Neopentyl and Trimethylsilylmethyl Compounds of Rhodium(III) and Iridium(III) with *ortho*-Metallated Triphenylphosphine. *X*-Ray Crystal Structure of $[\overline{\mathrm{Ir}(\mathrm{C_6H_4P}}\mathrm{Ph_2})(\mathrm{CH_2SiMe_3})(\eta^5\text{-}\mathrm{C_5Me_5})]$†

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The compound $[\mathrm{RhCl_2}(\eta^5\text{-}\mathrm{C_5Me_5})(\mathrm{PPh_3})]$ reacts with $\mathrm{Li(CH_2SiMe_3)}$ to give the *ortho*-metallated complex $[\overline{\mathrm{Rh}(\mathrm{C_6H_4P}}\mathrm{Ph_2})(\mathrm{CH_2SiMe_3})(\eta^5\text{-}\mathrm{C_5Me_5})]$ (**2**), and with $\mathrm{Mg(CH_2SiMe_3)Cl}$ in $\mathrm{CH_2Cl_2}$ (molar ratio 1 : 1) to yield $[\mathrm{RhCl(CH_2SiMe_3)}(\eta^5\text{-}\mathrm{C_5Me_5})(\mathrm{PPh_3})]$, (**3**). Complex (**3**) is converted by the action of $\mathrm{Li(CH_2SiMe_3)}$ into the *ortho*-metallated compound (**2**). The reaction of $[\mathrm{IrCl_2}(\eta^5\text{-}\mathrm{C_5Me_5})(\mathrm{PPh_3})]$ with $\mathrm{Mg(CH_2SiMe_3)Cl}$ in $\mathrm{CH_2Cl_2}$ gives $[\overline{\mathrm{Ir}(\mathrm{C_6H_4P}}\mathrm{Ph_2})(\mathrm{CH_2SiMe_3})(\eta^5\text{-}\mathrm{C_5Me_5})]$, (**6**), and $[\mathrm{IrCl(Me)}(\eta^5\text{-}\mathrm{C_5Me_5})(\mathrm{PPh_3})]$. Reaction of $[\mathrm{RhCl_2}(\eta^5\text{-}\mathrm{C_5Me_5})(\mathrm{PPh_3})]$ with $\mathrm{Mg(CH_2CMe_3)Cl}$ or $\mathrm{Li(CH_2CMe_3)}$ in diethyl ether affords a mixture of $[\overline{\mathrm{Rh}(\mathrm{CH_2CMe_2C}}\mathrm{H_2})(\eta^5\text{-}\mathrm{C_5Me_5})(\mathrm{PPh_3})]$, $[\overline{\mathrm{Rh}(\mathrm{C_6H_4P}}\mathrm{Ph_2})(\mathrm{CH_2CMe_3})(\eta^5\text{-}\mathrm{C_5Me_5})]$, and $[\mathrm{Rh}(\eta^5\text{-}\mathrm{C_5Me_5})(\mathrm{C_2H_4})(\mathrm{PPh_3})]$, while reaction in $\mathrm{CH_2Cl_2}$ in equimolar amounts gives $[\mathrm{RhCl(CH_2CMe_3)}(\eta^5\text{-}\mathrm{C_5Me_5})(\mathrm{PPh_3})]$. Reaction of $[\mathrm{IrCl_2}(\eta^5\text{-}\mathrm{C_5Me_5})(\mathrm{PPh_3})]$ with $\mathrm{Mg(CH_2CMe_3)Cl}$ gives $[\overline{\mathrm{Ir}(\mathrm{C_6H_4P}}\mathrm{Ph_2})(\mathrm{CH_2CMe_3})(\eta^5\text{-}\mathrm{C_5Me_5})]$. The *X*-ray crystal structure analysis of compound (**6**) has been carried out: $a = 17.537(7)$, $b = 11.304(4)$, $c = 15.410(7)$ Å, $\beta = 94.49(1)°$, space group $P2_1/n$, $Z = 4$, $R = 0.0361$ for 4 114 observed reflections. The 'piano-stool' metal co-ordination polyhedron is deformed by *ortho*-metallation which imposes a 67.0(2)° angle at iridium in the metallacycle, while the other angles, P–Ir–C(17) 89.0(2) and C(17)–Ir–C(36) 89.2(2)°, between the 'legs' of the 'stool' are near to 90°. The bulky $\mathrm{C_5Me_5}$ ligand (effective cone angle 146°), in approaching the metal, produces large widenings of the other co-ordination polyhedron angles: Cp–Ir–P 137.0(3), Cp–Ir–C(36)(benzene) 133.4(3)°, and Cp–Ir–C(17)(silyl) 122.6(3)° (Cp = centroid of $\mathrm{C_5Me_5}$). The *ortho*-metallated ring is nearly planar, (P–Ir–C) $\wedge$ (P–C–C) 5.3(3)°, and bent by only 6.6(2)° with respect to the metal-bound benzene ring which maintains its planarity; the only deformation this ring suffers involves the endocyclic angles at the carbon bound to phosphorus which widen to 124.5(5)° and at the *ortho*-carbons which narrow to 115.9(6) and 116.7(5)°.

The interaction of $[\mathrm{IrCl_2}(\eta^5\text{-}\mathrm{C_5Me_5})(\mathrm{PPh_3})]$ with $\mathrm{Mg(CH_2SiMe_3)Cl}$ has led to a dialkyl derivative, which can be thermally converted into a silairidacyclobutane complex with concomitant loss of tetramethylsilane. In contrast, by reaction of $[\mathrm{RhCl_2}(\eta^5\text{-}\mathrm{C_5Me_5})(\mathrm{PPh_3})]$ with $\mathrm{Mg(CH_2CMe_3)Cl}$ a rhodacyclobutane derivative is formed straightforwardly, the expected dialkyl derivative being too unstable to be isolated.[1]

During the study of these alkylation reactions it was found that *ortho*-metallation of co-ordinated triphenylphosphine may also occur depending upon the experimental conditions. Because of the interest in cyclometallation reactions which relate to the more general field of C–H bond activation by transition metals,[2] we have carried out a study of the factors that determine the course of the above reactions. The results of this study are now reported. A preliminary account of part of this research has been communicated.[3]

Results and Discussion

Reaction of $[\mathrm{MCl_2}(\eta^5\text{-}\mathrm{C_5Me_5})(\mathrm{PPh_3})]$ [M = Rh (**1**) *or* Ir (**5**)] *with* $\mathrm{Li(CH_2SiMe_3)}$.—The reactions of complexes (**1**) and (**5**) with $\mathrm{Li(CH_2SiMe_3)}$ in diethyl ether take different routes, leading in the case of iridium to a very complex mixture of compounds that we have not been able to isolate, and in the case of rhodium to an oily product identified as the *ortho*-metallated compound (**2**) (Scheme 1). The mass spectrum of (**2**) shows a molecular ion peak at m/z 586, a peak at m/z 513 ($M - \mathrm{SiMe_3}$), the base peak at m/z 73 ($\mathrm{SiMe_3}$), and the second most intense peak at m/z 364 corresponding to the $\overline{\mathrm{Rh}(\mathrm{C_6H_4P}}\mathrm{Ph_2})$ fragment. Both the ^{1}H and ^{13}C n.m.r. spectra show the triphenylphosphine signals as a complex pattern, which is different from that expected for co-ordinated triphenylphosphine and consistent with the complexity expected for *ortho*-metallated phosphine. In particular the ^{13}C n.m.r. spectrum shows ten signals (seven doublets and three singlets) of the fourteen signals expected for *ortho*-metallated triphenylphosphine; the four missing signals are due to the most substituted carbon atoms. Finally, the ^{31}P n.m.r. spectrum shows a high-field resonance (Table 1), which, according to Garrou,[4] is indicative of a structure in which the phosphorus atom is a part of a four-membered ring. It is worthwhile remembering that, upon alkylation of complex (**1**)

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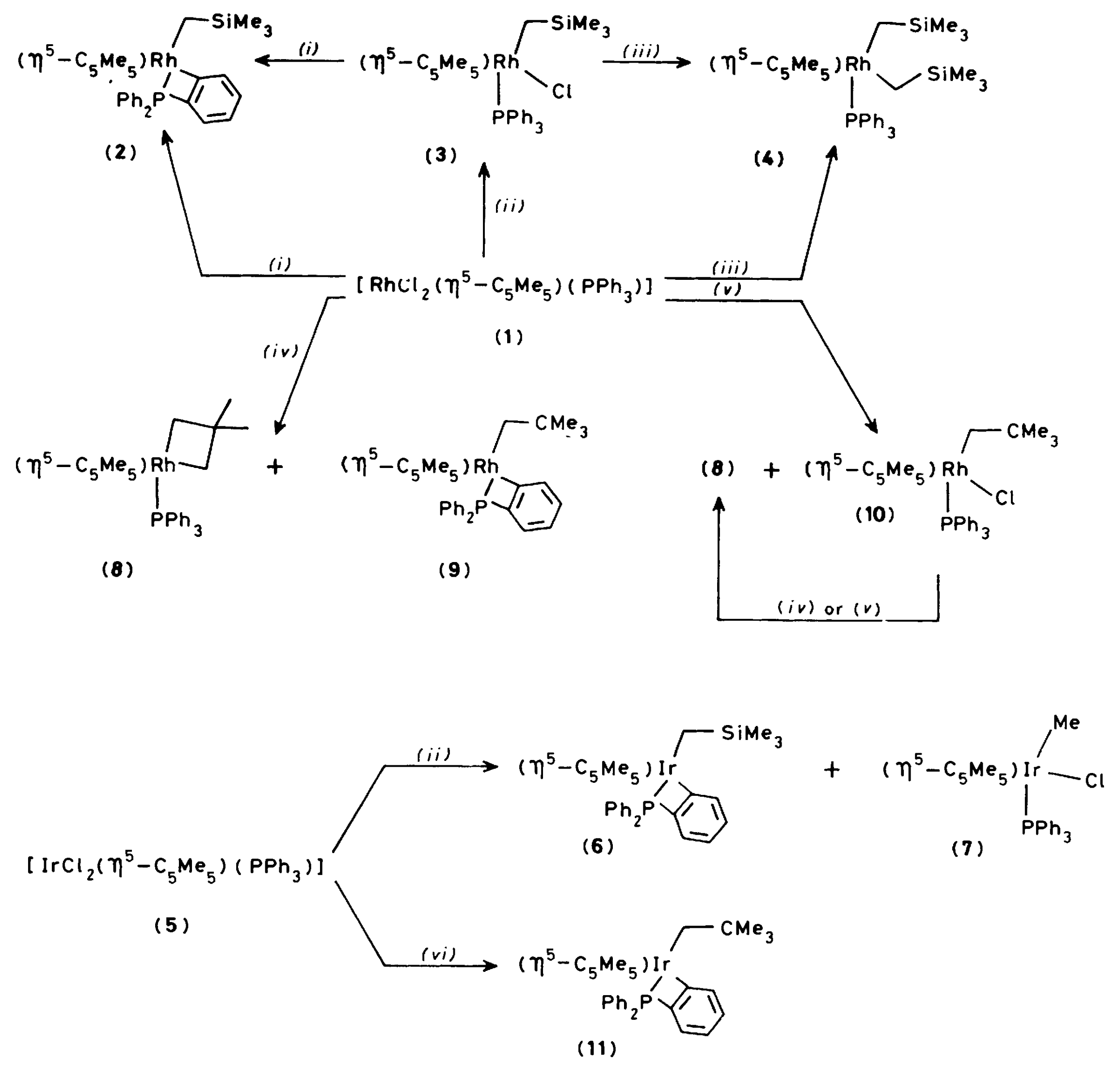
† (*o*-Diphenylphosphinophenyl-C^1P)(η-pentamethylcyclopentadienyl)trimethylsilylmethyliridium(III).

Supplementary data available (No. SUP 56410, 9 pp.): H-atom co-ordinates, thermal parameters, complete bond lengths and angles. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.



Scheme 1. (*i*) Li(CH$_2$SiMe$_3$), in Et$_2$O; (*ii*) Mg(CH$_2$SiMe$_3$)Cl, in CH$_2$Cl$_2$, Rh:Mg = 1; (*iii*) Mg(CH$_2$SiMe$_3$)Cl, in Et$_2$O; (*iv*) Li(CH$_2$CMe$_3$), in pentane; (*v*) Mg(CH$_2$CMe$_3$)Cl, in CH$_2$Cl$_2$; (*vi*) Mg(CH$_2$CMe$_3$)Cl, in pentane

Table 1. ^{31}P N.m.r. data[a]

Compound	Chemical shift	$\Delta_R = \delta_P - \delta_F$[b]
(4) [Rh(CH$_2$SiMe$_3$)$_2$(η^5-C$_5$Me$_5$)(PPh$_3$)][c]	+50.28 (d, 172.02)	+56.54
(2) [$\overline{\text{Rh(C}_6\text{H}_4\text{P}}Ph_2$)(CH$_2$SiMe$_3$)($\eta^5$-C$_5Me_5$)]	−26.45 (d, 119.64)	−20.19
[Ir(CH$_2$SiMe$_3$)$_2$(η^5-C$_5$Me$_5$)(PPh$_3$)][c]	+5.35	+11.61
(6) [$\overline{\text{Ir(C}_6\text{H}_4\text{P}}Ph_2$)(CH$_2$SiMe$_3$)($\eta^5$-C$_5Me_5$)]	−63.26	−57
(11) [$\overline{\text{Ir(C}_6\text{H}_4\text{P}}Ph_2$)(CH$_2CMe_3$)($\eta^5$-C$_5Me_5$)]	−63.42	−57.16
PPh$_3$	−6.26	

[a] In C$_6$D$_6$ solvent, referred to external 85% H$_3$PO$_4$ (δ 0.0), 40.5 MHz (positive values to low field); multiplicity and coupling constant (Hz) in parentheses. [b] δ_P, for co-ordinated triphenylphosphine, δ_F for free triphenylphosphine. [c] Ref. 1.

with Mg(CH$_2$SiMe$_3$)Cl in diethyl ether a different product is obtained, [Rh(CH$_2$SiMe$_3$)$_2$(η^5-C$_5$Me$_5$)(PPh$_3$)], (**4**).[1] This marked dependence of the nature of the reaction products upon the alkylating reagents could be explained assuming that the two reactions involve the same intermediate (**3**) (Scheme 1) which is further alkylated by the Grignard reagent to give the dialkyl derivative (**4**) or is deprotonated by the organolithium compound to give the *ortho*-metallated complex (**2**).

In order to verify this hypothesis we prepared the monoalkyl derivative (**3**) in good yields by treating (**1**), in CH$_2$Cl$_2$ solution, with an equimolar amount of Mg(CH$_2$SiMe$_3$)Cl. If the alkylation is carried out in diethyl ether the dialkyl derivative (**4**) is the only product. This is because complex (**1**) is virtually insoluble in Et$_2$O and consequently the Grignard reagent is always in excess in solution during the alkylation. Thus, complex (**3**) reacted with Li(CH$_2$SiMe$_3$) and with Mg(CH$_2$SiMe$_3$)Cl to give (**2**) and (**4**) respectively, as expected on the basis of the above hypothesis. A plausible explanation for the different courses of the alkylation reaction is that the substitution of the chloro ligand in (**3**) is relatively slow due to the increased steric restrictions around the rhodium atom caused by the presence of the bulky trimethylsilyl group. This allows alternative reaction patterns to take place: Li(CH$_2$SiMe$_3$), more basic than the analogous Grignard reagent, is probably acting as a base and removes a proton from one of the phenyl groups of co-ordinated phosphine. Similar deprotonation reactions

Table 2. Proton and ^{13}C n.m.r. data[a]

Compound	^{1}H N.m.r.		^{13}C N.m.r.	
	δ/p.p.m.[b]	Assignment	δ/p.p.m.[c]	Assignment
(2) $[\overline{\mathrm{Rh(C_6H_4P}}\mathrm{Ph_2)(CH_2SiMe_3)(\eta^5\text{-}C_5Me_5)}]$	−0.17 (s)	MeSi	1.89 (s)	MeSi
	0.13 (m)	CH_2	9.14 (s)	$C_5\mathit{Me}_5$
	1.56 (d, 4)	C_5Me_5	10.23 (m)	CH_2
			96.36 (m)	C_5Me_5
(3) $[\mathrm{RhCl(CH_2SiMe_3)(\eta^5\text{-}C_5Me_5)(PPh_3)}]$	0.25 (s)	MeSi		
	0.93 (m)	CH_2		
	1.21 (d, 3)	C_5Me_5		
(6) $[\overline{\mathrm{Ir(C_6H_4P}}\mathrm{Ph_2)(CH_2SiMe_3)(\eta^5\text{-}C_5Me_5)}]$	−0.15 (s)	MeSi		
	0.40 (m)	CH_2		
	1.56 (d, 3)	C_5Me_5		
(7) $[\mathrm{IrCl(Me)(\eta^5\text{-}C_5Me_5)(PPh_3)}]$[d]	0.90 (d, 6)	IrMe		
	1.35 (d, 2)	C_5Me_5		
(9) $[\overline{\mathrm{Rh(C_6H_4P}}\mathrm{Ph_2)(CH_2CMe_3)(\eta^5\text{-}C_5Me_5)}]$	0.76 (s)	CMe_3		
	2.16 (m)	CH_2		
	1.59 (d, 4)	C_5Me_5		
(10) $[\mathrm{RhCl(CH_2CMe_3)(\eta^5\text{-}C_5Me_5)(PPh_3)}]$	1.13 (s)	CMe_3		
	2.37 (m)	CH_2		
	1.27 (d, 3)	C_5Me_5		
(11) $[\overline{\mathrm{Ir(C_6H_4P}}\mathrm{Ph_2)(CH_2CMe_3)(\eta^5\text{-}C_5Me_5)}]$	0.80 (s)	CMe_3	9.07 (s)	$C_5\mathit{Me}_5$
	2.17 (m)	CH_2	32.95 (s)	$\mathit{C}Me_3$
	1.55 (d, 2,4)	C_5Me_5	91.94 (m)	C_5Me_5

[a] Resonances due to PPh_3 are omitted. [b] In C_6D_6 solvent, referred to $SiMe_4$ (δ 0.0), 60 MHz (unless otherwise stated); multiplicity and coupling constant (Hz) in parentheses. [c] In $CDCl_3$ solvent, referred to $SiMe_4$ (δ 0.0), 25.2 MHz. [d] In $CDCl_3$.

promoted by alkyl-lithium compounds to give cyclometallated phosphines have recently been reported.[5]

A more complicated reaction takes place when $[\mathrm{IrCl_2(\eta^5\text{-}C_5Me_5)(PPh_3)}]$ (**5**) is treated with $\mathrm{Mg(CH_2SiMe_3)Cl}$ in CH_2Cl_2 (Scheme 1): no monoalkyl derivative is formed and the *ortho*-metallated complex (**6**) is the main product, with small amounts of the unexpected compound (**7**). Complex (**6**), unlike (**2**) and the other *ortho*-metallated complexes described in this paper, has been obtained in a crystalline form. The ^{1}H n.m.r. spectrum is almost superimposable upon that of complex (**2**) (Table 2). The ^{31}P n.m.r. spectrum, according to Garrou,[4] is consistent with the phosphorus atom being part of an *ortho*-metallated system (Table 1). Although the analytical and spectroscopic data indicate that the structure of this product is almost certainly as displayed, we considered the compound and its mode of preparation to be of sufficient interest as to determine its structure by *X*-ray diffraction analysis (see later). Complex (**7**) has been characterized by elemental analysis, ^{1}H n.m.r. spectroscopy, and bromolytic decomposition (see Table 2 and Experimental section). The mechanism of formation of (**6**) and (**7**) is not obvious and at the moment we have no satisfactory explanation. These compounds could derive from a monoalkyl intermediate analogous to (**3**), which has been deprotonated by the Grignard reagent to give (**6**) or has decomposed with loss of the thermodynamically unstable $CH_2{=}SiMe_2$ fragment[6] to yield (**7**) (unless the CH_2Cl_2 solvent has some role in the formation of the methyl derivative).

Reaction of $[\mathrm{MCl_2(\eta^5\text{-}C_5Me_5)(PPh_3)}]$ [M = Rh (**1**) *or* Ir (**5**)] *with* $\mathrm{M'(CH_2CMe_3)}$ (M′ = Li *or* MgCl).—The course of the alkylation reactions of complex (**1**) with $\mathrm{Li(CH_2CMe_3)}$ or $\mathrm{Mg(CH_2CMe_3)Cl}$ is strongly dependent on the solvent and on the nature of the alkylating agent. We have already reported that by carrying out the reaction with $\mathrm{Mg(CH_2CMe_3)Cl}$ in pentane the rhodacyclobutane derivative (**8**) is the only product.[1] In contrast, by using $\mathrm{Li(CH_2CMe_3)}$ in pentane, the *ortho*-metallated complex (**9**) is formed along with (**8**) (Scheme 1). Complex (**9**) has been identified by ^{1}H n.m.r. spectroscopy (Table 2) and mass spectrometry.

Reaction of complex (**1**) with $\mathrm{Mg(CH_2CMe_3)Cl}$ or $\mathrm{Li(CH_2CMe_3)}$ in diethyl ether gives (**8**), (**9**), and comparable amounts of the ethylene complex $[\mathrm{Rh(\eta^5\text{-}C_5Me_5)(C_2H_4)(PPh_3)}]$ which has been identified by comparison of its properties with those of an authentic sample prepared according to the literature.[7] Deuterium-labelling studies have demonstrated that the ethylene is not derived from carbon–carbon cleavage of the rhodacyclobutane moiety: indeed, by treating (**1**) with $\mathrm{Li(CD_2CMe_3)}$ the ethylene derivative obtained is non-deuteriated.[1] We suggest that the ethylene is formed by C–O bond rupture in diethyl ether by the alkylating reagent and then trapped by rhodium(I) species formed *in situ*. A similar conclusion was drawn when a rhodacyclopentane derivative was prepared by allowing (**1**) to react with $\mathrm{BrMg(CH_2)_4MgBr}$ in diethyl ether.[7] By analogy with the formation of $[\overline{\mathrm{Rh(C_6H_4P}}\mathrm{Ph_2)(CH_2SiMe_3)(\eta^5\text{-}C_5Me_5)}]$, (**2**), it seemed reasonable that also in this case a plausible candidate for (**9**) is a monoalkylated compound. In order to verify this hypothesis, we carried out the reaction between complex (**1**) and $\mathrm{Mg(CH_2CMe_3)Cl}$ in CH_2Cl_2 and obtained the monoalkylated complex (**10**) together with traces of the rhodacyclobutane (**8**), most of the starting material being recovered (see Scheme 1). Complex (**10**) has been isolated as an orange-red crystalline compound after chromatographic purification of the reaction mixture.

Complex (**10**) was treated with $\mathrm{Li(CH_2CMe_3)}$ in pentane and, surprisingly, the rhodacyclobutane (**8**) was obtained as the only product. The same result has been obtained by using $\mathrm{Mg(CH_2CMe_3)Cl}$ in CH_2Cl_2 (see Scheme 1).

On this basis the amounts of complex (**8**) which are formed together with (**10**) from the reaction of (**1**) with the Grignard reagent (Rh:Mg = 1:1) are most probably due to further alkylation of (**10**) to an unstable dineopentylrhodium intermediate.[1] As for the origin of (**9**), it is possible that (**1**) is deprotonated to give an *ortho*-metallated halogeno compound which reacts with $\mathrm{Li(CH_2CMe_3)}$ to give (**9**). We are inclined to explain the different origins of the *ortho*-metallated complexes (**2**) and (**9**) on the basis of the difference in base strengths of $\mathrm{Li(CH_2CMe_3)}$ and $\mathrm{Li(CH_2SiMe_3)}$. The reaction of $[\mathrm{IrCl_2(\eta^5\text{-}C_5Me_5)(PPh_3)}]$ (**5**) with $\mathrm{Li(CH_2CMe_3)}$ in various solvents (Et_2O, C_6H_6,

Table 3. Fractional co-ordinates (× 10^4) and isotropic equivalent B values ($B_{equiv.}$ = one third trace of the diagonalized matrix) of complex (**6**) with standard deviations in parentheses

Atom	X/a	Y/b	Z/c	$B_{equiv.}$
Ir	−240.9(1)	2 631.8(2)	1 912.9(2)	2.71(1)
Si	−1 702(1)	2 158(2)	3 356(1)	3.53(5)
P	720(1)	2 106(1)	2 897(1)	2.95(4)
C(1)	−340(5)	4 373(5)	1 204(5)	4.73(24)
C(2)	−988(5)	3 676(6)	932(5)	4.99(24)
C(3)	−761(5)	2 652(6)	538(5)	5.04(22)
C(4)	60(5)	2 689(6)	525(4)	4.88(22)
C(5)	318(4)	3 739(7)	947(5)	4.57(22)
C(6)	−344(7)	5 578(6)	1 624(7)	9.15(43)
C(7)	−1 805(6)	4 105(9)	1 010(7)	8.44(37)
C(8)	−1 257(7)	1 757(8)	69(7)	10.03(43)
C(9)	535(6)	1 800(7)	49(6)	8.17(36)
C(10)	1 133(6)	4 142(9)	990(7)	8.65(38)
C(11)	1 674(4)	1 919(5)	2 531(5)	3.51(17)
C(12)	2 284(4)	2 652(6)	2 817(6)	5.24(23)
C(13)	2 992(5)	2 560(7)	2 460(7)	6.88(30)
C(14)	3 088(5)	1 721(8)	1 837(7)	6.53(30)
C(15)	2 512(5)	984(7)	1 563(6)	5.83(27)
C(16)	1 805(4)	1 074(5)	1 907(5)	4.35(21)
C(17)	−923(4)	3 068(5)	2 968(5)	3.48(17)
C(18)	−1 335(5)	959(7)	4 111(6)	6.25(28)
C(19)	−2 333(5)	3 140(7)	3 979(6)	6.06(27)
C(20)	−2 366(5)	1 539(7)	2 462(6)	6.05(27)
C(21)	889(3)	2 795(5)	3 954(4)	3.28(16)
C(22)	813(4)	4 001(6)	4 031(5)	4.24(21)
C(23)	954(5)	4 567(6)	4 829(6)	5.29(26)
C(24)	1 161(5)	3 918(8)	5 557(6)	5.67(27)
C(25)	1 233(5)	2 710(8)	5 502(5)	5.96(26)
C(26)	1 091(5)	2 147(6)	4 701(5)	4.80(22)
C(31)	301(4)	656(5)	2 922(4)	3.10(17)
C(32)	457(4)	−437(5)	3 316(5)	4.03(20)
C(33)	2(5)	−1 379(5)	2 999(6)	4.94(25)
C(34)	−580(4)	−1 213(5)	2 360(5)	4.54(22)
C(35)	−723(4)	−119(5)	1 985(5)	3.99(20)
C(36)	−285(4)	860(4)	2 271(4)	3.07(16)

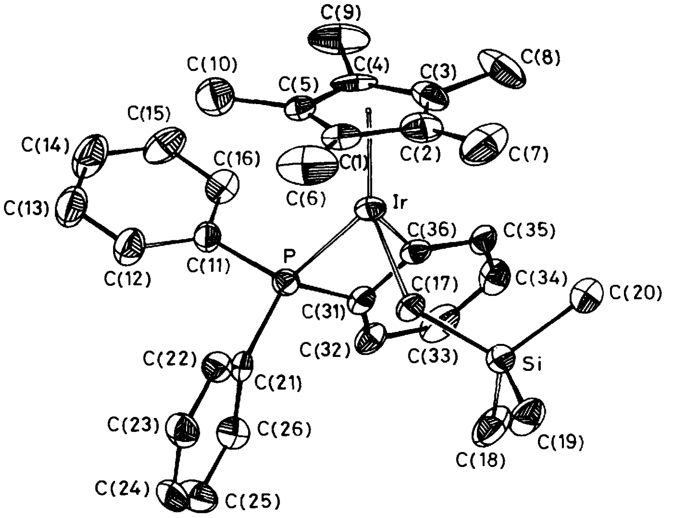


Figure 1. ORTEP drawing of complex (**6**) showing thermal ellipsoids at 30% probability

pentane), is very complicated. Proton n.m.r. spectroscopy of the crude reaction mixture reveals the presence of several compounds (as shown by the number of absorptions in the C_5Me_5 region). Attempted separation by chromatographic techniques failed due to considerable decomposition.

In contrast, the reaction of complex (**5**) with $Mg(CH_2CMe_3)Cl$ gives, after chromatographic separation, a yellow oil which was identified as the *ortho*-metallated compound (**11**) (see Scheme 1). The reaction gives poor yields (5%) when carried out in diethyl ether, much better (47%) in pentane. Compound (**11**) has been identified by elemental analysis and n.m.r. spectroscopy. In particular the ^1H n.m.r. spectrum is almost superimposable upon that of the rhodium analogue (**9**), and the ^{31}P n.m.r. spectrum shows a high-field signal (−63.42 p.p.m.) which, according to Garrou,[4] is consistent with a phosphorus atom in a four-membered ring (Table 1).

Crystal Structure Analysis of Complex (**6**).—Table 3 gives the atomic co-ordinates with the isotropic equivalent thermal parameters, while Table 4 shows the relevant bond distances (values corrected for thermal motion are in square brackets) and angles. The thermal motion analysis was carried out in the rigid-body approximation of Schomaker and Trueblood.[8] As shown in Table 5 a considerable improvement of fit is obtained by taking into account the internal motions according to the one-parameter model of Dunitz and White.[9,10] As expected, the best agreements are found for the atoms which execute small-amplitude librations and satisfy Hirshfeld's rigid-body postulate.[11,12] Throughout the paper the values quoted are means weighted according to the reciprocals of the variances. When two values, x_1 and x_2, are compared, the ratio $\Delta/\sigma = |x_1 - x_2|/(\sigma_1^2 + \sigma_2^2)^{\frac{1}{2}}$ is considered, where σ_1 and σ_2 are the estimated standard deviations (e.s.d.s) of x_1 and x_2, respectively.

Co-ordination polyhedron. As shown in Figure 1 the usual 'three-legged piano-stool' co-ordination, typical for these organometallic complexes, is observed. It is interesting to compare the geometry of this molecule with that of the iridasilacyclobutane complex $[\overline{Ir(CH_2SiMe_2CH_2})(\eta^5\text{-}C_5Me_5)(PPh_3)]$ (**12**) which we studied recently.[1] The closing of the Ir–P–C–C ring causes narrowing of the P–Ir–C(36) angle which reduces from 89.0(3)° in (**12**) to 67.0(2)°, while the opening of the ring involving the two carbons bound to Ir in (**12**) causes a widening of the C(17)–Ir–C(36) angle from 77.3(4) to 89.2(2)°. The angle Cp–Ir–P (Cp = centroid of C_5Me_5) increases from 131.1(3) to 137.0(3)° and Cp–Ir–C(18) [or C(36)] from 125.4(4) to 133.4(3)°, while Cp–Ir–C(17) decreases from 125.8(4) to 122.6(3)°. These differences are quite understandable considering that the constraints imposed by the metallasilacyclobutane are released, while those required by the *ortho*-metallation of phosphine become effective. The Ir–P distance increases from 2.236(2) Å in (**12**) to 2.257(2) Å and the difference is significant (Δ/σ = 7.4), while Ir–Cp decreases by the same amount, *i.e.* from 1.915(10) Å in (**12**) to 1.892(7) Å, but the difference is not significant (Δ/σ = 1.9) owing to the relatively high e.s.d.s of the carbon atom co-ordinates.

The C_5Me_5 ligand is perpendicular to the vector Ir–Cp [90.8(4)°] as found in (**12**), but because of its orientation [Figure 2(*a*)] the Ir–P and Ir–C bonds are less eclipsed by the M • • • C(Cp) directions than in (**12**). The 'effective' cone angle* of the C_5Me_5 ligand is 146°, *i.e.* in perfect agreement with that (147°) found in (**12**). As found for (**12**) and for the similar

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* Calculated as twice the angle formed by the Ir–Cp direction and the tangent from Ir to the most external hydrogen-atom sphere to which a van der Waals radius of 1.20 Å has been attributed.

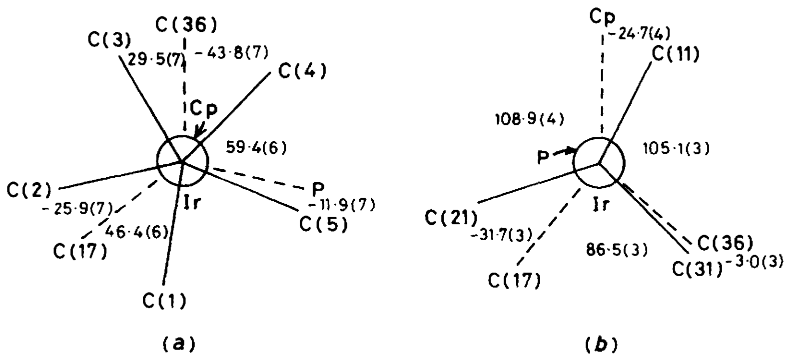


Figure 2. Newman projections along the Cp–Ir (*a*), and P–Ir directions (*b*)

Table 4. Selected bond lengths (Å) and angles (°). Values corrected for thermal motion are given in square brackets; the weighted averages of these values were calculated by assigning to them the e.s.d.s of the corresponding uncorrected values

Co-ordination sphere

Ir–C(1)	2.252(6) [2.256]	Ir–Cp	1.892(7) [1.896]
Ir–C(2)	2.256(8) [2.260]	Ir–P	2.257(2) [2.262]
Ir–C(3)	2.241(8) [2.246]	Ir–C(17)	2.149(7) [2.152]
Ir–C(4)	2.243(7) [2.247]	Ir–C(36)	2.080(5) [2.085]
Ir–C(5)	2.229(8) [2.233]		
av.	2.245(4) [2.249]		
Cp–Ir–P	137.0(3)	P–Ir–C(17)	89.0(2)
Cp–Ir–C(17)	122.6(3)	P–Ir–C(36)	67.0(2)
Cp–Ir–C(36)	133.4(3)	C(17)–Ir–C(36)	89.2(2)

C_5Me_5 ligand

C(1)–C(2)	1.419(11) [1.422]	C(1)–C(6)	1.508(10) [1.511]
C(2)–C(3)	1.380(11) [1.383]	C(2)–C(7)	1.525(13) [1.528]
C(3)–C(4)	1.443(12) [1.445]	C(3)–C(8)	1.483(13) [1.487]
C(4)–C(5)	1.410(10) [1.413]	C(4)–C(9)	1.530(12) [1.533]
C(5)–C(1)	1.440(12) [1.442]	C(5)–C(10)	1.498(13) [1.501]
av.	1.416(11) [1.419]	av.	1.509(8) [1.512]
C(5)–C(1)–C(2)	106.4(6)	C(3)–C(4)–C(5)	107.6(7)
C(1)–C(2)–C(3)	110.1(7)	C(4)–C(5)–C(1)	108.1(7)
C(2)–C(3)–C(4)	107.7(7)	av.	107.9(6)

Silyl ligand

Si–C(17)	1.848(7) [1.851]	C(17)–Si–C(18)	112.2(3)
Si–C(18)	1.868(9) [1.872]	C(17)–Si–C(19)	108.4(3)
Si–C(19)	1.883(9) [1.886]	C(17)–Si–C(20)	113.9(4)
Si–C(20)	1.867(9) [1.871]	C(18)–Si–C(19)	107.3(4)
av.	1.873(5) [1.876]	C(18)–Si–C(20)	110.6(4)
		C(19)–Si–C(20)	103.8(4)
		av.	109.6(14)
		Ir–C(17)–Si	125.9(3)

Triphenylphosphine ligand

P–C(11)	1.818(7) [1.821]	Ir–P–C(11)	118.6(2)
P–C(21)	1.810(7) [1.813]	Ir–P–C(21)	123.5(2)
P–C(31)	1.799(6) [1.803]	Ir–P–C(31)	88.2(2)
av.	1.808(6) [1.811]	av.	110.1(110)
C(11)–P–C(21)	103.9(3)	P–C(11)–C(12)	122.2(5)
C(11)–P–C(31)	106.8(3)	P–C(11)–C(16)	120.1(5)
C(21)–P–C(31)	114.3(3)	P–C(21)–C(22)	119.6(5)
av.	108.3(31)	P–C(21)–C(26)	122.2(5)
		P–C(31)–C(32)	138.6(5)
		Ir–C(36)–C(35)	135.2(5)

Phenyl rings*

C(31)–C(36)	1.398(9)		
C–C (av.)	1.386(3) [1.389]		
C–C(*ipso*)–C	av. 117.8(4)	C(32)–C(31)*i*–C(36)	124.5(5)
C–C(*ortho*)–C	av. 121.0(4)	C(31)–C(32)*o*–C(33)	115.9(6)
C–C(*meta*)–C	av. 119.8(4)	C(32)–C(33)*m*–C(34)	121.2(6)
C–C(*para*)–C	av. 120.6(6)	C(33)–C(34)*p*–C(35)	121.5(7)
		C(34)–C(35)*m*–C(36)	120.0(6)
		C(35)–C(36)*o*–C(31)	116.7(5)
Ir–P–C(11)–C(12)	115.0(6)	Ir–P–C(21)–C(22)	−40.8(6)
Ir–P–C(11)–C(16)	−60.9(6)	Ir–P–C(21)–C(26)	138.8(5)
sum	175.9(8)	sum	179.6(8)
		Ir–P–C(31)–C(32)	177.0(8)
		Ir–P–C(31)–C(36)	4.2(4)
		sum	181.2(9)
[C(11) ··· C(16)] ∧ [C(21) ··· C(26)]	92.6(3)		
[C(11) ··· C(16)] ∧ [C(31) ··· C(36)]	78.7(2)		
[C(21) ··· C(26)] ∧ [C(31) ··· C(36)]	39.0(2)		

* The C–C bond distances of the C(31) ··· C(36) ring are not significantly different from those in the other phenyl rings so they are averaged all together. The same cannot be done for the angles.

rhodacyclobutane (**8**), no regular trends are observed for the Ir–C(Cp) and C–C (ring) distances in the C_5Me_5 ligand, which is planar $[\Sigma(\Delta/\sigma)^2 = 5.4]$ with the methyl groups out of the plane by an average of 0.14(2) Å [corresponding to a (C ··· C) ∧ CH_3 angle of 5.1(7)°] in the opposite direction with respect to the metal.

It is interesting to compare the metal–C(Cp) and the metal–Cp distances found in the *ortho*-metallated complex (**6**) and in the irida- and rhoda-cyclobutane complexes, (**12**) and (**8**),[1] with those quoted in the literature for iridium(III) and rhodium(III) systems.[13] From the data collected in Table 6 it appears that both the Ir–C(Cp) and Rh–C(Cp) distances we find are larger than those quoted in the literature. Moreover, comparing the data for the three metallacycles we studied, it appears that these distances are influenced by the interactions of the metal with the other ligands. In particular the M–Cp distance decreases with increasing electron affinity of the other ligands. This effect is largest for the *ortho*-metallated complex, owing to the π character of the metallacycle bonds and the greater electron attraction by the trimethylsilylmethyl ligand, medium in the iridasilacyclobutane complex, owing to the presence of silicon in the metallacycle, and minimum in the

Table 5. Results of thermal motion analysis*

	Eigenvectors			(Eigenvalue)$^{\frac{1}{2}}$	I
(*a*) All non-H atoms, $N = 35$, $n = 210$, $m = 20$, rigid-body					
L tensor	−0.6101	−0.7852	0.1061	3.3°	3 584
	0.7632	−0.6184	−0.1875	2.8	4 153
	0.2129	−0.0334	0.9765	2.5	4 967
T tensor	0.9697	−0.2372	0.0582	0.196 Å	
	0.1645	0.8105	0.5622	0.173	
	−0.1805	−0.5356	0.8250	0.170	
$\bar{\Delta} = 0.013(21)$, $R' = 0.091$,$\sigma(\overline{\Delta U}) = 0.0021$, $\bar{\sigma}(U_o) = 0.0051$					
(*b*) All non-H atoms, four non-rigid-body groups (1) C(1) • • • C(10) librating about Ir–Cp, g.l.a. = 8.1(2)° (2) C(12) • • • C(16) librating about C(11)–P, g.l.a. = 6.6(13)° (3) C(22) • • • C(26) librating about C(21)–P, g.l.a. = 5.5(13)° (4) C(18) • • • C(20) librating about C(17)–Si, g.l.a. = 8.0(5)°					
L tensor	−0.5174	−0.8242	0.2301	3.0°	3 584
	0.7904	−0.5634	−0.2406	2.4	4 153
	0.3279	0.0574	0.9430	2.1	4 967
T tensor	0.9720	−0.2057	0.1136	0.198 Å	
	0.1478	0.1594	−0.9761	0.177	
	0.1827	0.9656	0.1854	0.173	
$\bar{\Delta} = 0.013(21)$, $R' = 0.051$, $\sigma(\overline{\Delta U}) = 0.0012$, $\bar{\sigma}(U_o) = 0.0051$					

* The eigenvectors (inertial frame) and eigenvalues are for the rigid-body model. N = Number of atoms, n = number of independent observations, m = number of independent parameters, $\bar{\Delta}$ = mean difference of the mean-square vibrational amplitudes along the interatomic directions for all pairs of atoms of the segment, $\Delta U = U_{ij}(\text{obs.}) - U_{ij}(\text{calc.})$, $R' = [\Sigma(wU)^2/\Sigma(wU_o)^2]^{\frac{1}{2}}$, $\sigma(\overline{\Delta U}) = [\Sigma(w\Delta U)^2/\Sigma w^2]^{\frac{1}{2}}$, $\bar{\sigma}(U_o)$ = mean e.s.d. of U_o values, g.l.a. = group libration amplitude, and I = moment of intertia (a.m.u. Å^2; 1 a.m.u. = 1.16 604 × 10^{-47} kg m^2), ***L*** = librational tensor, ***T*** = translational tensor.

rhodacyclobutane complex where these effects are missing. It is noteworthy that in the series $[Ir_2(C_5Me_5)_2X_4]$ the distance Ir–Cp increases from X = Cl (1.756 Å) to Br (1.771 Å) to I (1.801 Å),[13] *i.e.* with increasing donor character of the halogen.

The benzene ring involved in *ortho*-metallation becomes deformed only in the endocyclic angles at C(31), C(32), and C(36). The first, involving the carbon bound to the phosphorus, widens by *ca.* 6°, while the other two, which involve carbon atoms in the *ortho* positions (one being bound to the metal), each become narrower by *ca.* 5°. The whole benzene ring maintains its planarity $[\Sigma(\Delta/\sigma)^2 = 5.8]$; the other endocyclic angles and the C–C distances do not show significant variations. The benzene ring is tilted by only 6.6(2)° with respect to the mean plane through the metallaphosphacyclobutane ring. This ring shows a quite small deviation from planarity with a dihedral angle IrPC(36)^C(31)PC(36) of 5.3(3)°. This quite reduced puckering seems to be a characteristic feature of the large number of *ortho*-metallated complexes known, as shown by the data in Table 7, where relevant geometric parameters are compared.

The orientation of the phosphine ligand, as shown by the Newman projection of Figure 2(*b*), is determined by the coplanarity of the *ortho*-metallated ring which requires eclipsing of the P–C(31) with the Ir–C(36) bonds. The molecules are packed in the unit cell by van der Waals forces.

Conclusions

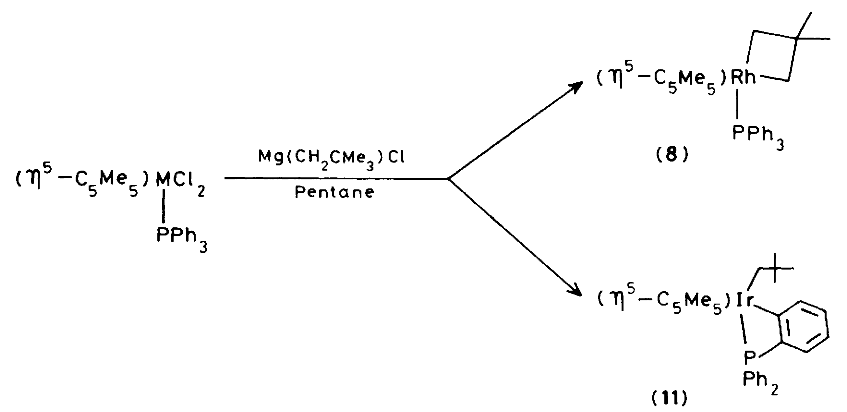
The results reported along with those on the formation of the metallacyclobutane (**8**) and (**12**)[1] allow the following conclusions.

(*i*) Bulky alkyl groups, like neopentyl and trimethylsilylmethyl, in sterically congested rhodium(III) and iridium(III) systems, have a great tendency to undergo cyclometallation reactions. When metallacyclobutanes are formed, these are derived from thermal decomposition reactions of dialkyl

Table 6. Comparison of metal–C_5Me_5 distances (Å) (M = Rh or Ir)

	M–C(Cp)[a]		M–Cp[b]	
Compound	av.	range	av.	range
(**6**) $[\overline{Ir(C_6H_4P}Ph_2)(CH_2SiMe_3)(\eta^5\text{-}C_5Me_5)]$	2.245(4)	2.229—2.256	1.892(7)	
(**12**) $[\overline{Ir(CH_2SiMe_2C}H_2)(\eta^5\text{-}C_5Me_5)(PPh_3)]$	2.262(9)	2.236—2.282	1.915(10)	
(**8**) $[\overline{Rh(CH_2CMe_2C}H_2)(\eta^5\text{-}C_5Me_5)(PPh_3)]$	2.304(9)	2.274—2.328	1.961(6)	
Rh^{III} (C_5Me_5) complexes[c]	2.154(6)	2.109—2.207	1.774(7)	1.745—1.815
Ir^{III} (C_5Me_5) complexes[c]			1.776(13)	1.756—1.801[d]

[a] C(Cp) = Carbon of the cyclopentadienyl ring. [b] Cp = Centroid of the cyclopentadienyl ring. [c] From ref. 13. [d] Data referred to $[Ir_2(C_5Me_5)_2X_4]$ with X = Cl, Br, or I.



Scheme 2.

Table 7. Comparison of relevant geometrical parameters for the M–P–C–C moiety in *ortho*-metallated compounds[a] (M = Ir, Pt, Mn, or Ru; R = conventional residual error index)

		Distance/Å						Angle/°				
Compound	R	M–P	M–C	P–C	C–C	M···C	P···C	M	P	C_M	C_P	(PMC) ∧ (PCC)
$[Ir(C_6H_4PPh_2)(CH_2SiMe_3)(\eta^5\text{-}C_5Me_5)]$[b]	0.0361	2.257(2)	2.080(5)	1.799(6)	1.398(9)	2.842(6)	2.399(6)	67.0(2)	88.2(2)	108.0(4)	96.5(4)	5.3(3)
$[Ir(C_6H_4PPh_2)_2H(PPh_3)]$[c]	0.040	2.396(4) 2.362(3)	2.063(11) 2.85(10)	1.807(16) 1.816(10)	1.40(2) 1.39(2)	2.841(11) 2.827(12)	2.48(2) 2.49(2)	67.1(3) 67.8(2)	83.8(3) 84.1(2)	108.6(6) 107.1(5)	100.3(7) 101.0(5)	4.1(8) 0.6(7)
$[Ir(C_6H_4PPh_2)H(Br)(PPh_3)_2]$[d]	0.095	2.341(6)	2.06(2)	1.80(2)	1.39(3)	2.84(2)	2.43(2)	66.6(6)	85.5(7)	109(1)	99(1)	6.9(14)
$[Ir(C_6H_4PPh_2)Cl\{(OCPh)_2CH\}(PPh_3)]$[e,*]	0.050	2.277(2)	2.027(8)					68.4(2)	85.6(3)	107.4(6)	98.4(6)	
$[Ir(C_6H_4PMe_2)H(PPhMe_2)_3]^+$[f,*]	0.057	2.380(3)	2.142(12)									
$[Ir(C_6H_4PPh_2)(C_2H_4)_2(PPh_3)]$[g,*]	0.056	2.370	2.070								101.2	
$[Ir(C_6H_4PPh_2)(CO)_2(PPh_3)]\cdot thf$[g,*]	0.058	2.374	2.113						83.7—85.7		101.9	
$[Pt(C_6H_4PBu^t_2)(NO_3)(PPhBu^t_2)]$[h]	0.043	2.318(5)	2.03(2)	1.81(2)	1.38(2)	2.746(14)	2.494(18)	69.7(5)	82.4(6)	106(1)	102(1)	3.9(10)
$[Mn\{MeC_6H_3P(C_6H_4Me)_2\}(CO)_4]$[i]	0.060	2.324(3)	2.097(9)	1.781(9)	1.385(10)	2.808(8)	2.464(9)	67.5(3)	85.2(3)	105.7(7)	101.5(7)	0.7(5)
$[Rh(C_6H_4PPh_2)H_2(PPh_3)_2]^-$[j,*]	0.089	A 2.347(3) B 2.339(3)	2.098(11) 2.069(10)	1.810(12) 1.837(11)	1.425(15) 1.405(14)			67.6(3) 67.4(3)	85.9(4) 85.6(4)	107.0(8) 109.4(8)	99.5(8) 97.7(8)	essentially planar
$[Pt(C_6H_4PPh_2)\{C(CO_2Me)=CHCO_2Me\}(PPh_3)]$[k]	0.047	2.329(11)	2.056(8)	1.794(9)	1.389(11)	2.792(8)	2.473(10)	68.2(2)	84.2(3)	106.6(6)	101.0(6)	1.8(5)

[a] For compounds indicated with an asterisk the atomic co-ordinates were not quoted so it was not possible to calculate the missing data. [b] Present work. [c] G. Del Piero, G. Perego, A. Zazzetta, and M. Cesari, *Cryst. Struct. Commun.*, 1974, **3**, 725. [d] K. Von Deuten and L. Dahlenburg, *Cryst. Struct. Commun.*, 1980, **9**, 421. [e] M. Cowle, M. D. Gauthier, S. J. Loeb, and I. R. McKeer, *Organometallics*, 1983, **2**, 1057. [f] R. H. Crabtree, J. M. Quirk, H. Felkin, T. Feelebeen-Khan, and C. Pascard, *J. Organomet. Chem.*, 1980, **187**, C32. [g] G. Perego, G. Del Piero, M. Cesari, M. G. Clerici, and E. Perrotti, *J. Organomet. Chem.*, 1973, **54**, C51. [h] R. Countryman and W. S. McDonald, *Acta Crystallogr., Sect. B*, 1977, **33**, 3580. [i] R. J. McKinney, C. B. Knobler, B. T. Huie, and H. D. Kaesz, *J. Am. Chem. Soc.*, 1977, **99**, 2988. [j] G. P. Pez, R. A. Grey, and J. Corsi, *J. Am. Chem. Soc.*, 1981, **103**, 7528; two anion A and B in the asymmetric unit. [k] N. C. Rice and J. D. Oliver, *J. Organomet. Chem.*, 1978, **145**, 121.

derivatives: in such cases no hydrogen abstraction from one of the phenyl groups of the phosphine takes place, but only a selective γ abstraction from one of the alkyl groups by the other.

(*ii*) *ortho*-Metallated complexes derive from the action of the alkylating agent on the starting dichloro complex (**1**) or (**5**), or on a monoalkylated derivative. The nature of the alkylating agent is very critical, as is clearly illustrated by the different products of the reaction between (**1**) and $Mg(CH_2SiMe_3)Cl$ or $Li(CH_2SiMe_3)$ respectively. Moreover all the reactions described in this paper show that the choice of a particular pathway is dependent not only on the nature of the alkylating agent, but also on the solvent, the nature of the alkyl group, and the transition metal. All these factors can operate together to create conditions favourable to the alkylation or deprotonation reaction. This could be the reason, for instance, for the different behaviour of complexes (**1**) and (**5**) towards $Mg(CH_2CMe_3)Cl$ in pentane (Scheme 2). It is quite possible that while the rhodium compound is alkylated to a dialkyl derivative [which rapidly decomposes to the rhodacyclobutane (**8**)], the iridium compound, owing to its relatively greater inertness towards chloro substitution, is first deprotonated to the halogeno *ortho*-metallated compound, which is then alkylated to (**11**). Further work is however necessary to get a better insight into these cyclometallation reactions.

Experimental

The reactions and manipulations of organometallics were carried out under dinitrogen or argon, using standard techniques. The solvents were dried and distilled prior to use. The compounds $[MCl_2(\eta^5\text{-}C_5Me_5)(PPh_3)]$ [M = Rh (**1**) or Ir (**5**)],[14] $Mg(CH_2CMe_3)Cl$,[15] $Mg(CH_2SiMe_3)Cl$,[16] $Li(CH_2CMe_3)$,[17] and $Li(CH_2SiMe_3)$[18] were prepared as described. Nuclear magnetic resonance spectra were recorded on Varian T60 (^1H) and XL 100 (^1H, ^{13}C, and ^{31}P) instruments. Mass spectra were obtained with a Varian MAT CH7 spectrometer. Microanalyses were performed by the Laboratorio di Microanalisi of the Istituto di Chimica Organica, Facoltà di Farmacia, Università di Pisa.

(o-Diphenylphosphinophenyl-C¹P)(η^5-pentamethylcyclopentadienyl)(trimethylsilylmethyl)rhodium(III) (**2**).—To a suspension of complex (**1**) (0.35 g, 0.61 mmol) in Et_2O (55 cm^3) was added $Li(CH_2SiMe_3)$ (0.41 g, 4.36 mmol) in diethyl ether (15 cm^3) at 0 °C (45 min). The reaction mixture was stirred at room temperature for another 2 h. The solvent was removed under vacuum and the residue extracted with pentane (50 cm^3). The solution was hydrolysed at 0 °C with water and the organic layer was desiccated over Na_2SO_4, concentrated to about 3 cm^3, and chromatographed on alumina at 0 °C whereupon pentane eluted a yellow band. After removal of the solvent a yellow oil was obtained (0.076 g, 21%) (Found: C, 64.8; H, 6.3. $C_{32}H_{40}PRhSi$ requires C, 65.5; H, 6.8%).

Chloro(η^5-pentamethylcyclopentadienyl)(trimethylsilylmethyl)(triphenylphosphine)rhodium(III) (**3**).—Complex (**1**) (0.308 g, 0.54 mmol) was dissolved in CH_2Cl_2 (12 cm^3) and a solution of $Mg(CH_2SiMe_3)Cl$ (1.93 cm^3 of a 0.28 mol dm^{-3} diethyl ether solution, 0.54 mmol) was slowly added at room temperature (1 h). The mixture was stirred for another 3 h, then evaporated to dryness. The residue was extracted with pentane (80 cm^3), filtered, and concentrated to 30 cm^3. After cooling overnight at −40 °C, red-orange crystals of complex (**3**) were obtained (0.202 g, 61%) (Found: C, 60.9; H, 7.1; Cl, 6.10. $C_{32}H_{41}ClPRhSi$ requires C, 61.6; H, 6.6; Cl, 5.6%). By using a molar ratio Grignard reagent:rhodium of 2:1, the complex $[Rh(CH_2SiMe_3)_2(\eta^5\text{-}C_5Me_5)(PPh_3)]$ (**4**) is obtained (40%).

Reactions of Complex (**3**).—*With* $Mg(CH_2SiMe_3)Cl$. To complex (**3**) (0.05 g, 0.08 mmol) in Et_2O (5 cm^3) was added $Mg(CH_2SiMe_3)Cl$ (1.55 cm^3 of a 0.26 mol dm^{-3} diethyl ether solution, 0.403 mmol) at 0 °C (30 min). The reaction mixture was stirred at 0 °C (1 h) and then at room temperature (1 h). After hydrolysis and extraction with pentane a solid residue was obtained, shown by ^1H n.m.r. spectroscopy to be a mixture of (**3**) (30%) and (**4**) (70%).

With $Li(CH_2SiMe_3)$. To complex (**3**) (0.07 g, 0.112 mmol) in Et_2O (10 cm^3) was added $Li(CH_2SiMe_3)$ (0.069 g, 0.73 mmol) in Et_2O (3 cm^3) at 0 °C. When the addition was complete (15 min) the brown-yellow mixture was allowed to react at 0 °C (1 h), then at room temperature (1.5 h). After hydrolysis, extraction with pentane and chromatographic separation on alumina at 0 °C (elution with pentane) gave a yellow band from which complex (**2**) was recovered (0.010 g, 16%).

Reaction between Complex (**5**) *and* $Mg(CH_2SiMe_3)Cl$ *in* CH_2Cl_2: *Formation of (o-Diphenylphosphinophenyl-C¹P)(η^5-pentamethylcyclopentadienyl)(trimethylsilylmethyl)iridium*(III) (**6**) *and Chloro(methyl)(η^5-pentamethylcyclopentadienyl)(triphenylphosphine)iridium*(III) (**7**).—To a solution of complex (**5**) (0.24 g, 0.36 mmol) in CH_2Cl_2 (10 cm^3), was added $Mg(CH_2SiMe_3)Cl$ (2.14 cm^3 of a 0.17 mol dm^{-3} diethyl ether solution, 0.364 mmol) at room temperature (1 h). The mixture was stirred at room temperature for 4 h, then the solvent was removed and the residue extracted with pentane (50 cm^3). The pentane solution, after filtration, was concentrated to 3 cm^3 and chromatographed on a column of alumina. By using pentane as eluant a yellow-green band (A) was eluted; by using a mixture of pentane–diethyl ether (1:1) a pale yellow band (B) was eluted. Band (A) gave a yellow residue of complex (**6**) (0.074 g, 30%) that can be crystallized from pentane at −20 °C to give yellow crystals (Found: C, 55.9; H, 5.8. $C_{32}H_{40}IrPSi$ requires C, 56.8; H, 5.9%). Band (B) gave a pale yellow residue of complex (**7**) (0.011 g, 5%) (Found: C, 53.65; H, 5.3; Cl, 5.0. $C_{29}H_{33}ClIrP$ requires C, 54.4; H, 5.2; Cl, 5.5%). Treatment of a sample (0.03 g) of (**7**) in $CDCl_3$ with an excess of bromine gave MeBr (according to ^1H n.m.r.).

Reaction of Complex (**1**) *with* $Li(CH_2CMe_3)$ *in* Et_2O: *Formation of (2,2-Dimethylpropane-1,3-diyl)(η^5-pentamethylcyclopentadienyl)(triphenylphosphine)rhodium*(III) (**8**), *(o-Diphenylphosphinophenyl-C¹P)neopentyl(η^5-pentamethylcyclopentadienyl)rhodium*(III) (**9**), *and Ethylene(η^5-pentamethylcyclopentadienyl)(triphenylphosphine)rhodium*(I).—To complex (**1**) (0.33 g, 0.58 mmol) in diethyl ether (50 cm^3) was added $Li(CH_2CMe_3)$ (0.271 g, 3.48 mmol) in Et_2O (10 cm^3) at −10 °C. The red solution was stirred at 0 °C for another 3 h, then the solvent was removed and the residue extracted with pentane (70 cm^3). The red solution was concentrated to *ca.* 5 cm^3, then chromatographed on a alumina column. Pentane eluted two yellow fractions. The first was evaporated *in vacuo* to give a yellow oil, which was crystallized from pentane at −30 °C to give complex (**8**) (0.033 g, 10%) (Found: C, 69.7; H, 7.2. $C_{33}H_{40}PRh$ requires C, 69.5; H, 7.0%). The second band gave, after evaporation, complex (**9**) as a yellow oil (0.04 g, 12%) (Found: C, 69.9; H, 7.3. $C_{33}H_{40}PRh$ requires C, 69.5; H, 7.0%). 15% Diethyl ether in pentane eluted a red fraction that was concentrated and cooled at −20 °C to give red-orange crystals of $[Rh(\eta^5\text{-}C_5Me_5)(C_2H_4)(PPh_3)]$ (0.062 g, 20%), identified by comparison of its properties with those of an authentic sample.[7] If the reaction of complex (**1**) with $Li(CH_2CMe_3)$ is carried out in pentane only (**8**) and (**9**) are obtained.

Chloro(neopentyl)(η^5-pentamethylcyclopentadienyl)(triphenylphosphine)rhodium(III) (**10**).—To a solution of complex (**1**) (0.262 g, 0.495 mmol) in CH_2Cl_2 (10 cm^3) was added

Table 8. Experimental data for the crystallographic analysis

Compound		$[\overline{\mathrm{Ir}(\mathrm{C_6H_4}\mathrm{P}}\mathrm{Ph_2})(\mathrm{CH_2SiMe_3})(\eta^5\text{-}\mathrm{C_5Me_5})]$
Formula		$C_{32}H_{40}IrPSi$
M		675.9
Space group		$P2_1/n$
a/Å		17.537(7)
b/Å		11.304(4)
c/Å		15.410(7)
β/°		94.49(1)
U/Å^3		3 046(2)
Z		4
D_c/Mg m^{-3}		1.474
Reflections for lattice parameters	number	25
	θ range	16—25
Radiation		Mo-K_{α_1}
λ/Å		0.709 300
F(000)		1 352
T/K		294
Crystal size/mm		0.18 × 0.34 × 0.53
Diffractometer		Philips PW1100
μ/mm^{-1}		4.47
Absorption correction (min.—max.)		1.0002—1.4695
Scan speed/° s^{-1}		0.10
Scan width/°		1.20
θ range/°		3—25
h range		20—20
k range		0—13
l range		0—18
Standard reflection		2 2 8
Intensity variation		None
Scan mode		$\omega/2\theta$
No of measured reflections		4 921
Condition for observed reflections		$I \geqslant 2\sigma(I)$
No. of reflections used in the refinement		4 114
Anisotropic least squares on F		Block-diagonal
Mean shift-to-error ratio		0.068
Min. and max. height in final difference map/e Å^{-3}		−0.14, 0.32
No. of measured reflections		477
$R = \Sigma\lvert\Delta F\rvert/\Sigma\lvert F_o\rvert$		0.0361
$R' = [\Sigma w(\Delta F)^2/\Sigma wF_o^2]^{\frac{1}{2}}$		0.0368
$S = [\Sigma w(\Delta F)^2/(N - P)]^{\frac{1}{2}}$ *		1.5800
w		$1/\sigma^2(F_o)$

* P = number of parameters, N = number of observations.

$Mg(CH_2CMe_3)Cl$ (2.19 cm^3 of a 0.21 mol dm^{-3} diethyl ether solution, 0.46 mmol) (1 h). The deep red solution was stirred for 3 h. The solvent was removed under vacuum and the residue extracted with pentane (80 cm^3). The extracts were filtered, concentrated to *ca.* 3 cm^3, and chromatographed on alumina at 0 °C. Pentane eluted a yellow band, that was evaporated to dryness to give complex (**8**) (0.005 g, 2%). Pentane–diethyl ether (1:1) eluted an orange band that was evaporated, dissolved in pentane (3 cm^3), and cooled at −40 °C to give complex (**10**) (0.025 g, 9%) as red-orange crystals (Found: C, 64.45; H, 6.35; Cl, 5.7. $C_{33}H_{41}ClPRh$ requires C, 65.3; H, 6.8; Cl, 5.8%).

Reactions of Complex (**10**).—*With* $Mg(CH_2CMe_3)Cl$. Complex (**10**) (0.03 g, 0.05 mmol) in CH_2Cl_2 (2 cm^3) was treated with $Mg(CH_2CMe_3)Cl$ (0.07 cm^3 of a 0.70 mol dm^{-3} diethyl ether solution, 0.049 mmol) for 3 h, at room temperature. Usual work-up gave a solid residue containing complexes (**8**) (65%) and (**10**) (35%) (according to ^{1}H n.m.r.).

With $Li(CH_2CMe_3)$. Complex (**10**) (0.025 g, 0.04 mmol) in pentane (5 cm^3) was treated at 0 °C with $Li(CH_2CMe_3)$ (0.017 g, 0.218 mmol) in pentane (1 cm^3), and stirred for 4 h at room temperature. Usual work-up gave complex (**8**) (0.01 g, 44%).

(o-*Diphenylphosphinophenyl*-C^{1}P)*neopentyl*(η^5-*pentamethylcyclopentadienyl*)*iridium*(III) (**11**).— Complex (**5**) (0.10 g, 0.15 mmol) in pentane (40 cm^3) was treated at room temperature with $Mg(CH_2CMe_3)Cl$ (2.5 cm^3 of a 0.74 mol dm^{-3} diethyl ether solution, 1.85 mmol). The mixture was stirred for 30 h to give a yellow solution and a white solid. The mixture was hydrolysed with water (0.5 cm^3) and the pentane solution was dried over Na_2SO_4. The solution was concentrated to *ca.* 3 cm^3 and chromatographed on alumina at 0 °C. Pentane eluted a green-yellow band, that, after removal of solvent, gave a yellow oil (0.047 g, 47%) (Found: C, 60.5; H, 6.6. $C_{33}H_{40}IrP$ requires C, 60.1; H, 6.1%). The analogous reaction carried out in diethyl ether gave complex (**11**) in 5% yield.

Crystal Structure Analysis of Complex (**6**).—The relevant data are summarized in Table 8. The lattice parameters were refined by a least-squares[19] procedure using the Nelson and Riley[20] extrapolation function. The reflection intensities were corrected for Lorentz and polarization effects, and the absorption was taken into account using the azimuthal-scan method.[21] The structure was solved by Patterson and Fourier techniques and refined by block-diagonal least squares (one block for the non-hydrogen-atom parameters, the other for hydrogens), using the SHELX 76 program.[22] All the hydrogen atoms were located from a Fourier difference synthesis and refined isotropically. The atomic scattering factors and anomalous scattering coefficients are from the literature.[23] The calculations were carried out on the GOULD-SEL 32/77 computer of the Centro di Studio per la Strutturistica Diffrattometrica del CNR (Parma). In addition to the quoted program, PARST,[24] THMV7,[25] ORTEP,[26] and PLUTO[27] programs were used.

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