

# Cyclometallation Reactions in Neopentyl and Trimethylsilylmethyl Systems of Rhodium(III) and Iridium(III). Formation and X-Ray Crystal Structures† of the Four-membered Metallacycles $[\text{Rh}(\text{CH}_2\text{CMe}_2\text{CH}_2)(\eta^5\text{-C}_5\text{Me}_5)(\text{PPh}_3)]$ and $[\text{Ir}(\text{CH}_2\text{SiMe}_2\text{CH}_2)(\eta^5\text{-C}_5\text{Me}_5)(\text{PPh}_3)]$

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The interaction of  $[\text{RhCl}_2(\eta^5\text{-C}_5\text{Me}_5)(\text{PPh}_3)]$  with  $\text{Mg}(\text{CH}_2\text{CMe}_2\text{Cl})$  in pentane gives the rhodacyclobutane  $[\text{Rh}(\text{CH}_2\text{CMe}_2\text{CH}_2)(\eta^5\text{-C}_5\text{Me}_5)(\text{PPh}_3)]$  (**2**). The analogous reaction of  $[\text{MCl}_2(\eta^5\text{-C}_5\text{Me}_5)(\text{PPh}_3)]$  ( $\text{M} = \text{Rh}$  or  $\text{Ir}$ ) with  $\text{Mg}(\text{CH}_2\text{SiMe}_2\text{Cl})$  allows the isolation of the dialkyl derivatives  $[\text{M}(\text{CH}_2\text{SiMe}_2)_2(\eta^5\text{-C}_5\text{Me}_5)(\text{PPh}_3)]$ . Thermolysis of  $[\text{Ir}(\text{CH}_2\text{SiMe}_2)_2(\eta^5\text{-C}_5\text{Me}_5)(\text{PPh}_3)]$  in cyclohexane leads to the iridasilacyclobutane derivative  $[\text{Ir}(\text{CH}_2\text{SiMe}_2\text{CH}_2)(\eta^5\text{-C}_5\text{Me}_5)(\text{PPh}_3)]$  (**6**). The mechanism of formation of the metallacyclobutane derivatives is discussed. The X-ray crystal structures of (**2**) and (**6**) have been determined. The two metallacycle compounds give isostructural crystals belonging to the  $P2_1/n$  space group with four molecules in the unit cell of dimensions for (**2**):  $a = 17.199(6)$ ,  $b = 10.987(4)$ ,  $c = 16.064(5)$  Å,  $\beta = 109.54(2)^\circ$ ; (**6**):  $a = 17.098(7)$ ,  $b = 11.294(5)$ ,  $c = 15.977(7)$  Å,  $\beta = 108.17(2)^\circ$ . Their crystal structures, refined to  $R = 0.0441$  and  $0.0389$  for (**2**) and (**6**) respectively, are built up of deformed 'three-legged piano stools', one leg being the  $\text{M-P}$  bond [ $\text{Rh-P} = 2.230(2)$ ,  $\text{Ir-P} = 2.236(2)$  Å], the other two being the  $\text{M-C}$   $\sigma$  bonds [ $\text{Rh-C} = 2.100(5)$  (av.),  $\text{Ir-C} = 2.159(7)$  Å (av.)] of the metallacyclobutane ring with  $\text{C-Rh-C} = 66.8(2)$  and  $\text{C-Ir-C} = 77.3(4)^\circ$ . These rings are puckered: angle between  $\text{M-C} \cdots \text{C}$  and  $\text{E-C} \cdots \text{C} = 16.5(4)$  and  $18.9(6)^\circ$  for (**2**) ( $\text{E} = \text{C}$ ) and (**6**) ( $\text{E} = \text{Si}$ ), respectively.

Carbon-hydrogen bond activation in neopentyl and trimethylsilylmethyl systems of transition metals has recently emerged as a route to metallacyclobutane derivatives.<sup>1</sup> In Group 8 transition-metal systems such a reaction is believed to proceed via internal oxidative-addition of a C-H bond, followed by elimination of an alkane, and has so far been observed in those cases where the formal oxidation state of the metal in the starting complex is a low one, and where a two-units higher oxidation state is easily accessible.

We have explored the feasibility of these reactions in rhodium(III) and iridium(III) systems, with  $\text{C}_5\text{Me}_5$  and triphenylphosphine as ancillary ligands, and have found that also in these cases  $\gamma$ -elimination reactions occur with the formation of metallacyclobutanes. Details concerning the synthesis and characterization of these compounds as well as the X-ray structural analyses of two of them are described herein. A brief account of some related aspects of this work has already been communicated.<sup>2</sup>

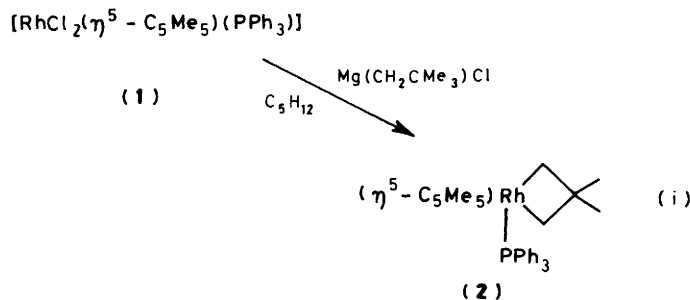
† (2,2-Dimethylpropane-1,3-diyl)( $\eta^5$ -pentamethylcyclopentadienyl)-(triphenylphosphine)rhodium(III) and (2,2-dimethyl-2-silapropane-1,3-diyl)( $\eta^5$ -pentamethylcyclopentadienyl)(triphenylphosphine)iridium(III) respectively.

Supplementary data available (No. SUP 56375, 17 pp.): H-atom coordinates, thermal parameters, full lists of 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.

Non-S.I. unit employed: a.m.u.  $\approx 1.660 \times 10^{-27}$  kg.

## Results and Discussion

**Chemical Reactions.**—(2,2-Dimethylpropane-1,3-diyl)( $\eta^5$ -pentamethylcyclopentadienyl)(triphenylphosphine)rhodium(III) (**1**). The reaction of  $[\text{RhCl}_2(\eta^5\text{-C}_5\text{Me}_5)(\text{PPh}_3)]$  (**1**) with  $\text{Mg}(\text{CH}_2\text{CMe}_2\text{Cl})$  in pentane does not yield the expected dineopentyl derivative but gives the rhodacyclobutane  $[\text{Rh}(\text{CH}_2\text{CMe}_2\text{CH}_2)(\eta^5\text{-C}_5\text{Me}_5)(\text{PPh}_3)]$  (**2**) in good yield [equation (i)]. The  $^1\text{H}$  n.m.r. spectrum of (**2**) (Table 1) is



consistent with the proposed structure: the methyl groups of the metallacyclobutane moiety have different chemical environments and appear as two distinct singlets ( $\delta$  0.11 and 1.04 p.p.m.), and the methylene groups appear as a complex multiplet at  $\delta$  0.37–0.53 p.p.m. The mass spectrum does not show the molecular ion, the highest  $m/z$  value being 500 ( $M - \text{C}_5\text{H}_{10}$ ) at

Table 1. N.m.r. data<sup>a</sup>

Compound	<sup>1</sup> H N.m.r.		<sup>13</sup> C N.m.r. <sup>b</sup>	
	δ/p.p.m.	Assignment	δ/p.p.m.	Assignment
(2) [Rh(CH <sub>2</sub> CMe <sub>2</sub> CH <sub>2</sub> )(η <sup>5</sup> -C <sub>5</sub> Me <sub>5</sub> )(PPh <sub>3</sub> )]	0.11 (s)	C-Me	-1.85 (dd, 9, 18)	CH <sub>2</sub>
	0.37-0.53 (m)	CH <sub>2</sub>	10.09 (s)	C <sub>5</sub> Me <sub>5</sub>
	1.04 (s)	C-Me	31.70 (s)	C-Me
	1.58 (d, 2)	C <sub>5</sub> Me <sub>5</sub>	34.02 (d, 2.8)	C-Me
	6.75-7.70 (m)	Ph	38.50 (d)	CMe <sub>2</sub>
(4) [Rh(CH <sub>2</sub> SiMe <sub>3</sub> ) <sub>2</sub> (η <sup>5</sup> -C <sub>5</sub> Me <sub>5</sub> )(PPh <sub>3</sub> )]	0.10 (s)	Si-Me	97.90 (d, 2)	C <sub>5</sub> Me <sub>5</sub>
	0.25 (m)	CH <sub>2</sub>	0.24 (dd, 15, 29)	CH <sub>2</sub>
	1.40 (d, 2.5)	C <sub>5</sub> Me <sub>5</sub>	5.60 (s)	Si-Me
	6.85-7.6 (m)	Ph	10.73 (s)	C <sub>5</sub> Me <sub>5</sub>
			99.15 (dd, 4, 3)	C <sub>5</sub> Me <sub>5</sub>
(5) [Ir(CH <sub>2</sub> SiMe <sub>3</sub> ) <sub>2</sub> (η <sup>5</sup> -C <sub>5</sub> Me <sub>5</sub> )(PPh <sub>3</sub> )]	0.13 (s)	Si-Me	5.90 (s)	Si-Me
	0.68 (dd, 3, 6)	CH <sub>2</sub>	10.27 (s)	C <sub>5</sub> Me <sub>5</sub>
	1.44 (d, 2)	C <sub>5</sub> Me <sub>5</sub>	19.21 (d, 7.7)	CH <sub>2</sub>
	6.85-7.5 (m)	Ph	94.01 (d, 3)	C <sub>5</sub> Me <sub>5</sub>
(6) [Ir(CH <sub>2</sub> SiMe <sub>2</sub> CH <sub>2</sub> )(η <sup>5</sup> -C <sub>5</sub> Me <sub>5</sub> )(PPh <sub>3</sub> )]	-0.28 (dd, 8, 11)	CH <sub>2</sub>		
	-0.62 (s)	Si-Me		
	0.15 (s)	Si-Me		
	1.45 (d, 2)	C <sub>5</sub> Me <sub>5</sub>		
	6.85-7.8 (m)	Ph		

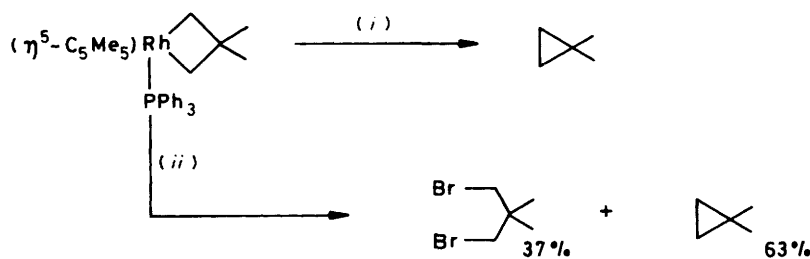
<sup>a</sup> In C<sub>6</sub>D<sub>6</sub>, referenced to SiMe<sub>4</sub> (δ 0.0 p.p.m.); J/Hz values are in parentheses. <sup>31</sup>P N.m.r. data (in C<sub>6</sub>D<sub>6</sub>, referenced to external 85% H<sub>3</sub>PO<sub>4</sub>): (2) +57.26 (*J*<sub>Rh</sub> 194.5); (4) +50.28 (*J*<sub>Rh</sub> 172 Hz); (5) +5.35 p.p.m. <sup>b</sup> Resonances due to the triphenylphosphine are omitted for clarity. These occur in the range δ 136-126 p.p.m.

70 eV. Complex (2) is the only observed product of the reaction. If the reaction is carried out in diethyl ether instead of pentane, the *ortho*-metallated product [Rh(C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>)(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)(CH<sub>2</sub>CMe<sub>3</sub>)] and the ethylene complex [Rh(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)(C<sub>2</sub>H<sub>4</sub>)(PPh<sub>3</sub>)] are also formed.<sup>2</sup> Complex (2) decomposes in a solution of CCl<sub>2</sub>FCF<sub>2</sub>Cl at 40 °C to give in almost quantitative yield 1,1-dimethylcyclopropane; on treatment with bromine 1,1-dimethylcyclopropane and 1,3-dibromo-2,2-dimethylpropane are formed, see Scheme.

are fairly stable as crystals and are soluble in most organic solvents. Solutions show signs of decomposition especially in the case of (4).

Thermolysis of the dialkyls has been followed by <sup>1</sup>H n.m.r. spectroscopy and by g.l.c. analysis: the results have been found to be strongly dependent on the metal and on the reaction solvent.

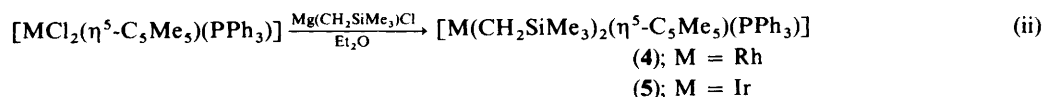
In the case of the rhodium derivative (4), by carrying out the reaction in various solvents (cyclohexane, neopentane, or

Scheme. (i) CCl<sub>2</sub>FCF<sub>2</sub>Cl, 40 °C; (ii) Br<sub>2</sub>, CCl<sub>2</sub>FCF<sub>2</sub>Cl

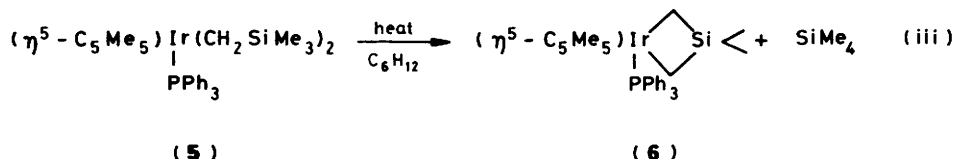
(2,2-Dimethyl-2-silapropane-1,3-diyl)(η<sup>5</sup>-pentamethylcyclopentadienyl)(triphenylphosphine)iridium(III) (6). Treatment of the dichlorides [MCl<sub>2</sub>(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)(PPh<sub>3</sub>)] (1) (M = Rh) or (3) (M = Ir) with an excess of Mg(CH<sub>2</sub>SiMe<sub>3</sub>)Cl in diethyl ether followed by chromatographic purification of the pentane soluble materials, yields yellow crystals of the bis(trimethylsilylmethyl) derivatives (4) and (5), respectively, identified on the basis of analytical and spectroscopic data (see Table 1 and Experimental section) [equation (ii)]. Compounds (4) and (5)

heptane) tetramethylsilane is formed as the only detectable organic product. As the reaction proceeds the solution becomes turbid and the <sup>1</sup>H n.m.r. signals of (4) decrease in intensity. Unfortunately we were not able to isolate any organometallic product.

Thermolysis of (5) in benzene has been investigated also. In addition to massive decomposition to metallic iridium, <sup>1</sup>H n.m.r. monitoring indicates the formation of tetramethylsilane, the doublet due to C<sub>5</sub>Me<sub>5</sub> disappears, and signals of a new



iridium complex emerge which indicate the presence of four non-equivalent methyls. Although we have not been able to isolate this compound, the data suggest a structure arising from the elimination of  $\text{SiMe}_4$  by abstracting a hydrogen atom from one of the methyl groups of the  $\text{C}_5\text{Me}_5$  ligand. By thermolysis of (5) in cyclohexane a different product is obtained: indeed, by keeping a solution of (5) in this solvent for seven days at  $50^\circ\text{C}$  the solution remains clear and  $\text{SiMe}_4$  is formed. After elimination of the organic materials under vacuum and crystallization from pentane, yellow crystals of the iridacyclobutane (6) are formed [equation (iii)]. The mass spectrum of (6) shows an



isotopic cluster molecular ion at  $m/z$  676 ( $^{193}\text{Ir}$ ), 661 ( $M - \text{CH}_3$ ), 633 ( $M - \text{SiCH}_3$ ), and 590 [ $\text{Ir}(\text{C}_5\text{Me}_5)(\text{PPh}_3)$ ]. The  $^1\text{H}$  n.m.r. spectrum is similar to that of (2) and shows the two methylene protons as a multiplet at  $\delta -0.28$  p.p.m. (Table 1).

**Crystal Structure Analysis of (2) and (6).**—The atomic co-ordinates are given in Table 2 and bond distances and angles are compared in Table 3, where the interatomic distances, corrected

for thermal motion, are indicated in square brackets. The thermal motion analysis was carried out first in the rigid-body approximation following Schomaker and Trueblood<sup>3</sup> and considering both the whole molecules and segments of them. The relevant data are collected in Table 4. From this analysis it appears that the treatment of each complex molecule as a rigid body, even if it gives a reasonable agreement between the observed and calculated  $U_{ij}$  values, nevertheless leaves groups of atoms with relevant discrepancies, particularly the  $\text{C}_5\text{Me}_5$  methyl carbon atoms and the phosphine phenyl groups as is indicated also by the thermal ellipsoids in the ORTEP drawings

of Figure 1. Thus the libration of these groups relative to the rigid-body core of the molecule was taken into account using the one-parameter model of Dunitz and White<sup>4</sup> (see also ref. 5) and sensible improvements in fit were obtained. The results quoted in Table 4 are quite reasonable both for librational and translational amplitudes. As expected, the best results are obtained with the segments in which the atoms execute small-amplitude librations and satisfy the Hirshfeld rigid-body postulate.<sup>6,7</sup>

**Table 2.** Fractional atomic co-ordinates ( $\times 10^4$ ) for  $[\text{M}(\text{CH}_2\text{E}(\text{Me}_2\text{CH}_2)(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3))]$  [ $\text{M} = \text{Rh}$ ,  $\text{E} = \text{C}(37)$  (2);  $\text{M} = \text{Ir}$ ,  $\text{E} = \text{Si}$  (6)]. Estimated standard deviations are given in parentheses

Atom	Complex (2)			Complex (6)		
	X/a	Y/b	Z/c	X/a	Y/b	Z/c
M	3 912.5(3)	1 041.5(4)	1 688.0(3)	3 919.6(2)	1 229.3(4)	1 721.9(2)
P	2 832(1)	1 419(1)	481(1)	2 838(2)	1 526(2)	520(2)
E	4 366(4)	−1 177(6)	1 222(4)	4 398(2)	−1 093(3)	1 290(2)
C(1)	3 830(4)	2 689(6)	2 555(4)	3 844(6)	2 899(9)	2 489(7)
C(2)	4 539(4)	2 869(6)	2 286(4)	4 586(6)	2 960(10)	2 236(6)
C(3)	5 086(4)	1 906(6)	2 645(4)	5 091(6)	2 015(10)	2 644(6)
C(4)	4 730(4)	1 137(6)	3 129(4)	4 676(7)	1 366(10)	3 139(6)
C(5)	3 941(4)	1 626(7)	3 080(4)	3 907(6)	1 908(10)	3 056(6)
C(6)	3 142(5)	3 604(6)	2 393(6)	3 166(7)	3 812(11)	2 280(8)
C(7)	4 731(4)	3 984(7)	1 838(5)	4 823(7)	3 989(10)	1 768(8)
C(8)	5 938(4)	1 782(7)	2 597(5)	5 952(6)	1 880(11)	2 590(8)
C(9)	5 134(5)	119(7)	3 754(5)	5 049(9)	361(12)	3 759(8)
C(10)	3 433(5)	1 204(7)	3 616(5)	3 322(8)	1 626(11)	3 551(7)
C(11)	1 805(4)	1 546(5)	597(4)	1 803(5)	1 572(8)	644(6)
C(12)	1 725(4)	1 406(5)	1 404(5)	1 712(6)	1 537(9)	1 471(7)
C(13)	951(5)	1 454(6)	1 511(5)	936(7)	1 596(11)	1 573(8)
C(14)	269(5)	1 625(8)	786(7)	258(7)	1 623(11)	820(10)
C(15)	333(4)	1 741(7)	−38(6)	329(7)	1 663(11)	12(9)
C(16)	1 104(4)	1 739(6)	−127(5)	1 095(6)	1 656(9)	−98(7)
C(17)	3 721(3)	−843(5)	1 658(4)	3 611(6)	−615(8)	1 783(7)
C(18)	4 501(3)	104(5)	921(4)	4 554(6)	390(9)	904(6)
C(19)	5 170(4)	−1 667(6)	1 905(5)	5 368(7)	−1 645(10)	2 135(9)
C(20)	4 066(4)	−2 099(7)	467(5)	4 088(7)	−2 285(12)	421(9)
C(21)	2 539(4)	389(6)	−489(4)	2 612(6)	481(9)	−414(6)
C(22)	2 090(4)	−659(6)	−459(5)	2 194(6)	−582(10)	−358(7)
C(23)	1 863(4)	−1 464(7)	−1 154(7)	1 989(7)	−1 351(12)	−1 060(8)
C(24)	2 063(5)	−1 253(10)	−1 903(6)	2 179(8)	−1 122(16)	−1 801(9)
C(25)	2 497(5)	−224(9)	−1 940(6)	2 570(8)	−87(13)	−1 889(8)
C(26)	2 737(4)	586(7)	−1 242(5)	2 776(7)	717(10)	−1 195(7)
C(31)	2 976(4)	2 892(6)	5(4)	2 934(6)	2 963(8)	5(6)
C(32)	2 470(4)	3 884(7)	−75(5)	2 368(6)	3 889(10)	−91(7)
C(33)	2 639(5)	4 998(7)	−392(5)	2 518(9)	4 951(10)	−446(8)
C(34)	3 316(6)	5 099(7)	−649(5)	3 182(10)	5 131(11)	−706(7)
C(35)	3 841(4)	4 122(7)	−559(5)	3 755(8)	4 227(12)	−616(8)
C(36)	3 685(4)	3 038(6)	−224(4)	3 637(7)	3 144(10)	−225(7)

**Table 3.** Selected bond lengths (Å) and angles (°) for complexes (2) and (6). Values corrected for thermal motion are given in square brackets. The weighted averages of these values are calculated by assigning them the e.s.d.s of the corresponding uncorrected values

	(2) (M = Rh)	(6) (M = Ir)	(2) (M = Rh)	(6) (M = Ir)
(a) Co-ordination sphere			(b) C <sub>5</sub> Me <sub>5</sub> ligand	
M–C(1)	2.317(7) [2.323]	2.275(11) [2.281]	C(1)–C(2)	1.437(11) [1.443] 1.448(16) [1.453]
M–C(2)	2.328(6) [2.334]	2.282(10) [2.288]	C(2)–C(3)	1.406(9) [1.411] 1.400(14) [1.405]
M–C(3)	2.295(6) [2.299]	2.264(9) [2.269]	C(3)–C(4)	1.419(11) [1.424] 1.419(16) [1.424]
M–C(4)	2.274(6) [2.278]	2.236(8) [2.241]	C(4)–C(5)	1.438(10) [1.443] 1.420(16) [1.425]
M–C(5)	2.312(8) [2.317]	2.271(11) [2.277]	C(5)–C(1)	1.415(10) [1.421] 1.422(15) [1.427]
av.	2.304(9) [2.309]	2.262(9) [2.267]	av.	1.422(6) [1.427] 1.421(8) [1.426]
M–cp	1.961(6) [1.965]	1.914(10) [1.919]	C(1)–C(6)	1.508(10) [1.514] 1.509(16) [1.515]
M–P	2.230(2) [2.234]	2.236(2) [2.241]	C(2)–C(7)	1.512(11) [1.518] 1.505(16) [1.509]
			C(3)–C(8)	1.499(10) [1.505] 1.509(16) [1.514]
M–C(17)	2.095(6) [2.100]	2.158(10) [2.164]	C(4)–C(9)	1.508(10) [1.514] 1.510(16) [1.518]
M–C(18)	2.106(7) [2.111]	2.160(11) [2.166]	C(5)–C(10)	1.490(12) [1.496] 1.490(18) [1.496]
av.	2.100(5) [2.105]	2.159(7) [2.165]	av.	1.504(5) [1.510] 1.505(7) [1.511]
cp–M–P	130.3(2)	131.1(3)	C(5)–C(1)–C(2)	109.6(6) 108.4(9)
cp–M–C(17)	126.7(3)	125.8(4)	C(1)–C(2)–C(3)	106.9(6) 107.5(9)
cp–M–C(18)	127.9(3)	125.4(4)	C(2)–C(3)–C(4)	108.7(6) 108.1(10)
P–M–C(17)	94.9(2)	92.0(3)	C(3)–C(4)–C(5)	108.7(6) 109.5(9)
P–M–C(18)	90.3(2)	89.0(2)	C(4)–C(5)–C(1)	106.1(6) 106.4(9)
C(17)–M–C(18)	66.8(2)	77.3(4)	av.	108.0(6) 108.0(5)
(c) Metallacyclic moiety [E = C(37) or Si]			(d) Triphenylphosphine ligand	
E–C(17)	1.539(10) [1.543]	1.840(12) [1.845]	P–C(11)	1.842(7) [1.846] 1.843(11) [1.847]
E–C(18)	1.531(9) [1.534]	1.833(11) [1.838]	P–C(21)	1.853(7) [1.857] 1.847(10) [1.852]
av.	1.535(7) [1.538]	1.836(8) [1.841]	P–C(31)	1.841(7) [1.846] 1.850(10) [1.855]
E–C(19)	1.547(8) [1.550]	1.888(11) [1.891]	av.	1.845(4) [1.850] 1.847(6) [1.852]
E–C(20)	1.532(10) [1.535]	1.888(14) [1.893]	M–P–C(11)	118.3(2) 118.5(3)
av.	1.541(7) [1.544]	1.888(9) [1.892]	M–P–C(21)	122.0(2) 120.5(3)
C(17)–E–C(18)	97.6(5)	94.5(5)	M–P–C(31)	109.6(2) 110.4(3)
C(17)–E–C(19)	111.7(6)	112.8(6)	av.	116.6(37) 116.5(31)
C(17)–E–C(20)	114.5(6)	116.7(5)	C(11)–P–C(21)	97.5(3) 98.0(4)
C(18)–E–C(19)	110.5(6)	110.8(5)	C(11)–P–C(31)	104.0(3) 104.1(4)
C(18)–E–C(20)	113.8(6)	116.1(5)	C(21)–P–C(31)	103.0(3) 103.1(4)
C(19)–E–C(20)	108.4(6)	105.9(6)	av.	101.5(20) 101.7(19)
av.	108.6(28)	109.5(35)		
(e) Phenyl rings				
C–C (av.)	1.379(3) [1.382]	1.386(5) [1.390]	M–P–C(21)–C(22)	80.3(6) 80.7(8)
C–C( <i>ipso</i> )–C (av.)	118.0(4)	118.8(5)	M–P–C(21)–C(26)	–99.4(6) –104.1(9)
C–C( <i>ortho</i> )–C (av.)	121.0(3)	120.0(4)	sum	179.7(9) 184.8(12)
C–C( <i>meta</i> )–C (av.)	120.0(4)	120.2(7)	M–P–C(31)–C(32)	–117.3(6) –118.4(8)
C–C( <i>para</i> )–C (av.)	119.9(7)	121.0(8)	M–P–C(31)–C(36)	57.4(6) 56.2(9)
M–P–C(11)–C(12)	–0.2(6)	6.0(10)	sum	174.7(9) 174.6(12)
M–P–C(11)–C(16)	–177.9(5)	–174.6(7)	[C(11) ... C(16)]–[C(21) ... C(26)]*	114.1(2) 114.7(4)
sum	178.1(8)	180.6(12)	[C(11) ... C(16)]–[C(31) ... C(36)]*	64.6(2) 67.4(3)
			[C(21) ... C(26)]–[C(31) ... C(36)]*	66.3(3) 68.6(4)

\* Angles between phenyl ring planes.

In the following discussion when values of the two compounds are quoted, the first one refers to complex (2) and the second to (6). Throughout the paper an averaged value is the weighted mean and the corresponding e.s.d. is the largest of the values of the 'internal' and 'external' deviations.<sup>8</sup> When two values  $x_1$  and  $x_2$  are compared the ratio  $\Delta/\sigma = |x_1 - x_2|/(\sigma_1^2 + \sigma_2^2)^{1/2}$  is considered, where  $\sigma_1$  and  $\sigma_2$  are the e.s.d.s of  $x_1$  and  $x_2$ , respectively. The e.s.d.s are given, in parentheses, in the last figure of the numbers they refer to.

**Co-ordination polyhedra.** The co-ordination polyhedra of the two complexes are quite similar and the differences involve only distances and angles influenced by the different nature of the two metal atoms. The polyhedra can be described as 'three-legged piano stools' deformed by the metallacyclobutane rings which impose C–M–C angles smaller than 90° (Figure 1). They can also be described as deformed octahedra if the C<sub>5</sub>Me<sub>5</sub>

ligand is assumed to be equivalent to three co-ordination sites, or as deformed tetrahedra, if the  $\eta^5$ -co-ordination of C<sub>5</sub>Me<sub>5</sub> is considered as a single co-ordination site. Steric effects due to interactions that the bulky C<sub>5</sub>Me<sub>5</sub> ligand exerts with the phenyls of the phosphine and the methyls and methylenes of the neopentyl (or silyl) moiety cause an increase in the cp–M–P and cp–M–C angles (cp is the centroid of the pentamethylcyclopentadienyl ligand) and a decrease in the P–M–C and C–M–C angles with respect to the tetrahedral values, the last being determined by the geometry of the four-membered metallacycle. These interactions, quoted in Table 5, condition the mutual orientation of the ligand as illustrated by the Newman projections of Figure 2. From projection (a) of Figure 2 it appears that the C<sub>5</sub>Me<sub>5</sub> ligand is oriented in such a way that the M ... C(cp) directions tend to eclipse the M–P and M–C bonds. This, together with the large value of the 'cone angle'<sup>9</sup> of C<sub>5</sub>Me<sub>5</sub>

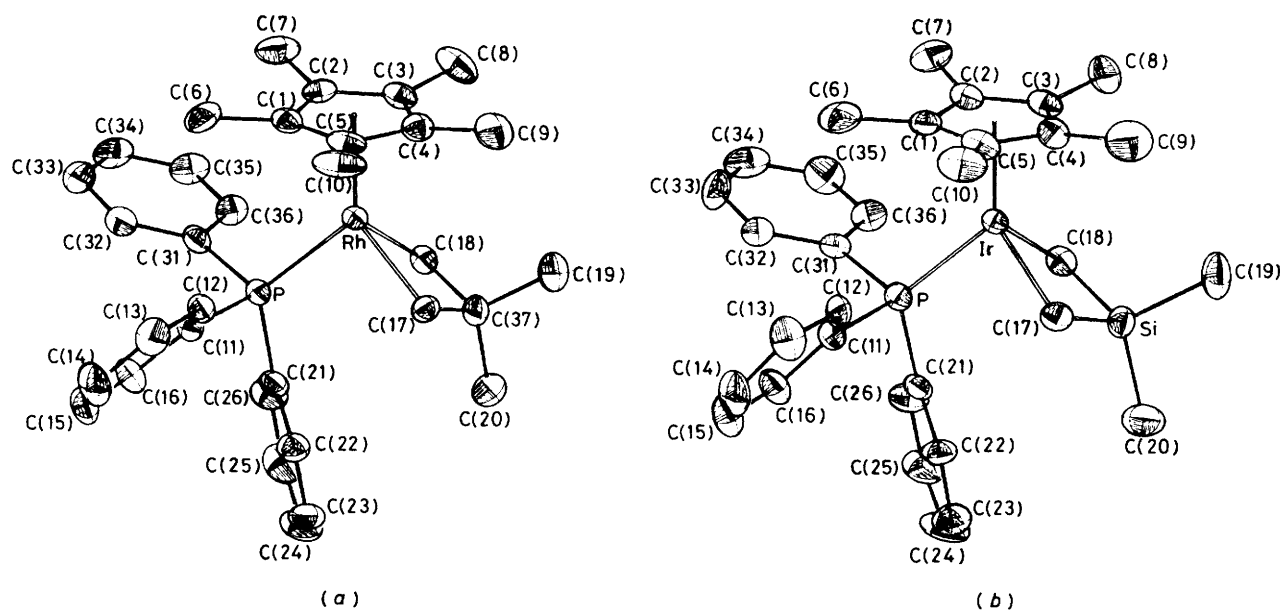


Figure 1. ORTEP Drawings of complexes  $[M(\text{CH}_2\text{CMe}_2\text{CH}_2)(\eta^5\text{-C}_5\text{Me}_5)(\text{PPh}_3)]$  [ $M = (a) \text{ Rh}$  or  $(b) \text{ Ir}$ ] showing that the thermal motion is essentially the same in the two compounds. The hydrogen atoms are omitted for clarity. Thermal ellipsoids are at 30% probability level

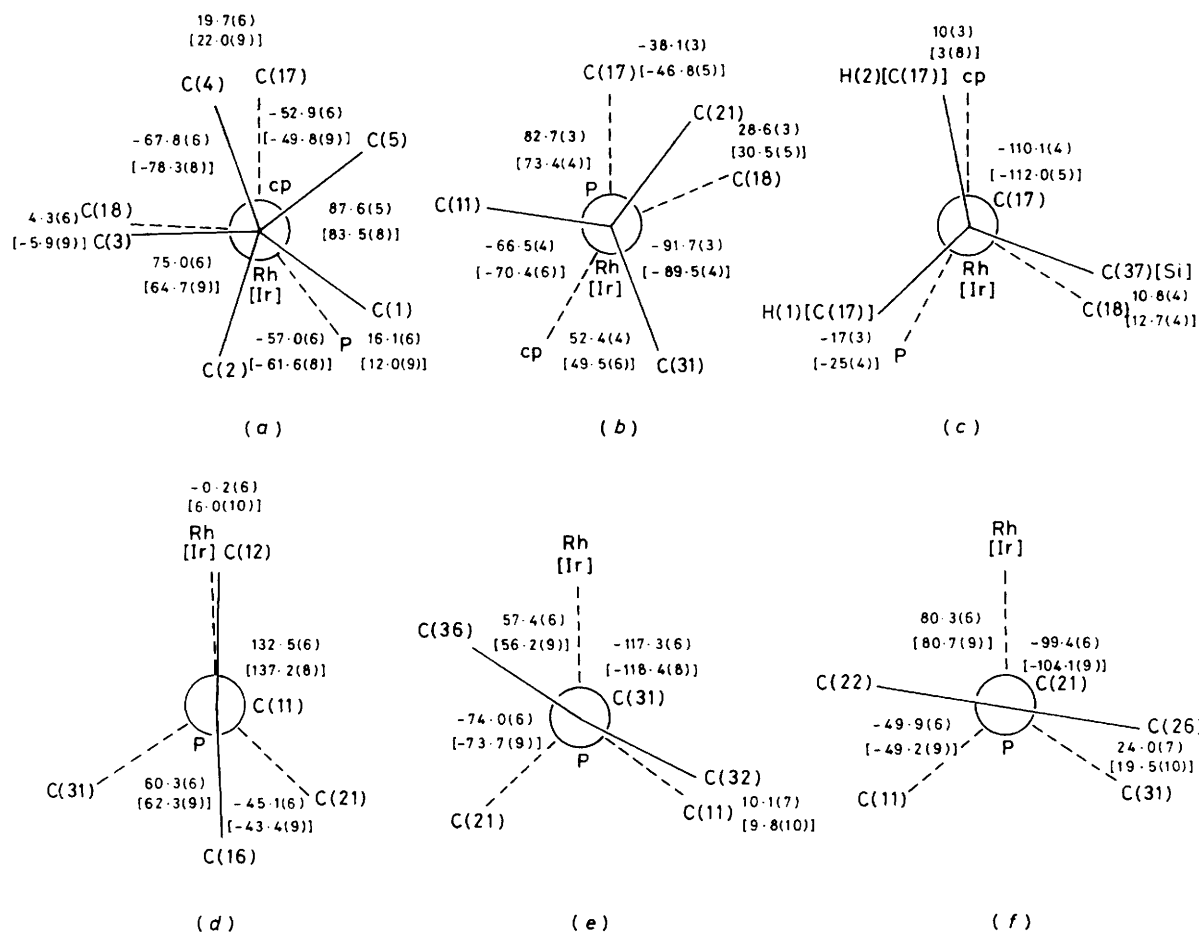


Figure 2. Newman projections along (a) cp-M, (b) P-M, (c) C(17)-M, (d) C(11)-P, (e) C(21)-P, (f) C(31)-P. cp = centroid of  $\text{C}_5\text{Me}_5$ . The values in square brackets refer to the Ir complex (6), the other values and the projections themselves correspond to the Rh complex (2)

**Table 4.** Results of thermal motion analysis. Eigenvectors (inertial frame) and eigenvalues are for the rigid-body model.  $\bar{\Delta}$  = mean difference of the mean-square vibrational amplitudes along the interatomic directions for all pairs of atoms of the segment,  $\Delta U = U_{ij}(\text{obs.}) - U_{ij}(\text{calc.})$ ,  $R'_v = [\Sigma(w\Delta U)^2/\Sigma(wU_o)^2]^{\frac{1}{2}}$ ,  $\sigma(\Delta U) = [\Sigma(w\Delta U)^2/\Sigma w^2]^{\frac{1}{2}}$ ,  $\bar{\sigma}$  = mean e.s.d. of  $U_o$ , g.l.a. = group libration amplitude,  $I$  = moment of inertia

	Rh					Ir				
	eigenvectors			(eigenvalues) <sup>†</sup>	<i>I</i> /a.m.u. Å <sup>2</sup>	eigenvectors			(eigenvalues) <sup>†</sup>	<i>I</i> /a.m.u. Å <sup>2</sup>
Segment: all non-H atoms										
<i>L</i> -tensor	0.9209	0.0398	−0.3878	3.4°	3 258	0.8264	0.1568	0.5408	3.4°	3 484
	−0.3859	−0.0485	−0.9213	2.8	4 168	0.4682	0.3424	−0.8146	2.8	4 323
	−0.0555	0.9980	−0.0293	2.6	4 570	−0.3131	0.9264	0.2095	2.7	4 960
<i>T</i> -tensor	−0.4594	−0.6783	−0.5734	0.189 Å		−0.6412	−0.7029	0.3079	0.198 Å	
	0.8882	−0.3489	−0.2989	0.172		0.6856	−0.7050	−0.1815	0.182	
	0.0027	−0.6466	0.7628	0.167		0.3446	0.0948	0.9339	0.164	
	$\bar{\Delta} = 0.010(14)$ , $R'_v = 0.118$ , $\sigma(\Delta U) = 0.0030$ , $\bar{\sigma} = 0.0046$					$\bar{\Delta} = 0.013(17)$ , $R'_v = 0.071$ , $\sigma(\Delta U) = 0.0018$ , $\bar{\sigma} = 0.0072$				
Segment: all non-H atoms, 4 non-rigid body groups										
(1) C(1) ... C(10) librating about M-cp; g.l.a. = 5.0(3)°						(1) C(1) ... C(10) librating about M-cp; g.l.a. = 4.7(4)°				
(2) C(12) ... C(16) librating about C(11)-P; g.l.a. = 3.4(22)						(2) C(12) ... C(16) librating about C(11)-P; g.l.a. = 2.1(46)				
(3) C(22) ... C(26) librating about C(21)-P; g.l.a. = 3.5(21)						(3) C(22) ... C(26) librating about C(21)-P; g.l.a. = 3.2(24)				
(4) C(32) ... C(36) librating about C(31)-P; g.l.a. = negative value*						(4) C(32) ... C(36) librating about C(31)-P; g.l.a. = 4.2(21)				
<i>L</i> -tensor	0.9233	−0.0349	−0.3824	3.2°	3 258	0.7954	0.1622	0.5839	3.2°	3 484
	−0.3810	−0.0414	−0.9236	2.6	4 168	−0.1999	0.9798	0.0002	2.6	4 323
	−0.0481	0.9985	−0.0250	2.2	4 570	−0.5721	−0.1169	0.8118	2.5	4 960
<i>T</i> -tensor	−0.3848	−0.6594	−0.6458	0.191 Å		−0.6056	−0.7241	0.3300	0.201 Å	
	0.6976	0.2504	−0.6713	0.172		0.6796	−0.6864	−0.2588	0.181	
	0.6044	−0.7088	0.3636	0.172		0.4139	0.0676	0.9078	0.167	
	$\bar{\Delta} = 0.010(14)$ , $R'_v = 0.093$ , $\sigma(\Delta U) = 0.0024$ , $\bar{\sigma} = 0.0046$					$\bar{\Delta} = 0.013(17)$ , $R'_v = 0.061$ , $\sigma(\Delta U) = 0.0016$ , $\bar{\sigma} = 0.0072$				
Segment: M, E, C(17), C(18), C(19), C(20)										
<i>L</i> -tensor	0.9743	0.1242	−0.1878	5.0°	69.4	−0.2380	0.5066	−0.8287	5.2°	97.8
	−0.2233	0.6404	−0.7348	4.1	350.3	−0.8940	−0.4478	−0.0170	3.8	556.6
	0.0290	0.7579	0.6517	3.7	355.7	−0.3797	0.7367	0.5595	2.4	567.2
<i>T</i> -tensor	0.7483	−0.0260	−0.6629	0.199 Å		0.9622	0.0816	−0.2598	0.203 Å	
	−0.6045	−0.4384	−0.6652	0.178		0.520	0.8816	0.4692	0.174	
	−0.2733	0.8984	−0.3437	0.165		0.2673	0.4649	0.8440	0.172	
	$\bar{\Delta} = 0.006(8)$ , $R'_v = 0.018$ , $\sigma(\Delta U) = 0.0004$ , $\bar{\sigma} = 0.0040$					$\bar{\Delta} = 0.012(17)$ , $R'_v = 0.021$ , $\sigma(\Delta U) = 0.0005$ , $\bar{\sigma} = 0.0060$				
Segment: M, P, C(11), C(21), C(31), C(17), C(18)										
<i>L</i> -tensor	0.9235	−0.0297	−0.3823	3.1°	186.9	0.9864	0.1174	−0.1152	3.7°	202.0
	−0.3288	0.4519	−0.8293	2.1	419.2	−0.1540	0.9049	−0.3967	2.2	474.7
	0.1974	0.8916	0.4075	0.8	443.0	0.0577	0.4090	0.9107	0.7	490.2
<i>T</i> -tensor	−0.5442	−0.5795	−0.6067	0.193 Å		−0.5323	−0.8335	−0.1481	0.204 Å	
	−0.0054	0.7256	−0.6882	0.179		0.7524	−0.5460	0.3684	0.187	
	0.8390	−0.3712	−0.3979	0.173		−0.3880	−0.0847	0.9178	0.168	
	$\bar{\Delta} = 0.004(5)$ , $R'_v = 0.032$ , $\sigma(\Delta U) = 0.0008$ , $\bar{\sigma} = 0.0031$					$\bar{\Delta} = 0.006(8)$ , $R'_v = 0.020$ , $\sigma(\Delta U) = 0.0005$ , $\bar{\sigma} = 0.0047$				

\* The negative mean square amplitude indicates that the data are not good enough or the model is not suitable to describe the libration of the group.

which is \* 142 and 147° in (2) and (6) respectively, justifies the large values for the cp-M-P and cp-M-C angles.

Projection (b) of Figure 2 shows that the P-C bonds of the triphenylphosphine ligand are staggered with respect to the M-C and M-cp bonds so as to reduce to a minimum the steric hindrance between the phosphine and the other two ligands. A perfectly planar metallacycle should impose an exact eclipsing of the M-C(18), M-P, and M-cp bonds by the C(17)-E [E = C(37) or Si], C(17)-H(1) [C(17)], and C(17)-H(2) [C(17)] bonds respectively, but the puckering of the metallacyclobutane ring reduces the hindrance of the eclipsing by a torsional angle of ca. 10° [Figure 2(c)]. Thus a compromise is reached between the required staggering, which should

correspond to the minimum hindrance, and the imposed eclipsing, which should give the maximum steric effect.

The M-cp vector is perpendicular to the cyclopentadienyl plane, the angles being 88.6(2) and 90.1(4)° in the two complexes. The M-C(cp) distances in both compounds do not show the regular trends found in other cases,<sup>10,11</sup> and the difference [0.042(13) \AA] between their mean values [2.304(9) and 2.262(9) \AA] is a little larger than the difference (0.02 \AA) of the metal atomic radii, as is the case for the M-C distances involving the metallacycle carbon atoms which are longer [av. 2.100(5) and 2.159(7) \AA] and show a difference of 0.059(9) \AA. On the contrary, the M-P distances, 2.230(2) and 2.236(2) \AA, are not significantly different.

**Pentamethylcyclopentadienyl ligand.** No significant distortion from five-fold symmetry, as observed in other cases,<sup>10,11</sup> has been found. The carbon atoms of the ring are perfectly coplanar in both compounds [ $\Sigma(\Delta/\sigma)^2 = 0.41$  and 0.43] and the differences in the endocyclic C-C distances [av. 1.427(6) and 1.426(8) \AA] are not significant. The C-C distances are similar

\* The 'effective' cone angle has been calculated as twice the angle formed by the 'axis' of the ligand, i.e. the M-cp (or M-P in the case of phosphine) direction, and the tangent from M to the most external hydrogen atom sphere to which a van der Waals radius of 1.20 \AA has been attributed.

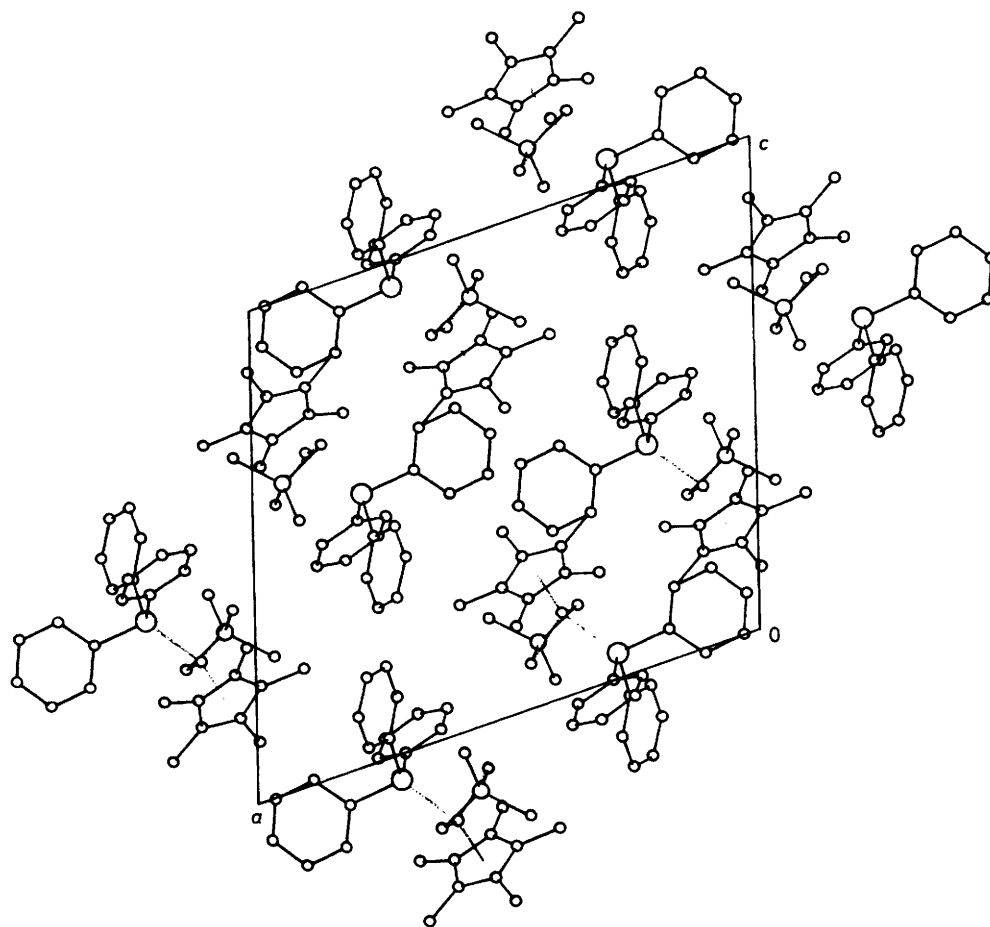


Figure 3. Packing of the complex molecules in the unit cell

**Table 5.** Selected intramolecular non-bonding contacts (Å) between ligands for complexes (2) and (6)

	Rh	Ir
P...C(1)	3.489(7)	3.45(1)
P...C(17)	3.187(6)	3.16(1)
P...C(18)	3.076(6)	3.08(1)
H(2)[C(6)]...H[C(32)]	2.93(9)	2.85(12)
H(1)[C(8)]...H(2)[C(18)]	2.82(9)	2.64(12)
H(1)[C(8)]...H(1)[C(19)]	2.60(11)	2.74(15)
H(1)[C(9)]...H(2)[C(17)]	2.40(7)	2.70(11)
H(1)[C(9)]...H(1)[C(19)]	2.75(11)	3.16(15)
H(2)[C(9)]...H(1)[C(19)]	2.31(10)	2.73(20)
H(2)[C(9)]...H(2)[C(19)]	3.54(8)	2.68(16)
H[C(22)]...H(1)[C(17)]	2.30(5)	2.25(10)
H[C(36)]...H(1)[C(18)]	2.42(6)	2.48(10)

and their mean values, 1.510(5) and 1.511(7) Å, correspond quite well to the expected value, 1.515(5) Å, for a  $C(sp^2)-C(sp^3)$  single bond.<sup>12</sup> All five methyl groups deviate significantly from the ring plane with mean displacements of 0.187(21) (range 0.120–0.231) and 0.170(17) (range 0.137–0.226) Å in a direction opposite to the metal atom. These displacements, which are commonly found in  $\eta^5-C_5Me_5$  metal complexes, seem to be due to the steric hindrance which the methyl groups experience when the ligand approaches the metal, their effect being to reduce the effective cone angle of the ligand.

**Metallacyclic ring.** In both complexes, the metallacyclic

moiety is not planar, as clearly indicated by the deviations from the mean plane [ $\Sigma(\Delta/\sigma)^2 = 871$  and 1 093] and puckering amplitudes:<sup>13</sup>  $Q = 0.048(2)$  and  $0.061(2)$  Å. From the data collected in Table 6, where the relevant parameters of metallacyclobutanes are compared, it appears that the hypothesis that puckering should be observed only with platinum complexes<sup>14</sup> is not verified. Probably, more than the nature of the metal, the relevant factors which influence the puckering are the presence and the number of substituents at the ring and the bulkiness and crowding of the other ligands. Moreover, puckering itself is effective in reducing the intraring strain, which, on the other hand, is smaller in the metallacyclobutane ring than in cyclobutane as a consequence of the ring expansion.<sup>14</sup> Substitution of rhodium by iridium and carbon by silicon results in an increase in the corresponding bond distances and non-bonding contacts in the ring, a large increase in the angle at the metal from 66.8(2) to 77.3(4)°, and a small decrease (3–4°) in the other angles. The two E–C endocyclic bond distances are similar within (2) and (6) and the difference, 0.303(11) Å, between their averaged values corresponds quite well to the difference, 0.34 Å, in the covalent radii of silicon and carbon. The same is true for the exocyclic E–C bond distances for which the difference between the averaged values is 0.348(11) Å. The exocyclic C–C and Si–C bonds are a little longer than the corresponding endocyclic ones, but the difference is significant only in the case of Si ( $\Delta/\sigma = 4.23$ ). The bond angles formed by C(37) and Si deviate considerably from the tetrahedral value [97.6(5)–114.5(6) and

**Table 6.** Comparison of relevant geometrical parameters of metallacyclobutanes (E = C or Si)

Compound	Ref. <sup>a</sup>	R	M–C/ Å	E–C/ Å	C...C/ Å	E...M/ Å	$\hat{M}/^\circ$	$\hat{C}/^\circ$	$\hat{E}/^\circ$	(MCC)–(CCE)) <sup>o</sup>
[Ti(CH <sub>2</sub> CHBu <sup>1</sup> CH <sub>2</sub> )(η <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> ]	b*	0.172	2.16 2.14	1.55 1.53	?	?	75	84 85	116	?
[Ti(CH <sub>2</sub> CHPhCH <sub>2</sub> )(η <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> ]	b*	0.036	2.127(3) 2.113(4)	1.546(5) 1.579(5)	?	?	75.3(1)	86.0(2) 85.7(2)	112.0(3)	3.2
[Ti(CH <sub>2</sub> CMe <sub>2</sub> CH <sub>2</sub> )(η <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> ]	b*	0.042	2.138(8) 2.152(7)	1.59(1) 1.58(1)	?	?	74.8(3)	87.2(4) 87.0(4)	110.9(6)	?
[Ti(CH <sub>2</sub> SiMe <sub>2</sub> CH <sub>2</sub> )(η <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> ]	c	0.047	A2.146(3) B2.169(4) 2.152(5) 2.095(6) 2.106(7)	1.863(3) 1.865(5) 1.855(5) 1.539(10) 1.531(9)	2.874(5) 2.883(6) 2.784(2)	2.772(2) 2.784(2)	84.1(2) 83.7(2) 87.0(2) 66.8(2)	87.2(1) 87.0(2) 87.7(2) 96.6(4) 96.4(4)	101.0(2) 101.6(2)	7.6(2) 0 16.5(4)
[Rh(CH <sub>2</sub> CMe <sub>2</sub> CH <sub>2</sub> )(η <sup>5</sup> -C <sub>5</sub> Me <sub>5</sub> )(PPh <sub>3</sub> ) <sub>3</sub> ]	d	0.044	2.253(9) B2.236(9) 2.243(9)	1.827(10) 1.844(10) 1.836(10)	2.797(11) 2.788(11)	2.956(2) 2.955(2)	77.0(4) 77.0(4)	91.9(3) 92.2(3) 92.3(3)	98.9(4) 98.5(4)	1.6(3) 0.5(3)
[Os(CH <sub>2</sub> SiMe <sub>2</sub> CH <sub>2</sub> )(PMe <sub>3</sub> ) <sub>4</sub> ]	e	0.0388	A2.241(9) 2.253(9) B2.236(9) 2.243(9)	1.855(10) 1.827(10) 1.844(10) 1.836(10)	2.797(11) 2.788(11)	2.956(2) 2.955(2)	77.0(4) 77.0(4)	91.9(3) 92.2(3) 92.3(3)	98.9(4) 98.5(4)	1.6(3) 0.5(3)
[Ir(CH <sub>2</sub> SiMe <sub>2</sub> CH <sub>2</sub> )(η <sup>5</sup> -C <sub>5</sub> Me <sub>5</sub> )(PPh <sub>3</sub> ) <sub>3</sub> ]	d	0.039	2.158(10) 2.160(11)	1.840(12) 1.833(11)	2.697(16)	2.894(3)	77.3(4)	92.4(4) 92.5(4)	94.5(5)	18.9(6)
[Pt(CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> )(bipy)]	f	0.036	2.030(10) 2.037(10)	1.534(14) 1.534(13)	2.329(15)	2.665(10)	69.9(4)	95.5(6) 95.8(6)	98.8(8)	3.3(6)
[Pt(CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> )Cl <sub>2</sub> (bipy)]	f	0.078	2.07(4)	1.63(6)	2.43(5)	2.75(9)	71.9(23)	96.0(30)	96.2(51)	0
[Pt(CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> )Cl <sub>2</sub> (C <sub>5</sub> H <sub>5</sub> N) <sub>2</sub> ]	g	0.094	2.04(5) 2.19(5)	1.48(8) 1.82(9)	2.55(10)	2.71(6)	74.2(19)	99.3(35) 84.3(27)	100.9(38)	12(4)
[Pt(CH <sub>2</sub> CMe <sub>2</sub> CH <sub>2</sub> )(PEt <sub>3</sub> ) <sub>2</sub> ]	h	0.032	2.086(6) 2.080(6)	1.536(9) 1.535(9)	2.309(9)	2.698(7)	67.3(3)	95.1(4) 95.4(4)	97.5(5)	22.4(4)
[Pt{C(CN) <sub>2</sub> CH <sub>2</sub> C(CN) <sub>2</sub> }(PPh <sub>3</sub> ) <sub>2</sub> ]	i	0.035	2.137(6) 2.139(6)	1.545(9) 1.584(9)	2.404(9)	2.712(6)	68.4(2)	93.5(4) 92.3(4)	100.4(5)	24.4(4)
[Pt(CHPhCHPhCH <sub>2</sub> )(C <sub>5</sub> H <sub>5</sub> N) <sub>2</sub> ]	j	0.097	A2.06(3) 2.11(5) B2.05(3) 2.17(3)	1.59(7) 1.48(5) 1.59(4) 1.71(4)	2.39(7) 2.60(4)	2.60(4) 2.62(3)	70(2) 76(1)	90(2) 91(3) 91(2) 84(2)	102(3) 104(2)	28(3) 22(2)
[Pt(CHCO <sub>2</sub> MeCOCHCO <sub>2</sub> Me)(PPh <sub>3</sub> ) <sub>2</sub> ]	k*	0.040	2.149(6) 2.128(6)	? ?	? ?	? ?	? ?	? ?	? ?	49.7
[Pt{C(CN) <sub>2</sub> CHPhC(CN) <sub>2</sub> }(PPh <sub>3</sub> ) <sub>2</sub> ]	l	0.029	2.137(6) 2.159(6)	1.557(9) 1.548(10)	2.394(9)	2.694(8)	67.7(2)	92.3(4) 91.7(4)	100.9(6)	28.6(6)
[Pt{C(CN) <sub>2</sub> CHPhC(CN)(CO <sub>2</sub> Et)}(PPh <sub>3</sub> ) <sub>2</sub> ]	l	0.056	2.158(14) 2.200(14)	1.556(19) 1.509(19)	2.403(20)	2.687(15)	66.9(2)	91.2(8) 90.8(8)	103.2(11)	29.7(13)
[Th(CH <sub>2</sub> SiMe <sub>2</sub> CH <sub>2</sub> )(η <sup>5</sup> -C <sub>5</sub> Me <sub>5</sub> ) <sub>2</sub> ]	m*	0.048	2.463(13) 2.485(14)	1.914(15) 1.931(14)	?	?	75.2(4)	90.6	103.4	5.8
[Zr(CH <sub>2</sub> SiMe <sub>2</sub> CH <sub>2</sub> )(η <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> ]	n	0.044	2.240(5)	1.870(5)	2.868(9)	2.875(2)	81.0(2)	88.3(2)	102.2(3)	4.7
[Nb(CH <sub>2</sub> SiMe <sub>2</sub> CH <sub>2</sub> )(η <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> ]	n	0.034	2.275(3)	1.848(4)	2.804(7)	2.983(1)	76.1(2)	92.1(1)	98.7(2)	10.4
[Mo(CH <sub>2</sub> SiMe <sub>2</sub> CH <sub>2</sub> )(η <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> ]	n	0.043	2.301(5)	1.831(5)	2.718(9)	3.061(2)	72.4(2)	94.9(2)	95.8(3)	14.3

<sup>a</sup> References marked with an asterisk do not quote the atomic co-ordinates, so it was not possible to calculate the missing data. For refs. c, e, and j, A and B refer to the two molecules in the asymmetric unit. <sup>b</sup> J. B. Lee, G. J. Gajda, W. P. Schaefer, T. R. Howard, T. Ikariya, D. A. Straus, and R. H. Grubbs, *J. Am. Chem. Soc.*, 1981, **103**, 7358. <sup>c</sup> W. R. Tikkanen, J. Z. Liu, J. W. Egan, jun., and J. L. Petersen, *Organometallics*, 1984, **3**, 825. <sup>d</sup> This work. <sup>e</sup> Ref. 1(d). <sup>f</sup> R. J. Klinger, J. C. Huffman, and J. K. Kochi, *J. Organomet. Chem.*, 1981, **206**, C7; *J. Am. Chem. Soc.*, 1982, **104**, 2147; bipy = 2,2'-bipyridyl. <sup>g</sup> R. D. Gillard, M. Keeton, R. Mason, M. F. Pilbrow, and D. R. Russell, *J. Organomet. Chem.*, 1971, **33**, 247. <sup>h</sup> J. A. Ibers, R. Di Cosimo, and G. M. Whitesides, *Organometallics*, 1982, **1**, 13. <sup>i</sup> D. J. Yarrow, J. A. Ibers, M. Lenarda, and M. Graziani, *J. Organomet. Chem.*, 1974, **70**, 133. <sup>j</sup> J. A. McGinnety, *J. Organomet. Chem.*, 1973, **59**, 429. <sup>k</sup> D. A. Clarke, R. D. W. Kemmitt, M. A. Mazid, M. D. Schilling, and D. R. Russell, *J. Chem. Soc., Chem. Commun.*, 1978, 744. <sup>l</sup> Ref. 14. <sup>m</sup> J. W. Bruno, T. J. Marks, and V. W. Day, *J. Am. Chem. Soc.*, 1982, **104**, 7357. <sup>n</sup> W. R. Tikkanen, J. W. Egan, jun., and J. L. Petersen, *Organometallics*, 1984, **3**, 1646.

94.5(5)—116.7(5)° as a consequence of the ring closure, but their averages coincide with the theoretical tetrahedral value.

**Triphenylphosphine.** The C—C distances and the endocyclic angles of the phenyl rings are normal and their averaged values are quoted in Table 3. The M—P—C angles within each compound are quite significantly different, however, the mean values of both compounds are practically the same [av. 116.6(37) and 116.5(31)°]. Also the C—P—C angles are significantly different within each ligand, but the means are equal in the two compounds [av. 101.5(20) and 101.7(19)°] and always smaller than the M—P—C angles. These observations can be easily justified by considering that the phenyl appendices are

folded backwards so as to reduce the effective cone angle,<sup>9</sup> which is 139 and 140° in (2) and (6), respectively. As is shown in Figure 2(b), the P—C bonds are staggered with respect to the M—cp and M—C bonds, and the phenyl rings are oriented in such a way as to minimize the hindrance between themselves and the C<sub>5</sub>Me<sub>5</sub> ligand and the metallacycle. This causes the P—M and P—C(11) bonds to be nearly eclipsed by the C(11)—C(12) and C(31)—C(32) bonds respectively [Figure 2(d) and (f)]. The phosphorus atoms do not lie exactly in the planes of the phenyl rings, and show small, but significant, displacements in the ranges 0.011(2)—0.087(2) and 0.014(3)—0.061(3) Å in (2) and (6), respectively.

**Packing.** The molecules are packed under the effect of van der Waals forces, as is indicated by the fact that there are no contacts less than the sum of the van der Waals radii. Figure 3, which shows the packing, is valid for both complexes, as their crystals are isostructural.

### Conclusions

Alkylation of  $[\text{RhCl}_2(\eta^5\text{-C}_5\text{Me}_5)(\text{PPh}_3)]$  with  $\text{Mg}(\text{CH}_2\text{CMe}_3)\text{-Cl}$  in pentane gives the rhodacyclobutane (2), while alkylation of  $[\text{MCl}_2(\eta^5\text{-C}_5\text{Me}_5)(\text{PPh}_3)]$  ( $\text{M} = \text{Rh}$  or  $\text{Ir}$ ) with  $\text{Mg}(\text{CH}_2\text{-SiMe}_3)\text{-Cl}$  gives the dialkyl derivatives (4) or (5) respectively. Complex (5) is converted to the iridasilacyclobutane (6) only after being heated for a week at  $50^\circ\text{C}$ . By assuming that thermolysis of (5) mimics the formation of the rhodacyclobutane derivative (2), one could imagine that in the alkylation of (1) an unstable dineopentyl derivative is formed which then decomposes to give the metallacyclobutane derivative (2).

Actually neopentyl complexes generally have a lower thermal stability than their trimethylsilyl analogues {for instance the average bond energy  $E(\text{M}-\text{C})$  is  $268\text{ kJ mol}^{-1}$  in the case of  $[\text{Ti}(\text{CH}_2\text{SiMe}_3)_4]$  and  $184\text{ kJ mol}^{-1}$  in the case of  $[\text{Ti}(\text{CH}_2\text{CMe}_3)_4]$ .<sup>15</sup> Although the way in which thermochemical and structural properties relate to each other is not obvious, steric hindrance factors could play an important role in determining the greater stability of trimethylsilylmethyl systems with respect to the neopentyl analogues: actually, the methyl groups are closer to the metal in neopentyl systems than in the trimethylsilylmethyl derivatives. Then it is quite plausible in systems like  $[\text{RhR}_2(\eta^5\text{-C}_5\text{Me}_5)(\text{PPh}_3)]$  where the cone angles of the ancillary ligands are high, that the replacement of silicon by carbon could cause a variation in the thermal stability great enough to preclude the isolation of the dineopentyl derivative.

Another point of interest is the mechanism by which these cyclometallation reactions proceed. Two major alternative mechanisms have been proposed in the literature: (i) oxidative addition of an alkyl ligand to give a metallacyclic intermediate, or (ii) a concerted mechanism in which one of the alkyl groups abstracts a hydrogen from the other.<sup>1</sup> By assuming that also in our case the stepwise mechanism proposed for other Group 8 transition-metal systems is operating, one could conclude that a species of rhodium(v) or iridium(v) is involved as an intermediate. This is a relatively high oxidation state for such metals; however a number of organometallic derivatives of rhodium(v) and iridium(v) have been prepared recently by Maitlis and co-workers<sup>15</sup> and rhodium(v) and iridium(v) intermediates have been proposed for some intermolecular C-H activation reactions.<sup>16</sup> Thus it is not unreasonable to consider such species as intermediates in a stepwise mechanism, even though it appears that steric effects are of fundamental importance in this case.

### Experimental

All reactions and manipulations of organometallics were carried out under dinitrogen or argon. The solvents were dried and distilled. The compounds  $[\text{MCl}_2(\eta^5\text{-C}_5\text{Me}_5)(\text{PPh}_3)]$  ( $\text{M} = \text{Rh}$  or  $\text{Ir}$ ),<sup>17</sup>  $\text{Mg}(\text{CH}_2\text{CMe}_3)\text{-Cl}$ ,<sup>18</sup> and  $\text{Mg}(\text{CH}_2\text{SiMe}_3)\text{-Cl}$ <sup>19</sup> were prepared as described previously. Hydrogen-1 n.m.r. spectra were run at 60 MHz on a Varian T60 instrument and at 100 MHz on a Varian XL100 spectrometer with  $\text{SiMe}_4$  as internal standard. Carbon-13 and phosphorus-31 n.m.r. spectra were run on a Varian XL100 instrument. Mass spectra were obtained with a Varian MAT model CH7 spectrometer. Microanalyses were performed by the Laboratorio di Microanalisi of the Istituto di Chimica Organica Facoltà Farmacia, Università di Pisa.

(2,2-Dimethylpropane-1,3-diyl)( $\eta^5$ -pentamethylcyclopentadienyl)(triphenylphosphine)rhodium(III) (2).—To a suspension of  $[\text{RhCl}_2(\eta^5\text{-C}_5\text{Me}_5)(\text{PPh}_3)]$  (1) (0.25 g, 0.438 mmol) in pentane ( $30\text{ cm}^3$ ) was added at  $0^\circ\text{C}$   $\text{Mg}(\text{CH}_2\text{CMe}_3)\text{-Cl}$  ( $3\text{ cm}^3$  of a  $0.74\text{ mol dm}^{-3}$  solution in  $\text{Et}_2\text{O}$ , 2.2 mmol). The reaction mixture was warmed to room temperature and stirred for a further 2 h. After removal of solvent the residue was extracted with pentane ( $50\text{ cm}^3$ ). The extract was reduced to *ca.*  $5\text{ cm}^3$  and applied to a chromatographic column constructed with Merck alumina 90 (activity grade II–III) as the absorbant. Elution with pentane gave a yellow band. After evaporation of the solvent to  $5\text{ cm}^3$ , the solution was cooled at  $-20^\circ\text{C}$  to give yellow crystals of (2) (0.12 g, 48%) (Found: C, 69.8; H, 7.1.  $\text{C}_{33}\text{H}_{40}\text{PRh}$  requires C, 69.5; H, 7.0%).

An  $^1\text{H}$  n.m.r. tube was charged with (2) (0.01 g) in  $\text{CCl}_2\text{FCF}_2\text{Cl}$  ( $1\text{ cm}^3$ ). A slight excess of bromine was added. After shaking, the tube was transferred to a n.m.r. probe. The  $^1\text{H}$  n.m.r. spectrum showed the formation of 1,3-dibromo-2,2-dimethylpropane (63%) ( $\delta_{\text{H}}$  1.18 and 3.40 p.p.m.) and 1,1-dimethylcyclopropane (37%) ( $\delta_{\text{H}}$  0.20 and 1.04 p.p.m.), these absorptions coinciding with those of authentic samples. An  $^1\text{H}$  n.m.r. tube was charged with (2) (0.01 g) and  $\text{CCl}_2\text{FCF}_2\text{Cl}$  ( $0.5\text{ cm}^3$ ), and thermostatted at  $30^\circ\text{C}$  for 2 d. The  $^1\text{H}$  n.m.r. spectrum showed formation of 1,1-dimethylcyclopropane.

( $\eta^5$ -Pentamethylcyclopentadienyl)bis(trimethylsilylmethyl)-(triphenylphosphine)rhodium(III) (4).— $[\text{RhCl}_2(\eta^5\text{-C}_5\text{Me}_5)(\text{PPh}_3)]$  (1) (0.400 g, 0.70 mmol) in diethyl ether ( $15\text{ cm}^3$ ) was treated at  $-78^\circ\text{C}$  with  $\text{Mg}(\text{CH}_2\text{SiMe}_3)\text{-Cl}$  ( $5.9\text{ cm}^3$  of  $0.59\text{ mol dm}^{-3}$  solution in diethyl ether, 3.48 mmol). The mixture was then stirred at room temperature for 2 h. The solvent was removed and the residue extracted with pentane ( $30\text{ cm}^3$ ). The pentane extracts were hydrolysed at  $0^\circ\text{C}$  with water ( $2\text{ cm}^3$ ) and the organic layer was separated and dried over sodium sulphate. The solution was concentrated to *ca.*  $3\text{ cm}^3$  and chromatographed at  $0^\circ\text{C}$  over an alumina column. Elution with pentane gave a golden yellow band. Removal of the solvent gave (4) as a solid compound (0.211 g, 45%). The compound can be crystallised from pentane at  $-20^\circ\text{C}$  to give golden yellow crystals (0.114 g) (Found: C, 64.3; H, 7.9; P, 5.1.  $\text{C}_{36}\text{H}_{52}\text{PRhSi}_2$  requires C, 64.1; H, 7.8; P, 4.6%).

( $\eta^5$ -Pentamethylcyclopentadienyl)bis(trimethylsilylmethyl)-(triphenylphosphine)iridium(III) (5).—To a suspension of  $[\text{IrCl}_2(\eta^5\text{-C}_5\text{Me}_5)(\text{PPh}_3)]$  (3) (0.38 g, 0.58 mmol) in diethyl ether ( $5\text{ cm}^3$ ) was added  $\text{Mg}(\text{CH}_2\text{SiMe}_3)\text{-Cl}$  ( $6.9\text{ cm}^3$  of a  $0.59\text{ mol dm}^{-3}$  solution in ether, 4.07 mmol) at  $-78^\circ\text{C}$ . The reaction mixture was stirred at room temperature for 4 h. The deep-red solution was evaporated, and the residue extracted with pentane ( $40\text{ cm}^3$ ). The pentane extracts were hydrolysed at  $0^\circ\text{C}$  with water ( $2\text{ cm}^3$ ) and the organic layer dried over sodium sulphate. The pentane solution was concentrated to *ca.*  $3\text{ cm}^3$  and chromatographed at  $0^\circ\text{C}$  through a column of neutral alumina. Elution with pentane gave a yellow-green band. Evaporation of the solvent gave a yellow solid, (5) (0.227 g, 51%). The product was crystallized from pentane at  $-20^\circ\text{C}$  to give yellow crystals (0.111 g) (Found: C, 57.0; H, 6.6.  $\text{C}_{36}\text{H}_{52}\text{IrPSi}_2$  requires C, 56.6; H, 6.9%). A second red band which developed slowly with pentane-ether (1:1) decomposed before elution was completed.

**Thermolysis of  $[\text{M}(\text{CH}_2\text{SiMe}_3)_2(\eta^5\text{-C}_5\text{Me}_5)(\text{PPh}_3)]$  ( $\text{M} = \text{Rh}$  or  $\text{Ir}$ ): General Procedure.**—Complex (4) or (5) (0.03 mmol) was dissolved in  $\text{C}_6\text{D}_6$  or  $\text{C}_6\text{D}_{12}$  ( $0.5\text{ cm}^3$ ). The solutions were transferred to an n.m.r. tube, sealed, and maintained at constant temperature. Decomposition was followed by monitoring by  $^1\text{H}$  n.m.r. spectroscopy. When decomposition was complete, g.l.c. analysis was performed on the solution for identification of organic products. When the thermolysis was carried out in a

**Table 7.** Experimental data for the crystallographic analyses of  $[\text{Rh}(\text{CH}_2\text{CMe}_2\text{CH}_2)(\eta^5\text{-C}_5\text{Me}_5)(\text{PPh}_3)]$  (2) and  $[\text{Ir}(\text{CH}_2\text{SiMe}_2\text{CH}_2)(\eta^5\text{-C}_5\text{Me}_5)(\text{PPh}_3)]$  (6) ( $N$  = number of observations,  $P$  = number of refined parameters)

Compound	(2)	(6)
Formula	$\text{C}_{33}\text{H}_{40}\text{PRh}$	$\text{C}_{32}\text{H}_{40}\text{IrPSi}$
$M$	570.56	675.95
Space group	$P2_1/n$	$P2_1/n$
$a/\text{\AA}$	17.199(6)	17.098(7)
$b/\text{\AA}$	10.987(4)	11.294(5)
$c/\text{\AA}$	16.064(5)	15.977(7)
$\beta/^\circ$	109.54(2)	108.17(2)
$U/\text{\AA}^3$	2 861(2)	2 931(2)
$Z$	4	4
$D_c/\text{Mg m}^{-3}$	1.325	1.532
$D_m/\text{Mg m}^{-3}$	1.31	1.35
Reflections for lattice parameters { number $\theta$ range/°	24 14.1–21.1	30 14.5–23.1
Radiation	Mo- $K_{\alpha 1}$	Mo- $K_{\alpha 1}$
$\lambda/\text{\AA}$	0.709 30	0.709 30
$F(000)$	1 192	1 352
$T/\text{K}$	294	294
Crystal size/mm	$0.14 \times 0.26 \times 0.29$	$0.24 \times 0.32 \times 0.31$
Diffractometer	Philips PW1100	Philips PW1100
$\mu/\text{mm}^{-1}$	0.660	4.648
Absorption correction (min, max.)		1.000 67, 1.168 53
Scan speed/° s <sup>-1</sup>	0.10	0.10
Scan width/°	1.20	1.50
$\theta$ -range/°	3–25	3–23.5
$h$ -range	$\overline{19}$ –19	$\overline{18}$ –18
$k$ -range	$\overline{13}$ –13	0–12
$l$ -range	0–19	0–17
Standard reflection	$\delta$ 2 3	$\delta$ 2 3
Intensity variation	< 3%	< 2%
Scan mode	$\theta/2\theta$	$\omega/2\theta$
No. of measured reflections	6 964	4 752
Condition for observed reflections	$I \geq 3\sigma(I)$	$I \geq 2\sigma(I)$
No. of observed reflections	4 236	3 143
No. of reflections used in the refinement	2 782	3 031
$R_{\text{int}} = \Sigma(I - \langle I \rangle)/\Sigma I$	0.337	0.0365
Anisotropic least-squares on $F$	Block-diagonal	Block-diagonal
Max. least-squares shift-to-error ratio	0.10	0.40
Min., max. height in final Fourier map, $\Delta\rho/\text{e \AA}^{-3}$	–0.12, 0.18	–0.19, 0.22
No. of refined parameters	477	477
$R = \Sigma\Delta F/\Sigma F_o $	0.0441	0.0389
$R' = [\Sigma w(\Delta F)^2/\Sigma wF_o^2]^{\frac{1}{2}}$	0.0406	0.0394
$S = [\Sigma w(\Delta F)^2/(N - P)]^{\frac{1}{2}}$	1.396	1.352
$w$	$1/\sigma^2(F)$	$1/\sigma^2(F)$

solution of hexane or neopentane, Schlenk tubes and rubber septums were used and samples analysed by g.l.c. and, after evaporation of the solvent, by  $^1\text{H}$  n.m.r.

**Thermal Decomposition of  $[\text{Ir}(\text{CH}_2\text{SiMe}_2)_2(\eta^5\text{-C}_5\text{Me}_5)(\text{PPh}_3)]$  (5):** Preparation of  $[\text{Ir}(\text{CH}_2\text{SiMe}_2\text{CH}_2)(\eta^5\text{-C}_5\text{Me}_5)(\text{PPh}_3)]$  (6).— $[\text{Ir}(\text{CH}_2\text{SiMe}_2)_2(\eta^5\text{-C}_5\text{Me}_5)(\text{PPh}_3)]$  (5) (0.120 g, 0.157 mmol) and cyclohexane (5 cm<sup>3</sup>) were put in a cylindrical vial having a central neck and a side arm which was connected to a vacuum nitrogen system. The vial was sealed off and set in a water-bath maintained at 50 °C. After 7 d, the organic products were removed under vacuum, collected into a trap cooled at –78 °C, and analysed by g.l.c. The residue was extracted with pentane (20 cm<sup>3</sup>), filtered, and the resulting solution concentrated under vacuum to 2 cm<sup>3</sup>. By cooling at –20 °C overnight, yellow crystals of (6) were obtained (0.042 g, 40%) [Found: C, 56.7; H, 6.0%;  $M^+$ , 676 ( $^{193}\text{Ir}$ ).  $\text{C}_{32}\text{H}_{40}\text{IrPSi}$  requires C, 56.9; H, 6.0%;  $M$ , 676].

**Crystal Structure Analyses.**—Table 7 summarizes the relevant data concerning the crystal structure analysis. The

lattice parameters were refined by a least-squares procedure<sup>20</sup> using the Nelson and Riley<sup>21</sup> extrapolation function. All reflections were corrected for Lorentz and polarization, while absorption effects were corrected only for the iridium compound (6) using the azimuthal scan method.<sup>22</sup> The structures were 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 SHELX76 program.<sup>23</sup> All hydrogen atoms were located from difference Fourier syntheses and refined isotropically. Atomic scattering factors and anomalous scattering coefficients were taken from the literature.<sup>24</sup> The calculations were carried out on the GOULD-SEL 32/77 computer of the Centro di Studio per la Strutturistica Diffattometrica del CNR (Parma). In addition to the quoted program, PARST,<sup>25</sup> THMV7,<sup>26</sup> ORTEP,<sup>27</sup> and PLUTO<sup>28</sup> programs were used.

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