3 [d, C_{ipso}] $^2J_{CP}$ = 12.9 111.7 [s, $C_{ring}CH_3$] 121.6 [s, $C_{ring}CH_3$] 30.1 [d,CH_2] J_{CP} = 14.0 13.25 [d, P(CH_3)$_2$] J_{CP} = 15.0 11.6 [d, $C_{ring}CH_3$] $^4J_{CP}$ = 4.2 10.5 [s, $C_{ring}CH_3$] ^{31}P{^{1}H} pyridine-d_5 −44.5 [s, $P(CH_3)_2$]
[Hf(η-$C_5H_4CMe_2PMe_2)_2Cl_2$] (**16**) Cream solid C 41.7 (41.2) H 5.6 (5.5) P 10.6 (10.6)	^{1}H C_6D_6 6.26 [m, 4H, $C_{ring}H$] 6.25 [m, 4H, $C_{ring}H$] 1.50 [d, 6H, P(CH_3)$_2$] $^2J_{PH}$ = 14 0.65 [d, 12H, C(CH_3)$_2$] $^3J_{PH}$ = 4 ^{13}C{^{1}H} C_6D_6 138.7 [d, C_{ring}] $^2J_{PC}$ = 5 114.2 [d, C_{ring}] $^3J_{PC}$ = 4 112.1 [s, C_{ring}] 35.1 [d, C(CH_3)$_2$] $^2J_{PC}$ = 16 23.6 [d, CCH_3] $^1J_{PC}$ = 17 10.7 [d, P(CH_3)$_2$] $^1J_{PC}$ = 21 ^{31}P{^{1}H} C_6D_6 −8.0 [s, $P(CH_3)_2$]
[Zr(η-$C_5H_4CMe_2PMe_2)_2Me_2$] (**17**) White microcrystals C, 55.5 (57.9) H, 8.4 (8.4) Zr, 20.0 (20.0)	^{1}H CD_2Cl_2 6.06 [m, 4H, $C_{ring}H$] 6.02 [m, 4H, $C_{ring}H$] 1.29 [d, 12H, P(CH_3)$_2$] $^2J_{PH}$ = 13.5 0.76 [d, 12H, C(CH_3)$_2$] $^3J_{PH}$ = 4.0 −0.26 [s, 6H, Zr(CH_3)$_2$] ^{13}C{^{1}H} C_6D_6 134.0 [d, C_{ring}] J_{PC} = 5.5 110.0, [s, C_{ring}] 108.8 [d, C_{ring}] J_{PC} = 4.0 33.8 [d, C(CH_3)$_2$] $^2J_{PC}$ = 14.5 31.4 [s, Zr(CH_3)$_2$] 24.0 [d, C(CH_3)$_2$] $^1J_{PC}$ = 18.5 10.4 [d, P(CH_3)$_2$] $^1J_{PC}$ = 20.0 ^{31}P{1H} CD_2Cl_2 −12.0 [s, $P(CH_3)_2$]

Table 1 (*Continued*)

Compound and analysis [a]	NMR data [b]
{[Zr(η-$C_5Me_4CH_2PMe_2)_2$]Cl}-{($C_6F_5)_3BClB(C_6F_5)_3$} (**18**) Pale yellow	^{1}H toluene-d_8 2.52 [d, 2H, CH_2] $^2J_{HP}$ = 7.0 1.66 [s, 6H, $C_{ring}CH_3$] 1.65 [s, 6H, $C_{ring}CH_3$] 0.62 [d, 6H, P(CH_3)$_2$] $^2J_{HP}$ = 10.6 ^{19}F toluene-d_8 −163.0 [m, 1F, *p*-C_6F_5] −158.0 [m, 2F, *m*-C_6F_5] −133.0 [m, 2F, *o*-C_6F_5] ^{13}C{^{1}H} toluene-d_8 149.2 [d, *o*-C_6F_5] J_{CF} = 247 140.7 [d, *p*-C_6F_5] J_{CF} = 252 1 37.8 [d, *m*-C_6F_5] J_{CF} = 257 124.4 [s, $C_{ring}CH_3$] 123.4 [s, $C_{ring}CH_3$] 118.0 [d, C_{ipso}] $^2J_{CP}$ = 7.25 115.4 [s, C_{ipso}] 22.4 [d, CH_2] J_{CP} = 31.4 13.9 [s, $C_{ring}CH_3$] 11.6 [s, $C_{ring}CH_3$] 7.89 [d, P(CH_3)$_2$] J_{CP} = 36.7 ^{11}B{^{1}H} toluene-d_8 −13.0 [s, $B(C_6F_5)_3$] ^{31}P{^{1}H} toluene-d_8 8.26 [s, $P(CH_3)_2$]
[Zr(η-$C_5Me_4CH_2PMe_2)_2Cl_2PtI_2$] (**19**) Yellow–orange C, 28.5 (28.8) H, 4.1 (4.5) MS (FAB) *m*/*z* 747 [M−2I] 50%	^{31}P{^{1}H} THF-d_8 −12.0 [s, $P(CH_3)_2$] Pt satellites J_{PPt} = 2304
[Mn(η-$C_5Me_4CH_2PMe_2)_2$] (**20**) Orange crystals C, 62.8 (64.7) H, 10.4 (9.1) P, 13.6 (13.9) MS (FAB) *m*/*z* 445 [M$^+$] 50%	^{1}H C_6D_6 4.96 [s, 6H, P(CH_3)$_2$] −2.51 [br s, 6H, $C_{ring}CH_3$] −4.21 [br s, 6H, $C_{ring}CH_3$] −11.29 [br s, 2H, CH_2] ^{31}P{^{1}H} toluene-d_8 210.0 [s, $P(CH_3)_2$]
[Mn{(η-$C_5Me_4CH_2PMe_2B$-($C_6F_5)_3$}$_2$] (**21**) Yellow–orange C, 42.5 (42.8) H, 6.36 (6.36) MS (FAB) *m*/*z* 1469 [M$^+$] 5% *m*/*z* 957 [M−B($C_6F_5)_3$] 10% *m*/*z* 445 [M-2 B($C_6F_5)_3$] 100%	
[Pb(η-$C_5H_4CMe_2PMe_2)_2$] (**23**) Orange crystals C, 43.2 (44.4) H, 6.0 (6.0) ^{13}C{^{1}H}- and ^{1}H-NMR spectra were assigned using a ^{1}H–^{13}C correlation HMQC experiment	^{1}H toluene-d_8 5.73 [m, 2H, $C_{ring}H$] 5.68 [m, 2H, $C_{ring}H$] 1.22 [d, 6H, P(CH_3)$_2$] $^2J_{HP}$ = 12.0 0.77 [d, 6H, C(CH_3)$_2$] $^3J_{HP}$ = 3.5 ^{31}P{^{1}H} toluene-d_8 −15.6 [s, $P(CH_3)_2$] $^3J_{PPb}$ = 276 ^{207}Pb{^{1}H} toluene-d_8

Table 1 (*Continued*)

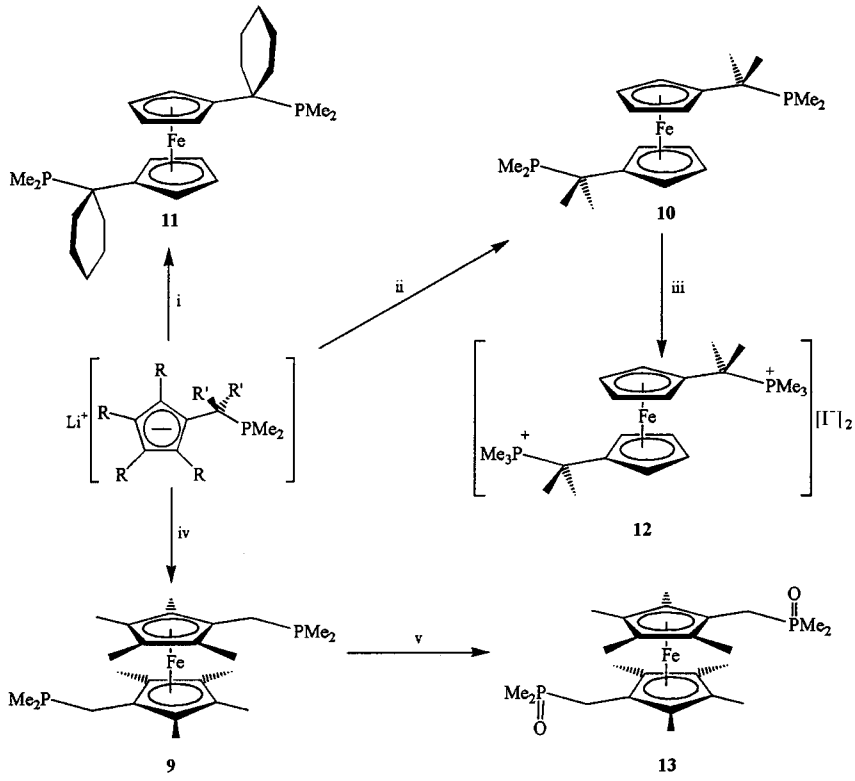
Compound and analysis [a]	NMR data [b]
	−4925.2 [t, *Pb*] $^3J_{PbP} = 270$
	$^{13}C\{^1H\}$ toluene-d_8
	139.5 [s, C_{ipso}]
	109.4 [d, $C_{ring}H$] $J_{CPb} = 106$
	108.8 [d, $C_{ring}H$] $J_{CPb} = 82$
	31.7 [d, $C(CH_3)_2$] $J_{CP} = 16$
	26.8 [d, $P(CH_3)_2$] $J_{CP} = 13$
	11.8 [d, $C(CH_3)_2$] $^2J_{CP} = 21$
[Sn(η-$C_5H_4CMe_2PMe_2)_2$] (**24**)	^1H toluene-d_8
Yellow	5.67 [m, 2H, $C_{ring}H$]
C, 51.6 (53.0)	5.62 [m, 2H, $C_{ring}H$]
H, 7.3 (7.1)	1.26 [d, 3H, $P(CH_3)_2$]
	$^2J_{HP} = 11.5$
	0.74 [d, 6H, $C(CH_3)_2$]
	$^3J_{HP} = 3.5$
$^{13}C\{^1H\}$- and ^1H-NMR spectra were assigned using a ^1H–^{13}C correlation HMQC experiment	$^{119}Sn\{^1H\}$ toluene-d_8
	−2162.8 [t, *Sn*] $^3J_{Sn-P} = 110$
	$^{13}C\{^1H\}$ toluene-d_8
	140.0 [s, C_{ipso}]
	109.9 [s, $C_{ring}H$]
	107.9 [s, $C_{ring}H$]
	31.8 [d, $C(CH_3)_2$] $J_{CP} = 16$
	26.6 [d, $P(CH_3)_2$] $^4J_{CSn117} = 360$
	$^4J_{CSn119} = 180$; $J_{CP} = 13$
	10.0 [d, $C(CH_3)_2$] $^3J_{CSn117} = 471$
	$^3J_{CSn119} = 230$; $^2J_{CP} = 21$
	$^{31}P\{^1H\}$ toluene-d_8
	−21.4 [s, $P(CH_3)_2$] $^3J_{PSn} = 111$
[Pb{η-$C_5H_4CMe_2PMe_2B(C_6F_5)_3\}_2$] (**25**)	^1H pyridine-d_5
Yellow	5.84 [m, 2H, $C_{ring}H$]
C, 42.5 (42.7)	5.82 [m, 2H, $C_{ring}H$]
H, 2.6 (2.1)	1.13 [d, 6H, $P(CH_3)_2$]
	$^2J_{HP} = 12.0$
P, 3.43 (3.96)	0.65 [d, 6H, $C(CH_3)_2$]
	$^3J_{HP} = 3.0$
	$^{11}B\{^1H\}$ pyridine-d_5
	0.61 [d, $(C_6F_5)_3BPMe_2$]
	$J_{BP} = 70.5$
	$^{13}C\{^1H\}$ pyridine-d_5
	149.5 [br, C_6F_5]
	147.5 [br, C_6F_5]
	139.4 [br, C_6F_5]
	116.3 [s, C_{ipso}]
	109.5 [s, $C_{ring}H$]
	108.4 [s, $C_{ring}H$]
	32.12 [d, $C(CH_3)_2$] $J_{CP} = 11.8$
	26.82 [d, $P(CH_3)_2$] $J_{CP} = 15.9$
	10.94 [d, $C(CH_3)_2$] $^2J_{CP} = 19.6$
	$^3P\{^1H\}$ pyridine-d_5
	−11.6 [s, $P(CH_3)_2$]
[Pb(η-$C_5H_4CMe_2PMe_2)_2PtI_2$] (**26**)	$^{31}P\{^1H\}$ THF-d_8
Yellow–orange	−4.67 [s, $P(CH_3)_2$] Pt satellites $J_{PPt} = 2320$
C, 25.1 (24.3)	
H, 3.6 (3.3)	
P, 6.4 (6.3)	
Pb, 19.8 (20.9)	
MS (FAB) m/z 863 [M−I] 40%, m/z 736 [M−2I] 25%	
[Rh(η,κ*P*-$C_5Me_4CH_2PMe_2$)-(C_2H_4)] (**29**)	^1H C_6D_6
Yellow–brown	3.36 [d, 2H, CH_2] $^2J_{PH} = 8.6$
C, 51.47 (51.55)	2.17 [s, 6H, $C_{ring}CH_3$]
H, 7.28 (7.42)	2.01 [d, 6H, $C_{ring}CH_3$]
	$^4J_{PH} = 3.2$
P, 9.16 (9.49)	1.86 [d, 6H, $P(CH_3)_2$] $^2J_{PH} = 13$
Rh, 30.19 (31.54)	$^{31}P\{^1H\}$ C_6D_6
	−29.6.[d, $P(CH_3)_2$]
	$J_{RhP} = 198.4$
[Rh(η,κ*P*-$C_5Me_4CH_2PMe_2)I_2$] (**30**)	^1H toluene-d_8
Brown	3.91 [d, 2H, CH_2] $^2J_{PH} = 8.7$
C, 25.98 (26.11)	2.19 [s, 6H, $C_{ring}CH_3$]
H, 3.60 (3.65)	2.01 [d, 6H, $C_{ring}CH_3$]
	$^4J_{PH} = 2.8$
P, 5.02 (5.61)	1.88 [d, 6H, $P(CH_3)_2$]
	$^2J_{PH} = 11.6$
I, 42.14 (46.12)	$^{31}P\{^1H\}$ C_6D_6
Rh, 17.21 (18.64)	−22.2.[d, $P(CH_3)_2$]
	$J_{RhP} = 136.8$
[Ir(η,κ*P*-$C_5Me_4CH_2PMe_2)I_2$] (**31**)	^1H CD_2Cl_2
Brown	3.89 [d, 2H, CH_2] $^2J_{PH} = 8.6$
C, 22.06 (22.48)	2.15 [s, 6H, $C_{ring}CH_3$]
H, 3.11 (3.14)	2.08 [d, 6H, $C_{ring}CH_3$]
	$^4J_{PH} = 3.3$
P, 4.39 (4.83)	1.81 [d, 6H, $P(CH_3)_2$]
	$^2J_{PH} = 12.9$
I, 35.76 (39.58)	$^{31}P\{^1H\}$ CD_2Cl_2
Ir, 28.22 (29.97)	−27.5.[s, $P(CH_3)_2$]

[a] Analytical data given as: found (calculated)%.

[b] Room temperature. Data given as: chemical shift (δ), [multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad), relative intensity, assignment], and coupling constant (in Hz).

PMe$_2$)$_2$] (**9**) in 45–49% yield. Crystals of **9** suitable for X-ray diffraction were grown by evaporation of a benzene-d_6 solution. The crystal structure of **9** has been determined and the molecular structure is shown in Fig. 1. Selected interatomic distances and bond angles are shown in Table 2. A solution of **9** in perdeuterobenzene was exposed to air for 72 h to give crystals of [Fe{η-$C_5Me_4CH_2P(O)Me_2\}_2$] **13**. The crystal structure of **13** has been determined and the molecular structure is shown in Fig. 2. Selected distances and angles are given in Table 3.

Comparison of the structures of **9** and **13**, shows that the bond lengths and angles of the ferrocene skeletons seem to be relatively unaffected by the oxidation of the tertiary phosphine. The Fe–C_{Cp} distance in **9** is 2.0517 Å, whilst in **13** it is 2.042 Å. The two rings are slightly eclipsed, as shown by the angles between opposite carbon atoms through the metal centre (177.71 and



Scheme 2. (i) For R = H, $R'_2 = (CH_2)_5$: anhydrous $FeCl_2$ in THF at room temperature, ca. 15%. (ii) For R = H, R′ = Me: anhydrous $FeCl_2$ in THF at −78 °C; warm to room temperature, 21%. (iii) MeI in pentane for 5 h, >90%. (iv) For R = Me, R′ = H: anhydrous $FeCl_2$ at −78 °C, 46–49%. (v) Expose to air for 2 days.

174.8°, respectively, for **9** and **13**). The tertiary phosphine fragments of the two complexes are more affected by the oxidation. The length of the P–Me bond, for instance, decreases from 1.829 Å in **9** to 1.760 Å in **13**. Similarly, the P–CH_2 bond length decreases from 1.856 to 1.792 Å.

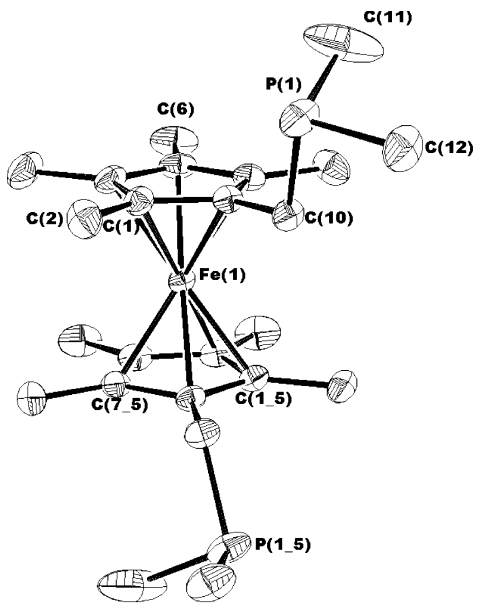


Fig. 1. Molecular structure of **9**.

Addition of half an equivalent of anhydrous ferrous chloride to a mixture formed from 6,6-(pentamethylene)fulvene and $LiPMe_2$, followed by stirring overnight, yields an orange solution. Orange crystals of [Fe{η-$C_5Me_4C(CH_2)_5PMe_2$}$_2$] (**11**) suitable for X-ray diffraction were obtained and the molecular structure and selected data are given in Fig. 3 and Table 4, respectively.

The cyclohexyl ring of **11** appears to modify the angle between the Cp ring and the phosphorus atom: compared to **9** and **13**, where the effect of the substituents on the bridge can be assumed to be minimal, the Cp–C–PMe_2 angle is 112.05(13) and 113.3(4)°, re-

Table 2
Selected bond lengths (Å) and bond angles (°) for **9**

Bond lengths	
Fe(1)–C(1)	2.0517(16)
C(1)–C(2)	1.434(2)
C(9)–C(10)	1.502(2)
P(1)–C(10)	1.8562(18)
P(1)–C(11)	1.829(2)
Bond angles	
C(1)–Fe(1)–C(24)	177.71(7)
P(1)–C(10)–C(1)	112.05(13)
C(10)–P(1)–C(11)	99.40(9)
Fe(1)–C(1)–C(2)	69.59(9)

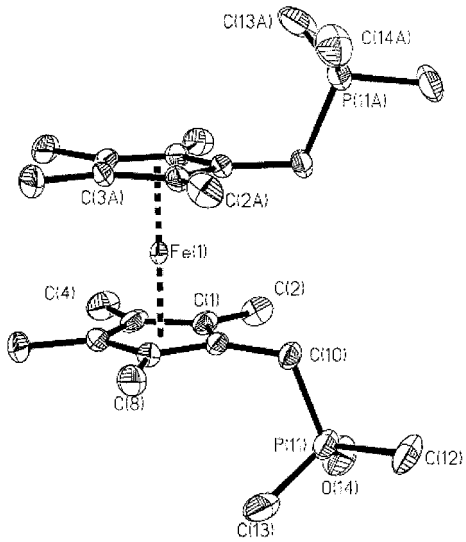


Fig. 2. Molecular structure of **13**.

Table 3
Selected bond lengths (Å) and bond angles (°) for **13**

Bond lengths	
Fe(1)–C(3)	2.042(6)
P(11)–O(14)	1.450(5)
P(11)–C(13)	1.760(7)
C(10)–P(11)	1.792(6)
C(1)–C(2)	1.488(8)
Bond angles	
C(1)–Fe(1)–C(3)	174.8(3)
C(9)–C(10)–P(11)	113.3(4)
O(14)–P(11)–C(10)	115.6(3)
C(2)–C(1)–Fe(1)	129.5(4)
C(3)–C(1)–C(2)	126.9(6)

spectively; in **11**, where the effect is likely to be larger, it is 110.49(14)°, about 1.5 and 2.8° more acute, respectively.

Treatment of zirconium tetrachloride with a selection of the salts of dimethylphosphinoalkylcyclopentadienide anions gave the corresponding dimethylphosphinoalkylcyclopentadienylzirconocene derivatives $\{[Zr(\eta\text{-}C_5R_4CR'_2PMe_2)_2]Cl_2\}$, where R = H, R′ = Me (**14**), or R = Me, R′ = H (**15**). The hafnium analogue of **14** namely $[Hf(\eta\text{-}C_5H_4CMe_2PMe_2)_2Cl_2]$ (**16**) was prepared in a similar manner (see Scheme 3). In a typical preparation a stirred THF solution of $ZrCl_4(THF)_2$ at 0 °C was added dropwise to a THF solution of compound **2**. The compound $[Zr(\eta\text{-}C_5Me_4CH_2PMe_2)_2Cl_2]$ (**15**) was isolated as a pale-yellow air-sensitive microcrystalline solid, soluble in dichloromethane, pyridine and THF.

Treatment of the dichloro derivative $[Zr(\eta\text{-}C_5H_4CMe_2PMe_2)_2Cl_2]$ (**14**) with methyllithium gives the corresponding dimethyl derivative $[Zr(\eta\text{-}C_5H_4CMe_2\text{-}PMe_2)_2Me_2]$ (**17**).

Treatment of **15** in toluene with two equivalents of the Lewis acid $[B(C_6F_5)_3]$ gave a pale-yellow solution, the NMR spectra of which may be assigned to the stoichiometry $\{[Zr(\eta\text{-}C_5Me_4CH_2PMe_2)_2]Cl\}\{(C_6F_5)_3\text{-}BClB(C_6F_5)_3\}$ (**18**). The $^{11}B\{^1H\}$-NMR spectrum of **18** displays a single peak at δ −13.0. The value for the $^{11}B\{^1H\}$-NMR spectrum of the $[ClB(C_6F_5)_3]^-$ anions is around δ −3.0 [19a], while the value of δ −13.0 resembles more closely the resonance found for $[MeB(C_6F_5)_3]^-$ [19a]. Given that two equivalents of $[B(C_6F_5)_3]$ were used in the reaction and there is a single ^{11}B signal, we tentatively propose the presence of the anion $[(C_6F_5)_3B\text{–}Cl\text{–}B(C_6F_5)_3]^-$ in **18**. By analogy with the structure determined for the compound $[Zr(\eta^5,\kappa P\text{-}C_5H_4CR_2PAr_2)_2Cl][ClB(C_6F_5)_3]_2$ [19a] we tentatively propose that **18** has the structure shown in Scheme 3.

Compound **15** in THF was added to $[Pt(COD)I_2]$ to give a yellow powder $[Zr\{(\eta\text{-}C_5Me_4CH_2PMe_2)_2Cl_2\}PtI_2]$ (**19**) in 45% yield. Compound **19** is poorly soluble in common solvents and decomposed on exposure to air.

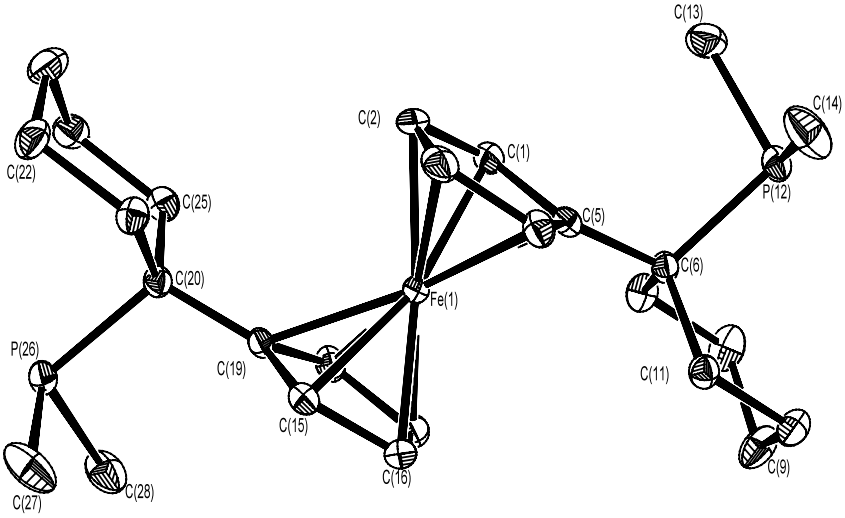


Fig. 3. Molecular structure of **11**.

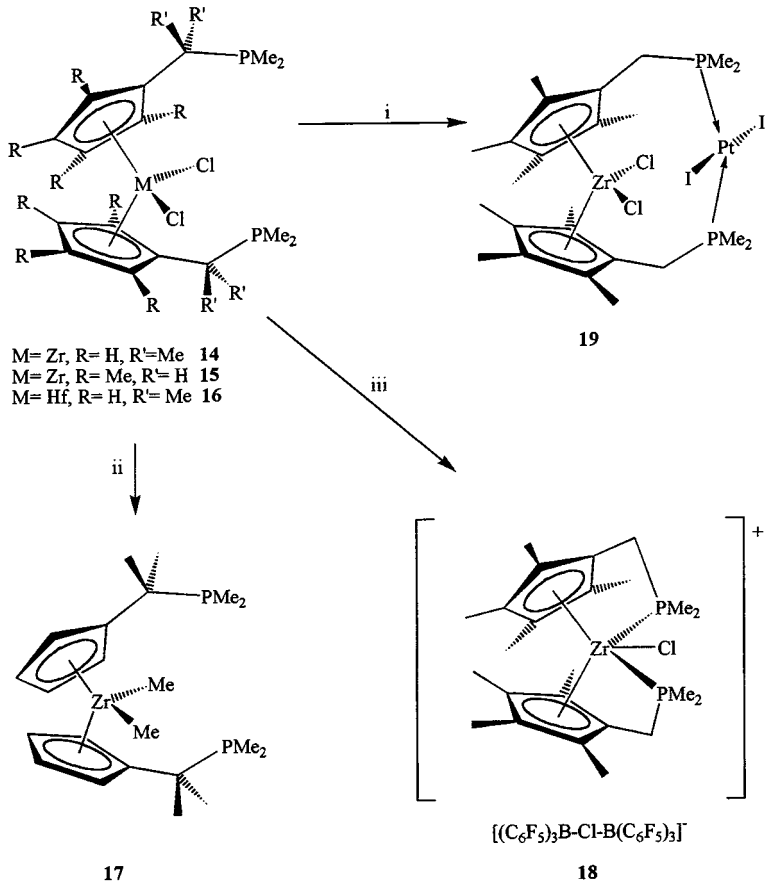
Table 4
Selected bond lengths (Å) and bond angles (°) for **11**

Bond lengths	
Fe(1)–C(1)	2.046(2)
C(5)–C(6)	1.503(3)
C(6)–P(12)	1.904(2)
P(12)–C(14)	1.838(3)
Bond angles	
C(16)–Fe(1)–C(2)	163.57(10)
C(6)–C(5)–Fe(1)	130.60(14)
C(5)–C(6)–P(12)	110.49(14)
C(14)–P(12)–C(6)	102.70(10)

The ^{31}P-NMR spectrum shows a band at δ −12.0 which shows sidebands assignable to ^{195}Pt satellites ($J_{P-Pt} = 2304$ Hz). This suggests that both the tertiary phosphine groups are coordinated to the platinum nucleus. Supporting the formulation of **19** as a bimetallic complex is the positive mode fast atom bombardment (FAB) mass spectrum which displays a signal at m/z 747 with the correct isotope pattern for the $[M^+ - 2I]$ fragment. The magnitude of J_{P-Pt} corresponds to *trans*-arrangement of phosphine groups around the platinum centre given that the *cis*-isomers are normally of the magnitude of 3500 Hz [25,30,31]. We note that Erker and coworkers [3] have reported that the compounds $[Zr(\eta\text{-}C_5H_4CMe_2PAr_2)_2Cl_2]$ (Ar = phenyl, *p*-tolyl) can act as chelating diphosphine ligands.

A THF solution of compound **2** was added to manganese dichloride ($MnCl_2$) at −78 °C to give the compound $[Mn(\eta\text{-}C_5Me_4CH_2PMe_2)_2]$ (**20**) as cubic, red–orange crystals which decomposed. The ^{31}P-NMR spectrum showed a singlet due to the tertiary phosphine group at δ −210.0, which is a relatively high-field chemical shift. However, compound **20** is not diamagnetic. The ^{1}H-NMR spectrum of **20** exhibits the expected number of signals with appropriate integrals. The signal at δ 4.96 can be assigned to the phosphinodimethyl hydrogens, with further signals at δ −2.51, −4.21 and −11.29 assigned to the two pairs of C_5-methyl groups and to the backbone CH_2 hydrogens, respectively.

The crystal structure of **20** has been determined and the molecular structure is shown in Fig. 4. The η-cyclopentadienyl rings adopt a parallel, staggered conformation such that the pendant dimethylphosphinomethyl groups are as far away from each other as possible. The view afforded by Fig. 4b demonstrates that both PMe_2 groups point up and away from the manganese centre so as to minimise steric interaction.



Scheme 3. (i) In THF at −78 °C, add $[PtI_2(COD)]$, 30%. (ii) In Et_2O at 0 °C, add MeLi, 32%. (iii) In toluene-d_8, add two equivalents $[B(C_6F_5)_3]$.

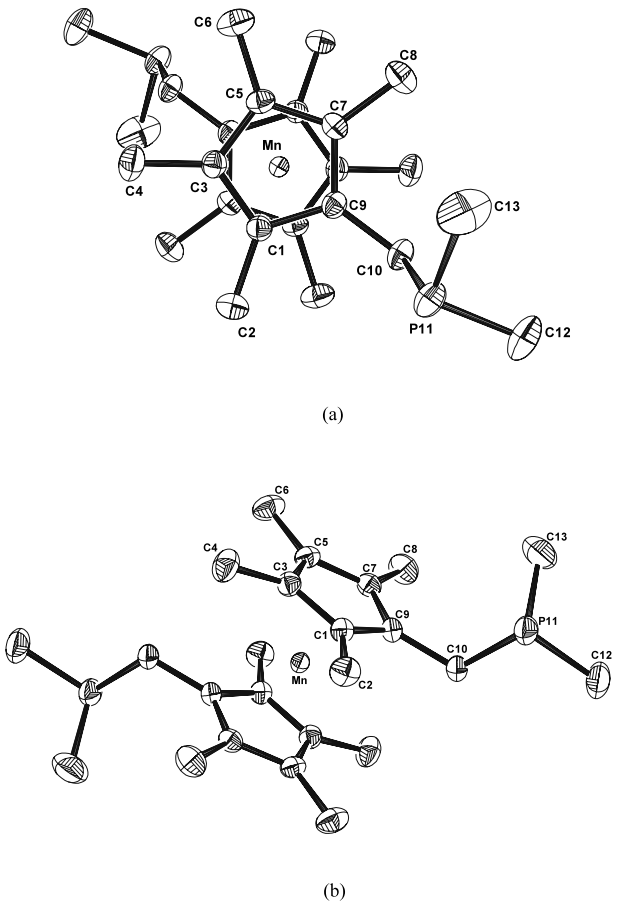


Fig. 4. Molecular structure of **20**: (a) view along the Cp–Mn–Cp axis; (b) a side-on view.

Selected Mn–C_{ring} bond lengths and angles for **20** are listed in Table 5. The Mn–C distances found for **20** broadly agree with the Mn–C bond lengths found for low-spin [Mn(η-$C_5Me_5)_2$], with values in the range of 2.092(2)–2.127(2) Å (see Table 6). Taken on their own, these bond length data could suggest that **20** has a low-spin, $^2E_{2g}$ character.

Substituted manganocene complexes exhibit several electronic states and spin equilibria [32–41]. The magnetic susceptibility of **20** in a toluene solution as a function of temperature has been determined using the Evans' NMR method [42,43]. An effective magnetic moment (298 K) of 2.64 BM was found. This value is higher than that expected for a system with one unpaired electron (1.73 BM) [41]. Thus, compound **20** has a predominantly low-spin character as suggested by the similarity of bond length data to those of [Mn(η-$C_5Me_5)_2$], but also contains a contribution from the

Table 5
Selected bond lengths (Å) and bond angles (°) for **20**

Bond lengths	
Mn–C(1)	2.099(2)
Mn–C(3)	2.120(2)
Mn–C(5)	2.127(2)
Mn–C(7)	2.105(2)
Mn–C(9)	2.092(2)
Mn–$C_{centroid}$	1.725
Bond angles	
C(1)–Mn–C(1)	180.0
C(1)–C(7)–C(9)	107.9(2)
$C_{centroid}$–Mn–$C_{centroid}$	180.0

Table 6
Comparison between Mn–C bond lengths in structurally characterised manganocenes and their electronic spin state

Compound	Selected Mn–C bond lengths [a] (Å)	Spin state	Reference
[Mn(η-$C_5Me_5)_2$]	2.105(2)	$^2E_{2g}$	[37]
[Mn(η-$C_5^iPr_4H)_2$]	2.450(5)	$^6A_{1g}$	[38]
[Mn(η-$C_5Me_4H)_2$]	–	$^2E_{2g}$	[39]
[Mn(η-$MeC_5H_4)_2$]	2.114(12) and 2.433(8)	$^2E_{2g}\leftrightarrow{}^6A_{1g}$	[40]
[Mn(η-$C_5H_5)_2$]	2.380(6)	$^6A_{1g}$	[40]
[Mn(η-$C_5^iPr_3H_2)_2$]	2.131(3)	$^2E_{2g}$	[40]
[Mn(η-$C_5^tBu_3H_2)_2$]	–	$^6A_{1g}$	[41]
[Mn(η-$C_5^iPrMe_4)_2$]	–	$^2E_{2g}$	[41]
[Mn(η-$C_5^iPr_3Me_2)_2$]	–	$^2E_{2g}\leftrightarrow{}^6A_{1g}$	[41]

[a] For [Mn(η-$C_5Me_4CH_2PMe_2)_2$], Mn–C-ring = 2.092(2)–2.127(2) Å.

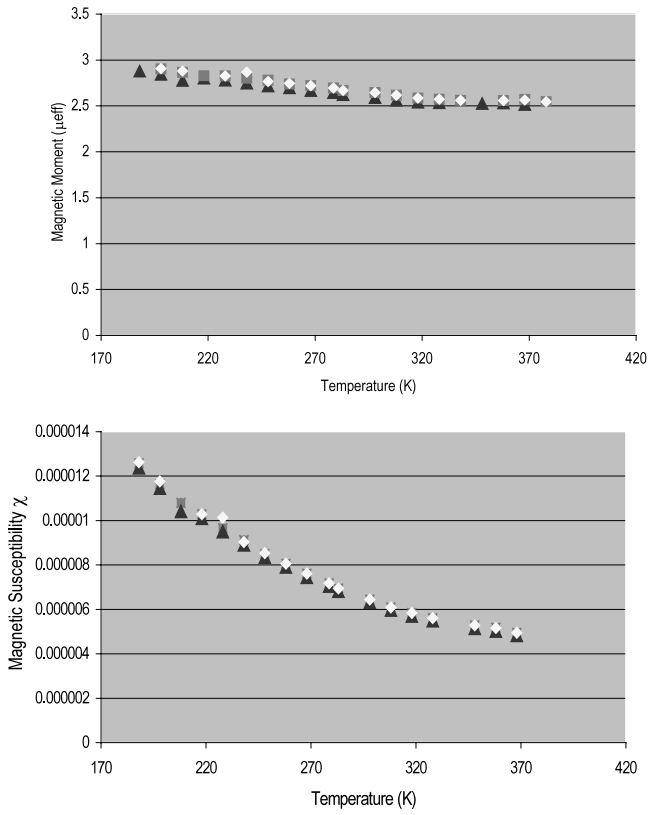


Fig. 5. (a) Variation of effective magnetic moment of **20** in toluene with temperature. (b) Variation of magnetic susceptibility χ of **20** in toluene with temperature.

high-spin $^6A_{1g}$ configuration. Fig. 5a shows the plot of effective magnetic moment (μ_{eff}) versus temperature (T). The graph shows a slight decrease in μ_{eff} with increasing temperature levelling off at around 2.5 BM. In addition, a plot of magnetic susceptibility versus temperature, shown in Fig. 5b, exhibits behaviour typical of a normal paramagnetic species where $\chi \propto 1/T$ [41].

Treatment of **20** with two equivalents of the Lewis acid $[B(C_6F_5)_3]$ gave the compound $[Mn\{\eta\text{-}C_5Me_4CH_2PMe_2B(C_6F_5)_3\}_2]$ (**21**) as an orange powder in quantitative yield. This compound is relatively stable in air but poorly soluble in common solvents. The low solubility of the complex precluded solution NMR studies and the sole characterising data for **21** is the microanalysis and the FAB mass spectrum. The latter shows a peak at m/z 1469 with the correct isotope pattern, which corresponds to the molecular ion $[M^+]$. Further signals at m/z 957 and 445 are attributable to fragments. The new manganocenes are shown in Scheme 4.

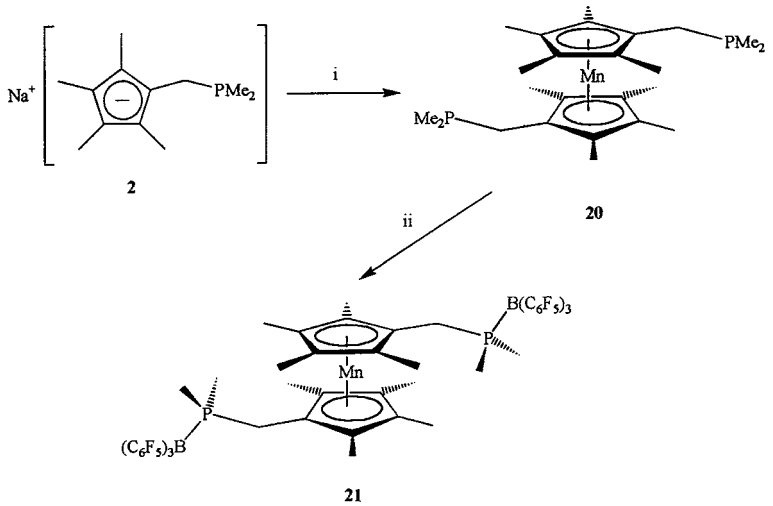
Addition of compound **20** in THF to $[Pt(COD)I_2]$ gave an orange powder in 45% yield. The microanalysis corresponds to the formulation $[Mn(\eta\text{-}C_5Me_4CH_2PMe_2)_2PtI_2]_n$ (**22**). Compound **22** appears relatively stable in air but insoluble in all common solvents. The evidence does not permit distinction between a mono- ($n = 1$) or poly-molecular ($n = 2$ or more) structure for compound **22**.

In the absence of light, a mixture of $PbCl_2$ and $[Li(C_5H_4CMe_2PMe_2)]$ in THF was stirred at -78 °C to give orange microcrystals of stoichiometry corresponding to $[Pb(\eta\text{-}C_5H_4CMe_2PMe_2)_2]$ (**23**) in 78% yield. Compound **23** is moderately stable towards light in the solid state but solutions in pentane show signs of decomposition within a few minutes.

The $^{31}P\{^1H\}$-NMR spectrum shows coupling to the ^{207}Pb nuclei ($I = 1/2$, 22.6% abundance) with a value of $J = 276$ Hz indicative of a $^3J_{P-Pb}$ or $^4J_{P-Pb}$ coupling and these are about one tenth the size of direct lead–phosphorus couplings found in tertiary phosphine–lead complexes [44]. This suggests the P atom is not directly bonded to the lead centre. An HMQC 2D-correlation experiment was carried out in order to assist in the assignment of the ^{13}C- and ^1H-NMR spectra.

The tin compound $[Sn(\eta\text{-}C_5H_4CMe_2PMe_2)_2]$ (**24**) was prepared in a similar manner to **23** and was isolated as a fine yellow powder, in 70% yield. The compound **24** at room temperature decomposes in the light both in the solid state and in pentane solution. The $^{31}P\{^1H\}$-NMR spectrum of **24** is diagnostic of the formation of a stannocene given that the signal at δ -21.4 is accompanied by ^{119}Sn and ^{117}Sn satellites ($I = 1/2$, 8.58 and 7.61% abundance, respectively). Resolution of the two sets of satellites was not possible. The coupling-value, $^3J_{P-Sn} = 111$ Hz, is similar with other $^3J_{P-Sn}$ values reported [44–47]. An HMQC 2D-correlation spectrum assisted the assignment of the ^{13}C- and ^1H-NMR spectra. The $^{119}Sn\{^1H\}$-NMR spectrum of **24** in toluene-d_8 at 298 K shows a binomial triplet at δ -2163 ($^3J_{Sn-P} = 110$ Hz) referenced to $SnMe_4$ (δ 0), which compares favourably with the chemical shifts recorded for other metallocenes of Sn(II) [45,48–51]. The coupling value for $^3J_{Sn-P}$ is consistent with that found in the $^{31}P\{^1H\}$-NMR spectrum and confirms that the pendant tertiary phosphine groups are not directly attached to the Sn(II) centre.

Addition of a $[B(C_6F_5)_3]$ solution in toluene to **23** gave a compound with a stoichiometry corresponding to $[Pb\{\eta\text{-}C_5H_4CMe_2PMe_2B(C_6F_5)_3\}_2]$ (**25**) as a yellow powder, in quantitative yield. It decomposes in air and is soluble in polar solvents. The ^1H- and ^{13}C-NMR spectra of **25** in pyridine-d_5, are similar to that obtained for the parent plumbocene. The $^{31}P\{^1H\}$-NMR spectrum displays a singlet at δ -11, which is a downfield



Scheme 4. (i) Anhydrous $MnCl_2$ in THF at -78 °C, 66%. (ii) $[B(C_6F_5)_3]$ in toluene at room temperature, for 12 h, 63%.

shift of approximately 5 ppm from that of the parent complex **23**. In addition, the three-bond P–Pb coupling is no longer evident. This is likely to be a result of the interaction between the ^{11}B nucleus and the P-group. The $^{11}B\{^1H\}$ spectrum displays a doublet at δ 0.65 ($J_{B-P} = 70.5$ Hz) typical of a neutral, tetracoordinate boron species which is well within the realms of PR_3–borane coupling constants [52,53].

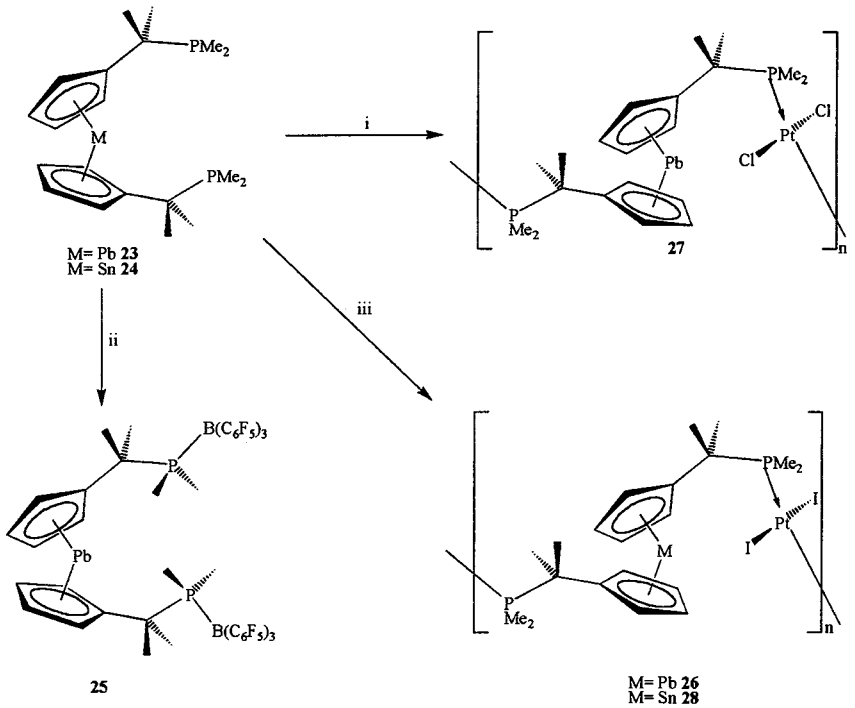
The compound $[PtI_2(COD)]$ in THF was treated with compound **23** in THF at room temperature giving an air-sensitive orange powder of stoichiometry $[Pb(\eta\text{-}C_5H_4CMe_2PMe_2)_2PtI_2]_n$ (**26**), in 50% yield. Compound **26** is an air-sensitive orange solid, which is sparingly soluble in THF. The FAB mass spectrum (NOBA matrix) of compound **26** contains two peaks and although the signal due to the molecular ion ($m/z = 990$) is not present, signals at $m/z = 863$ [M − I] and $m/z = 736$ [M − 2I] with the correct isotope patterns are observed. Complex **26** exhibits a $^{31}P\{^1H\}$-NMR resonance at δ −4.7, which is shifted upfield by about 11 ppm from the parent compound **23** and the ^{195}Pt isotope ($I = 1/2$, 33.7% relative abundance) accounts for a splitting due to the ^{31}P–^{195}Pt coupling. The data do not allow distinction between a monomolecular bimetallic structure and a bi- or poly-nuclear structure (see Scheme 5). Oligomeric structures of similar compounds have been reported by Graham and Erker [3,17,26,54].

Addition of $[Pd(COD)Cl_2]$ in THF to **23** gave yellow–orange $[Pb(\eta\text{-}C_5H_4CMe_2PMe_2)_2PdCl_2]_n$ (**27**) which is only sparingly soluble in THF. The $^{31}P\{^1H\}$-NMR spectrum (THF-d_8, 298 K) showed two peaks indicating that some ligand dissociation may be occurring or both *cis*- and *trans*-isomers may be present.

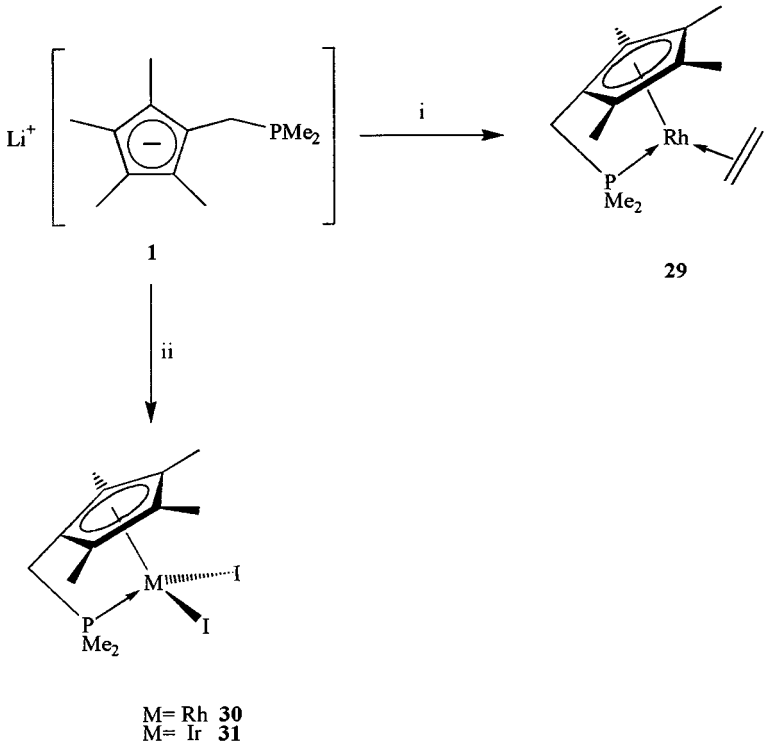
Treatment of $[PtI_2(COD)]$ in THF with **24** in THF at room temperature gave an orange compound with a stoichiometry corresponding to $[Sn(\eta\text{-}C_5H_4CMe_2\text{-}PMe_2)_2PtI_2]_n$ (**28**) in 60% yield. Low solubility precluded NMR studies.

Treatment of the rhodium ethylene chloride dimer $[Rh(C_2H_4)_2Cl]_2$ with one equivalent of $[Li(C_5Me_4CH_2\text{-}PMe_2)]$ (**1**) gave $[Rh(\eta,\kappa P\text{-}C_5Me_4CH_2PMe_2)(C_2H_4)]$ (**29**) that was isolated as a dark yellow solid in 40% yield. The ^{31}P-NMR spectrum in benzene-d_6 shows a doublet at δ −29.6 ($J_{Rh-P} = 198.4$ Hz). Complex **29** was oxidised with iodine leading to a brown microcrystalline product $[Rh(\eta,\kappa P\text{-}C_5Me_4CH_2PMe_2)I_2]$ (**30**). The ^{31}P resonance appears as a doublet at δ −25.2 with $J_{Rh-P} = 136.6$ Hz. The reaction of the ligand precursor **1** with the iridium cyclooctene chloride dimer $[Ir(\text{-}COE)_2Cl]_2$ gave a dark brown solid and this was treated with one equivalent of iodine. $[Ir(\eta,\kappa P\text{-}C_5Me_4CH_2\text{-}PMe_2)I_2]$ (**31**) was obtained in 38% yield as a brown microcrystalline solid. The ^{31}P resonance of complex **31** in CD_2Cl_2 is observed at δ −27.5. The structures proposed for **29**–**31** are shown in Scheme 6.

The rhodium and iridium derivatives described above are not stable for long periods in solution. After two days very shielded resonances appear in the ^{31}P-NMR spectra at δ −166 and −160 for the solutions of **30** and **31**, respectively. Simultaneously, the ^1H-NMR



Scheme 5. (i) M = Pb: $[PdCl_2(COD)]$ in THF at room temperature, for 12 h, 32%. (ii) $[B(C_6F_5)_3]$ in toluene at room temperature, for 12 h, 50%. (iii) $[PtI_2(COD)]$ in THF at room temperature, for 12 h, 36% (**26**) and 32% (**28**).



Scheme 6. (i) $[Rh(C_2H_4)_2Cl]_2$ in THF at 0 °C, for 6 h, 40%. (ii) For M = Rh (**30**): $[Rh(C_2H_4)_2Cl]_2$ in THF at 0 °C, for 6 h; then I_2 in toluene at room temperature, for 4 h, 52%. For M = Ir (**31**): $[Ir(COE)_2Cl]_2$ in THF at 0 °C, for 8 h; then I_2 in toluene at room temperature, for 4 h, 43%.

spectra show the broadening of all the signals and the appearance of new resonances in the range δ 1.3–2.0.

3. Experimental

All manipulations of air- and/or moisture-sensitive materials were performed under an inert atmosphere of pure argon or dry dinitrogen using standard Schlenk line techniques or in an inert atmosphere dry box containing dinitrogen. Inert gases were purified firstly by passage through columns filled with activated molecular sieves (4 Å) and then either manganese(II) oxide suspended on vermiculite, for the Schlenk line, or BASF catalyst, for the dry box. Celite® filtration aid was purchased from Fluka Chemie and oven-dried at 150 °C prior to use. Filtrations were generally performed using modified stainless steel cannulae, which had been fitted with glass fibre filter discs. All glassware and cannulae were dried overnight at 150 °C before use.

Solvents were pre-dried over activated 4 Å molecular sieves and then distilled from Na–K alloy (light petroleum ether (b.p. 40–60 °C), Et_2O, pentane and DME), from Na (petroleum ether (b.p. 100–120 °C) and toluene), from K (THF), P_2O_5 (MeOH) or from CaH_2 (CH_2Cl_2), under a slow continuous stream of dinitrogen. Glassware was thoroughly degassed by the pump–fill technique followed by re-admission of dinitrogen or by purging with dinitrogen for ca. 15 min prior to use. Solvents and solutions were transferred, using a positive pressure of nitrogen, through stainless-steel cannulae (diameter 0.5–2.0 mm) and mixtures were filtered in a similar way using modified cannulae which could be fitted with glass-fibre filter discs (Whatman GF/C). Deuterated NMR solvents (Aldrich, Goss Scientific) were refluxed and distilled from potassium metal (benzene-d_6, toluene-d_8, THF-d_8), from CaH_2 (CD_2Cl_2 and pyridine-d_5) or from $MgSO_4$ (acetone-d_6), distilled, degassed by the freeze–pump–thaw technique prior to use and stored in Young's ampoules under argon. D_2O was degassed by purging with argon for approximately 15 min prior to use. NMR solvents were transferred using a teat pipette in an inert atmosphere dry box, or by vacuum distillation using an all-glass apparatus.

The compounds $MnCl_2$, $TiCl_4$, NH_4PF_6, $KN(SiMe_3)_2$, $NaN(SiMe_3)_2$, $ZnMe_2$ (2.0 M solution in hexanes), Li^{t}Bu (1.7 M solution in pentane), Li^{n}Bu (2.5 M solution in light petroleum ether (b.p. 40–60 °C)), LiMe (1.6 M solution in Et_2O), HCl (1.0 M solution in Et_2O), naphthalene (C_8H_{10}) and CH_3I, were purchased from Aldrich Chemical Company and used without further purification. 1,2,3,4-Tetramethylcyclopent-2-enone was purchased from Aldrich and distilled before use. $ZrCl_4$ and $HfCl_4$ were purchased from Aldrich and sublimed prior to use. $LiN(SiMe_3)_2$ was purchased from Aldrich and was recrystallised from THF before use.

Trimethylphosphine (PMe_3) [55], $ZrCl_4(THF)_2$ and $HfCl_4(THF)_2$ [56], tetramethyl dithiodiphosphane [57a], dimethylphosphine [57b], tetramethylcyclopentenone [58–61], 1,2,3,4-tetramethylfulvene [61], 6,6-dimethylfulvene and 6,6-pentamethylenefulvene [62], $[Rh(C_2H_4)_2Cl]_2$ [63] and $[Ir(COE)_2Cl]_2$ [64], were prepared as described.

Solution NMR spectra were recorded using either a Varian Mercury 300 (^{1}H 300 MHz, ^{13}C 75.5 MHz, ^{19}F 282.3 MHz, ^{31}P 121.6 MHz, ^{119}Sn 111.9 MHz and ^{207}Pb 62.7 MHz) or a Varian UNITYplus (^{1}H 500 MHz, ^{11}B 160.4 MHz, ^{13}C 125.7 MHz, ^{31}P 202.4 MHz) spectrometer and are at room temperature (r.t.) unless otherwise stated. The spectra were referenced internally relative to the residual protio-solvent (^{1}H) and solvent (^{13}C) resonances relative to Me_4Si (^{1}H, ^{13}C, $\delta = 0$) or externally to $BF_3{\cdot}Et_2O$ (^{11}B, $\delta = 0$); 85% H_3PO_3 (^{31}P, $\delta = 0$); $SnMe_4$ (^{119}Sn, $\delta = 0$); $PbOAc_4$ (^{207}Pb, $\delta = -2675$) or $CFCl_3$ (^{19}F, $\delta = 0$). Chemical shifts (δ) are expressed in ppm and coupling constants (J) in Hz.

Electrospray mass spectra were recorded using a Micromass LC TOF electrospray ionisation mass spectrometer. FAB mass spectrometry was performed by the EPSRC Mass Spectrometry Service at Swansea. Elemental analyses were performed by the Microanalytical Department of the Inorganic Chemistry Laboratory, Oxford.

3.1. Synthesis of $[Li(C_5Me_4CH_2PMe_2)]$ (1)

3.1.1. Method A

1,2,3,4-Tetramethylfulvene (1.4 g, 10.45 mmol) in THF (50 ml) was added to $LiPMe_2{\cdot}0.22Et_2O$, (1.02 g, 10.45 mmol) in THF (50 ml) stirred with a glass encased magnetic stir bar at -78 °C. The red solution of the fulvene instantly changes colour upon contact with the other reagent. The solution was allowed to warm gradually to r.t. overnight. The solvent was removed under vacuum and the pale green product washed with three portions of Et_2O and thoroughly dried in vacuo, to yield 1.4g (64%) of a white pyrophoric solid, which was shown to have no THF coordinated to it by NMR spectroscopy. On scaling up, the same reaction product needed recrystallising from THF.

3.1.2. Method B

To a stirred THF solution (25 ml) of $[HC_5Me_4CH_2PMe_2]$ (**8**) (0.80 g, 4.0 mmol) at -78 °C was added via a cannula, a THF solution (25 ml) of $LiN(SiMe_3)_2$ (0.63 g, 4.1 mmol). The solution was allowed to warm to r.t. and stirred for 12 h. The solvent was removed under reduced pressure from the resulting yellow solution. The off-white product was washed with pentane (2×10 ml) and isolated by filtration. After the residual solvent was removed under reduced pressure compound **1** was obtained as a pyrophoric, white powder. Yield: 0.60 g (74%).

3.2. Synthesis of $[Na(C_5Me_4CH_2PMe_2)]$ (2)

To a THF (25 ml) solution of **8** (1.34 g, 6.2 mmol) at -78 °C was added via a cannula, a THF solution (25 ml) of $NaN(SiMe_3)_2$ (1.05 g, 6.2 mmol). The solution was allowed to warm to r.t. and stirred for 12 h. The solvent was removed under reduced pressure from the resulting yellow solution. The off-white product was washed with pentane (2×10 ml) and isolated by filtration. After the residual solvent was removed under reduced pressure compound **2** was obtained as a pyrophoric, white powder. Yield: 1.19 g, (87%).

3.3. Synthesis of $[K(C_5Me_4CH_2PMe_2)]$ (3)

To a THF solution (25 ml) of **8** (1.00 g, 5.1 mmol) at -78 °C was added via a cannula, a THF solution (25 ml) of $KN(SiMe_3)_2$ (1.03 g, 5.1 mmol). The solution was allowed to warm to r.t. and stirred for 12 h. The solvent was removed under reduced pressure from the resulting yellow solution. The off-white product was washed with pentane (2×10 ml) and isolated by filtration. After the residual solvent was removed under reduced pressure compound **3** was obtained as a pyrophoric, white powder. Yield: 0.95 g, (79%).

3.4. Synthesis of $[Li(C_5H_4CMe_2PMe_2)]$ (4)

To a stirred solution of $LiPMe_2{\cdot}0.22Et_2O$ (3.58 g, 43 mmol) in THF (40 ml) at -78 °C was added dropwise a THF solution of 6,6-dimethylfulvene (5.42 g, 51 mmol) and the reaction mixture left to stir overnight after slowly warming to r.t. The solvent was then removed from the yellow solution under reduced pressure affording a sticky yellow solid. The product was triturated and then washed with pentane (3×15 ml) and filtration of the supernatant followed by removal of residual volatiles under reduced pressure yielded the compound $[Li(C_5H_4CMe_2PMe_2)]$ (**4**) as a fine, white powder. Yield: 4.7g (63%).

3.5. Synthesis of $[Li\{C_5H_4C(CH_2)_5PMe_2\}]$ (5)

The compound $LiPMe_2{\cdot}0.22Et_2O$ (100 mg, 1.2 mmol) was suspended in THF and cooled to -78 °C. A solution of 6,6-pentamethylenefulvene (176 mg, 1.2 mmol) in THF was slowly added with stirring. The resulting pale yellow solution was allowed to warm to r.t. overnight. All volatiles were removed in vacuo to yield a very sticky yellow material. Washing with a pentane–Et_2O mixture and trituration converts this into a free-flowing white powder. Yield: 40%.

3.6. Synthesis of $[HC_5Me_4CH_2PMe_2H][Cl]$ (6)

To a yellow solution of $LiCH_2PMe_2$ (3.12 g, 38 mmol) in THF (125 ml) at −78 °C was added dropwise via a cannula, a THF solution (75 ml) of tetramethylcyclopent-2-enone (5.25 g, 38 mmol). The resulting yellow solution was allowed to warm to r.t. and was stirred for a further 12 h. Upon further cooling to −78 °C, a 1.0 M solution of HCl in Et_2O (79.8 ml, 2.1 equivalents) was added over 2.5 h and formation of a white precipitate ensued. The mixture was then stirred for 2 h and the white solid isolated on a glass frit after transfer via a wide bore Teflon cannula. The product was washed with THF (2 × 20 ml) and pentane (2 × 30 ml) before residual solvent was removed under reduced pressure to yield compound **6** as a white powder. Crude yield: 7.2 g (80%).

3.7. Synthesis of $[HC_5Me_4CH_2PMe_2H][PF_6]$ (7)

To a pale yellow solution of **6** (12.19 g, 52 mmol) in degassed H_2O (50 ml) at r.t. was added via cannula a solution of NH_4PF_6 (10.24 g, 57 mmol) in degassed H_2O (50 ml) with the immediate precipitation of a white solid. The product was transferred to a glass frit and filtered then washed with degassed H_2O (2 × 30 ml). Residual water was removed from the resulting white solid under reduced pressure to yield compound **7** as a white powder. Yield: 15.1 g (85%).

3.8. Synthesis of $[HC_5Me_4CH_2PMe_2]$ (8)

3.8.1. Method A

To a suspension of **7** (13.81 g, 40 mmol) in MeOH (50 ml) was added a solution of KOH (2.25 g, 40 mmol) in MeOH (20 ml). The suspension changed to a cloudy solution with the concomitant evolution of a phosphine odour. Pentane (50 ml) was added to the solution, which was stirred for 10 min. On separation of the two layers, the top pentane layer was transferred via a cannula into a Schlenk vessel containing $MgSO_4$ (3.0 g) and the suspension stirred. The suspension was then filtered into a clean Schlenk vessel to yield a colourless solution from which solvent was removed under reduced pressure. Compound **8** was isolated as a very pale yellow oil. Yield: 3.50 g (45%).

3.8.2. Method B

The compound $[HC_5Me_4CH_2PMe_2H][PF_6]$, (**7**) (170 mg, 0.5 mmol) was suspended in degassed water (50 ml) and KOH (100 mg, 1.7 mmol) was added. The liquid was stirred under nitrogen for 10 min, and then pentane (20 ml) was added with stirring. The two phases were allowed to separate and then the organic layer was carefully decanted into another flask via a cannula. This process was repeated three times, and then the combined organic fractions were dried under vacuum leaving a very air sensitive, pale yellow oil. Yield: 79%.

3.9. Synthesis of $[Fe(\eta\text{-}C_5Me_4CH_2PMe_2)_2]$ (9)

The salt **1** (1.0 g, 5 mmol) and anhydrous $FeCl_2$ (320 mg, 2.5 mmol) were placed in a Schlenk vessel and THF was added at −78 °C. The mixture was allowed to warm to r.t. overnight to give a dark brown solution. The solvent was removed in vacuo and the brown residue was extracted three times with pentane. Concentration and crystallisation at −78 °C yielded orange blocks. Yield: 45–49%. The product, occasionally contaminated with a dark, tarry substance, could be further purified by vacuum sublimation, filtration through silica gel or further recrystallisation. Crystals of **9** suitable for X-ray diffraction were grown by dissolving a small amount in ca. 2 ml of benzene and allowing the solvent to slowly evaporate under a very slow stream of nitrogen gas.

3.10. Synthesis of $[Fe(\eta\text{-}C_5H_4CMe_2PMe_2)_2]$ (10)

A solution of **4** (280 mg, 1.6 mmol) in THF was treated with anhydrous $FeCl_2$ (100 mg, 0.8 mmol) in THF at −78 °C. The orange coloured reaction mixture was left to stir for 3 h during which time it was allowed to warm to r.t. All volatiles were then removed under vacuum and the residue extracted with pentane to yield an orange crystalline solid. Yield: 130 mg (21%).

3.11. Synthesis of $[Fe\{\eta\text{-}C_5H_4C(CH_2)_5PMe_2\}_2]$ (11)

A solution of $[LiC_5H_4C(CH_2)_5PMe_2]$ (**5**) in THF was made up by treating 6,6-pentamethylenefulvene (350 mg, 2.4 mmol) with $LiPMe_2{\cdot}0.22Et_2O$ (200 mg, 2.4 mmol). Anhydrous $FeCl_2$ (1.2 mmol, 150 mg, half an equivalent) was suspended in THF and added as a slurry to the solution of the lithium salt. The yellow solution turned cloudy with $FeCl_2$ crystals, and the reaction could be monitored by the dissolution of the particulates and concomitant formation of an orange tint. After 3 h the reaction was deemed to be complete and all volatiles were removed under vacuum, the residue extracted with pentane and then dried under vacuum. Analytically pure crystals could be grown by crystallisation at −20 °C in a minimum amount of Et_2O. Yield: 100 mg first crop, 50 mg second crop (10% first crop, 5% second crop).

3.12. Synthesis of $[Fe(\eta\text{-}C_5H_4CMe_2PMe_3)_2I_2]$ (12)

A pentane solution of **10** (40 mg, 0.1 mmol) was treated with a large excess of MeI (0.5 ml, ca. 1.5 mmol) and the mixture was stirred for 5 h. A flocculent

pale yellow precipitate formed, which was found to be the title compound, in almost quantitative yield. Recrystallisation from MeOH at −78 °C yielded analytically pure microcrystals of **12**.

3.13. Synthesis of [Fe(η-$C_5Me_4CH_2P(O)Me_2)_2$] (13)

A sample of **9** in benzene-d_6 in an NMR tube was opened to air and left to evaporate for 2 days. Orange crystals of the bisphosphine oxide derivative **13** were formed, and they were found to be suitable for an X-ray structural investigation.

3.14. Synthesis of [Zr(η-$C_5H_4CMe_2PMe_2)_2Cl_2$] (14)

Compound **4** (1.74 g, 10 mmol) and $ZrCl_4$ (1.16 g, 5 mmol) were suspended in toluene in two separate Schlenk vessels. The suspension of the lithium salt was added to the other at −78 °C with stirring and allowed to warm overnight to r.t. A light brown flocculent solid formed with a red supernatant solution. The solvent was removed in vacuo, the residue was extracted with CH_2Cl_2 until the solution was colourless and filtered through Celite to remove any suspended LiCl. A pale yellow solid formed which could be purified by overnight recrystallisation at −20 °C from CH_2Cl_2 to yield 1.25 g (2.53 mmol, 50%) of the desired product. Note that the product is not stable for long periods in CH_2Cl_2.

3.15. Synthesis of [Zr(η-$C_5Me_4CH_2PMe_2)_2Cl_2$] (15)

To a stirred THF solution (25 ml) of $ZrCl_4(THF)_2$ (259 mg, 0.69 mmol) at 0 °C was added dropwise a solution of **2** (306 mg, 1.40 mmol) in THF (20 ml). The colour changed from pale yellow to orange before reverting to yellow again on warming to r.t. The yellow solution was then stirred for 12 h. The solvent was removed under reduced pressure and the yellow solid triturated with pentane (2 × 10 ml) then extracted into dichloromethane (2 × 20 ml). The solvent was removed from the resulting yellow solution under reduced pressure to yield compound **15** as pale yellow microcrystals. Yield: 267 mg (70%).

3.16. Synthesis of [Hf(η-$C_5H_4CMe_2PMe_2)_2Cl_2$] (16)

The lithium salt **4** (350 mg, 2 mmol) and $HfCl_4(THF)_2$ (465 mg, 1 mmol) were each loaded into separate Schlenk vessels and suspended in cold (−78 °C) THF. The suspension of the lithium salt was then added to the other with stirring and allowed to warm to r.t. overnight. The resulting yellow–green solution was pumped down under vacuum, and the residue taken up in CH_2Cl_2. The resulting suspension was filtered through Celite. The filtrate was concentrated and cooled to −80 °C. Yield: 170 mg (30%).

3.17. Synthesis of [Zr(η-$C_5H_4CMe_2PMe_2)_2Me_2$] (17)

A suspension of **15** (992 mg, 2 mmol) in Et_2O was treated with LiMe (1.4 M in Et_2O, 2.86 ml, 4 mmol) at −78 °C and allowed to warm to r.t. The resulting yellow suspension was filtered through Celite and washed through with Et_2O. All volatiles were removed under vacuum and the residue was washed with a small amount of petroleum ether (b.p. 40–60 °C). Yield: 300 mg (32%).

3.18. Synthesis of {[Zr(η-$C_5Me_4CH_2PMe_2)_2$]Cl}-{$(C_6F_5)_3BClB(C_6F_5)_3$} (18)

To a Young's tap NMR tube was added a toluene-d_8 solution of compound **15** (10.0 mg, 0.018 mmol) and two equivalents of $B(C_6F_5)_3$ (18.5 mg, 0.036 mmol). This compound was characterised by NMR only.

3.19. Synthesis of [Zr(η-$C_5Me_4CH_2PMe_2)_2Cl_2PtI_2$] (19)

To a Schlenk vessel containing stirred THF (25 ml) at −78 °C were simultaneously added dropwise via two cannulae, solutions of **15** (100 mg, 0.18 mmol) and PtI_2(COD) (105 mg,0.18 mmol) in THF (25 ml each) over 30 min. The resulting orange solution was stirred at r.t. for 1 h after which time a pale orange precipitate began to form. The solution was filtered and solvent was removed under reduced pressure. The resulting red–orange solid was triturated with pentane (10 ml), solvent was removed under reduced pressure and compound **19** was isolated as an orange solid. Yield: 53 mg (30%).

3.20. Synthesis of [Mn(η-$C_5Me_4CH_2PMe_2)_2$] (20)

To a stirred solution of **2** (1.0 g, 4.6 mmol) in THF (30 ml) at −78 °C was added via a solid addition Schlenk vessel, $MnCl_2$ (289 mg, 2.3 mmol). The mixture was slowly warmed to 40 °C using a water bath and maintained at that temperature for 1 h. The resulting orange solution was stirred for a further 12 h, cooling slowly to r.t. Solvent was removed under reduced pressure and the oily, orange product triturated with pentane (30 ml). The orange product was then extracted into pentane (3 × 30 ml) and filtered via a cannula into a Schlenk vessel. The solvent was removed under reduced pressure to leave a concentrated solution (20 ml) which was cooled to 4 °C for 2 days. Compound **20** was isolated as orange, cubic, X-ray quality crystals. Yield: 0.68 g (66%).

3.21. Synthesis of [Mn{η-$C_5Me_4CH_2PMe_2B(C_6F_5)_3$}$_2$] (21)

To a stirred solution of **20** (98 mg, 0.22 mmol) in toluene (50 ml) at r.t. was added via a cannula, a toluene solution (25 ml) of $B(C_6F_5)_3$ (225 mg, 0.44 mmol). The orange solution was stirred for a further 12 h. The solvent was removed from the resulting yellow suspension under reduced pressure and the solid, pale orange–yellow product washed with pentane (30 ml) and residual volatiles were removed under reduced pressure. The compound **21** was isolated as a yellow solid. Yield: 203 mg (63%).

3.22. Synthesis of [Mn(η-$C_5Me_4CH_2PMe_2$)$_2$$PtI_2$] (22)

To a solution of [PtI_2(COD)] (131 mg, 0.22 mmol) in THF (25 ml) at r.t. was added a THF solution of **20** (100 mg, 0.22 mmol) over 60 min. The orange–red mixture was stirred for 2 h after which the solution was filtered and solvent was removed under reduced pressure. The resulting red–orange solid was triturated with pentane (10 ml), remaining volatiles were removed under reduced pressure and the compound **22** was isolated as a red–orange solid. Yield: 86 mg (44%). Microanalysis results for a compound with the empirical formula $C_{24}H_{40}I_2MnP_2Pt$ (MW = 894.36 amu): Found: C, 32.7; H, 4.5; P, 6.8. Calc.: C, 32.2; H, 4.8; P, 6.9%.

3.23. Synthesis of [Pb(η-$C_5H_4CMe_2PMe_2$)$_2$] (23)

To a foil-covered Schlenk vessel containing a mixture of $PbCl_2$ (300 mg, 1.1mmol) and **4** (368 mg, 2.2 mmol) was added THF (30 ml) at −78 °C. The resulting yellow suspension was stirred for 12 h. The orange solution containing a white precipitate was filtered via a cannula to yield a dark yellow solution from which the solvent was removed under reduced pressure. An orange, oily solid resulted. The product was triturated with pentane (10 ml) and the solid then extracted into pentane and stored at −40 °C overnight. Compound **23** was isolated as a microcrystalline, orange solid. Yield: 400 mg (68%).

3.24. Synthesis of [Sn(η-$C_5H_4CMe_2PMe_2$)$_2$] (24)

To a foil-covered Schlenk vessel containing a mixture of $SnCl_2$ (300 mg, 1.6 mmol) and **4** (555 mg, 3.2 mmol) was added THF (20 ml) at −78 °C. The resulting yellow suspension was stirred for 12 h. The dark yellow solution containing a white precipitate was filtered via a cannula to yield a yellow solution from which the solvent was removed under reduced pressure. A yellow, waxy solid was isolated. The product was triturated with pentane (10 ml) and the solid then extracted into pentane and the solvent removed under reduced pressure. Compound **24** was isolated as a waxy, yellow solid and stored at −40 °C in the dark. Yield: 650 mg (91%).

3.25. Synthesis of [Pb{η-$C_5H_4CMe_2PMe_2B(C_6F_5)_3$}$_2$] (25)

A solution of [$B(C_6F_5)_3$] (95 mg, 0.18 mmol) in toluene (25 ml) was added dropwise to a solution of **23** (50 mg, 0.09 mmol) in toluene (25 ml) at r.t. The resulting yellow solution was stirred for 72 h. The solvent was removed under reduced pressure from the yellow solution and the resulting yellow solid washed with pentane (2 × 20 ml). Final removal of volatiles under reduced pressure yielded compound **25** as a yellow powder. Yield: 70 mg (50%).

3.26. Synthesis of [Pb(η-$C_5H_4CMe_2PMe_2$)$_2$$PtI_2$]$_n$ (26)

A yellow solution of [PtI_2(COD)] (83 mg, 0.14 mmol) in THF (30 ml) was slowly added to a solution of **23** (77 mg, 0.14 mmol) in THF (20 ml) at r.t. The resulting yellow solution was stirred for 12 h. Volatiles were removed under reduced pressure from the yellow–orange solution and the yellow solid washed with pentane (2 × 20 ml). Removal of residual pentane under reduced pressure yielded compound **26** as an orange powder. Yield: 50 mg (36%).

3.27. Synthesis of [Pb(η-$C_5H_4CMe_2PMe_2$)$_2$$PdCl_2$]$_n$ (27)

A yellow solution of [$PdCl_2$(COD)] (52 mg, 0.18 mmol) in THF (30 ml) was slowly (10 min) added to an orange solution of **23** (100 mg, 0.18 mmol) in THF (20 ml) at r.t. The resulting orange solution was stirred for 12 h. The solvent was removed under reduced pressure from the yellow–orange solution and the yellow solid washed with pentane (2 × 10 ml). Removal of residual pentane under reduced pressure yielded compound **27** as an orange–yellow powder. Yield: 40 mg (32%). Microanalysis results for a compound with the empirical formula $C_{20}H_{32}Cl_2PbP_2Pd$ (MW = 718.9 amu): Found: C, 33.4; H, 4.5. Calc.: C, 33.4; H, 4.5%. $^{31}P\{^1H\}$-NMR spectrum (pyridine-d_5): δ −3.4 (s), −5.7 (s).

3.28. Synthesis of [Sn(η-$C_5H_4CMe_2PMe_2$)$_2$$PtI_2$]$_n$ (28)

A yellow solution of [PtI_2(COD)] (103 mg, 0.18 mmol) in THF (30 ml) was slowly (10 min) added to an orange solution of **24** (80 mg, 0.18 mmol) in THF (20 ml) at r.t. The resulting orange solution was stirred for 12 h. The solvent was removed under reduced pressure from the yellow–orange solution and the yellow solid washed with pentane (2 × 10 ml). Removal of residual pentane under reduced pressure yielded compound **28**

as an insoluble orange–yellow powder. Yield: 40 mg (32%). Microanalysis results for a compound with the empirical formula $C_{20}H_{32}I_2SnP_2Pt$ (MW = 902.01 amu): Found: C, 26.7; H, 3.6. Calc.: C, 26.6; H, 3.6%.

3.29. Synthesis of [Rh(η,κP-$C_5Me_4CH_2PMe_2$)(C_2H_4)] (29)

A THF solution of the ligand precursor **1** (202 mg, 1.0 mmol) was slowly added at 0 °C to a solution of $[Rh(C_2H_4)_2Cl]_2$ (195 mg, 0.5 mmol) in the same solvent. The solution darkened immediately and a white precipitate formed. The mixture was stirred at r.t. for 6 h and the solvent was then evaporated to dryness. The brown residue obtained was extracted in Et_2O to give an orange–brown solution that was filtered and evaporated to dryness. The slightly oily product formed was frozen in liquid N_2 and scratched with a spatula leading to a brown powder on heating to r.t. The product was dissolved in pentane and the solution filtered through neutral alumina (grade I, 2 cm height column). A yellow–brown crystalline solid formed when the solution was concentrated and cooled at −80 °C. Yield: 130 mg (40%).

3.30. Synthesis of [Rh(η,κP-$C_5Me_4CH_2PMe_2$)I_2] (30)

The first part of this synthesis was similar to that described for **29**: a solution of **1** (202 mg, 1.0 mmol) and $[Rh(C_2H_4)_2Cl]_2$ (195 mg, 0.5 mmol) in THF was reacted for 6 h and the solvent was evaporated to dryness. The residue was extracted in Et_2O and filtered. A solution of I_2 (254 mg, 1.0 mmol) in toluene was added to the previous solution and the resulting mixture was stirred for 4 h. The solvent was evaporated to dryness and a tiny amount of I_2 sublimed. The residue was re-extracted in toluene and the solution was filtered through a small column (ca. 2 cm height) of neutral alumina. The resulting orange–brown solution was collected, concentrated and layered with pentane. Cooling to −80 °C afforded brown microcrystals of **30**. Yield: 287 mg (52%).

3.31. Synthesis of [Ir(η,κP-$C_5Me_4CH_2PMe_2$)I_2] (31)

Treatment of a THF solution of $[Ir(COE)_2Cl]_2$ (448 mg, 0.5 mmol) with a solution of **1** (202 mg, 1.0 mmol) in THF at 0 °C led to the formation of a white precipitate and a brown solution. The mixture was reacted for 8 h at r.t. and the solvent was then evaporated to dryness. The residue was extracted in Et_2O and the solution was filtered and evaporated to dryness. The brown powder obtained was weighed (413 mg, 0.83 mmol) and redissolved in toluene. A toluene solution of I_2 (210 mg, 0.83 mmol) was added dropwise at r.t. and the mixture stirred for 4 h. The solvent was removed in vacuum and a small excess of I_2 sublimed out. The brown solid was redissolved in toluene and filtered through a column of neutral alumina (ca. 2 cm height). The solution was concentrated, layered with pentane and cooled to −80 °C overnight. Brown crystals of **31** formed. Yield: 275 mg (43%).

Table 7
Crystal data and structure refinement parameters

	9	**13**	**11**	**20**
Empirical formula	$C_{24}H_{40}FeP_2$	$C_{24}H_{40}FeO_2P_2$	$C_{26}H_{40}FeP_2$	$C_{24}H_{40}MnP_2$
Temperature (K)	150	150	150	150
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	*C*2/*c*	*C*2/*c*	$Pna2_1$	$P2_1/c$
Crystal description	Yellow prism	Yellow–green prism	Orange block	Orange block
Unit cell dimensions				
a (Å)	11.624(2)	11.263(2)	25.257(5)	8.653(1)
b (Å)	21.254(4)	20.969(4)	6.4030(13)	16.202(1)
c (Å)	9.811(2)	10.172(2)	14.588(3)	8.610(1)
α (°)	90	90	90	90
β (°)	96.78(3)	98.05(3)	90	97.945(3)
γ (°)	90	90	90	90
Z	4	4	4	4
Crystal size (mm)	0.3 × 0.3 × 0.5	0.2 × 0.3 × 0.6	0.3 × 0.3 × 0.3	0.2 × 0.2 × 0.3
Data measured	4583	2302	4059	2449
Unique data	2428	2302	2519	2449
R_{int}	0.020	0	0.031	0
Refinement on	F	F^2	F^2	F^2
Parameters refined	123	138	266	131
R (all data)	0.0472	0.1027	0.0196	0.0594
R_w (all data)	0.0415	0.1781	0.0520	0.0957

3.32. X-ray crystallography

Crystals were isolated under N_2, covered with perfluoropolyether oil and mounted on a glass fibre. Data were collected using an Enraf–Nonius DIP2000 image-plate diffractometer using Mo–K_α radiation ($\lambda =$ 0.71069 Å). Structure solution was performed using the SHELXS-97 program [65]. For compound **9**, subsequent refinement was performed using the CRYSTALS package [66], whereas the SHELXL-93 package [67] was used for compounds **13**, **11** and **20**. All non-hydrogen atoms were refined with anisotropic thermal displacement parameters. Hydrogen atoms were positioned geometrically and subsequently allowed to ride on their parent atoms with fixed isotropic thermal parameters. Crystallographic data are summarised in Table 7. Diagrams of the molecular structures (ORTEP-3 [68]) are shown in Figs. 1–4.

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