

## Synthesis, X-Ray Structure, and Reactivity with Lewis Acids of Metallacyclopentane Derivatives of Rhodium(III) and Iridium(III). Observation of the First Boron Trifluoride-promoted C–H Bond Activation in Transition Metal Alkyls †

Roberto Bertani, Pietro Diversi, Giovanni Ingrassio,\* Antonio Lucherini, and Fabio Marchetti  
Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via Risorgimento 35, 56100 Pisa, Italy  
Victor Adovasio and Mario Nardelli\*

Istituto di Chimica Generale ed Inorganica dell'Università di Parma, Centro di Studio per la Strutturistica  
Diffraattometrica del CNR, Viale delle Scienze, 43100 Parma, Italy

Sergio Pucci

Centro di Studio del CNR per le Macromolecole Stereordinate ed Otticamente Attive, Via Risorgimento 35,  
56100 Pisa, Italy

The metallacyclopentanes  $[M\{\text{CH}_2\text{CH}(\text{R})\text{CH}(\text{R}')\text{CH}_2\}(\eta^5\text{-C}_5\text{Me}_5)(\text{PPh}_3)]$  [(1b) M = Rh, R = Me, R' = H; (1c) M = Rh, R = R' = Me; (1e) M = Ir, R = Me, R' = H; (1f) M = Ir, R = R' = Me; (1g) M = Ir, R = Pr, R' = H] were prepared by reacting the appropriate alkylating reagent  $M'[\text{CH}_2\text{CH}(\text{R})\text{CH}(\text{R}')\text{CH}_2]M'$  (M' = Li or MgCl) with the dichlorides of formula  $[MCl_2(\eta^5\text{-C}_5\text{Me}_5)(\text{PPh}_3)]$ . Complexes (1) were characterized by elemental analysis,  $^1\text{H}$  n.m.r., and mass spectrometry. The X-ray crystal structures of (1c), (1e), and (1f) have been determined. (1c) and (1f) give isostructural  $P2_1/c$  crystals, while (1e) crystallizes in the space group  $C2/c$ . The cell constants are: (1c),  $a = 14.982(9)$ ,  $b = 11.058(6)$ ,  $c = 18.421(10)$  Å,  $\beta = 101.13(2)^\circ$ ,  $Z = 4$ ,  $R$  (3 964 reflections, 493 parameters) = 0.0443; (1e),  $a = 33.63(4)$ ,  $b = 9.29(1)$ ,  $c = 20.56(2)$  Å,  $\beta = 116.6(2)^\circ$ ,  $Z = 8$ ,  $R$  (3 196, 476) = 0.0472; (1f),  $a = 15.01(2)$ ,  $b = 11.10(1)$ ,  $c = 18.44(2)$  Å,  $\beta = 100.90(4)^\circ$ ,  $Z = 4$ ,  $R$  (4 136, 446) = 0.0334. All compounds possess a structure of the 'three-legged piano stool' type, the major differences lying in the puckering of the metallacyclopentane rings which is larger in the dimethylated derivatives (1c) and (1f) than it is in (1e), where the metallacyclic moiety is rather flattened. The endocyclic  $C_\alpha\text{-}C_\beta$  bond in (1e) is 1.34(3) Å, while it is 1.51(1) and 1.52(1) Å in (1c) and (1f), respectively. The rhoda- and irida-cyclopentanes (1a) (M = Rh, R = R' = H), (1b), (1c), and (1d) (M = Ir, R = R' = H), (1e), and (1f) react under very mild conditions, with  $\text{BF}_3\cdot\text{Bu}^n\text{O}$  and with  $[\text{CPh}_3][\text{PF}_6]$  to give the  $\eta^3$ -allyl complexes  $[M\{\eta^3\text{-CH}_2\text{C}(\text{R})\text{C}(\text{R}')\text{Me}\}(\eta^5\text{-C}_5\text{Me}_5)(\text{PPh}_3)][\text{BF}_4]$  (2) and  $[M\{\eta^3\text{-CH}_2\text{C}(\text{R})\text{C}(\text{R}')\text{Me}\}(\eta^5\text{-C}_5\text{Me}_5)(\text{PPh}_3)][\text{PF}_6]$  (3) [(a) M = Rh, R = R' = H; (b) M = Rh, R = Me, R' = H; (c) M = Rh, R = R' = Me; (d) M = Ir, R = R' = H; (e) M = Ir, R = Me, R' = H; (f) M = Ir, R = R' = Me], respectively, via the regiospecific hydrogen abstraction from the alkyl-substituted  $\beta$ -carbon atom by Lewis acids. Complexes (2) and (3) were characterized by elemental analysis,  $^1\text{H}$  n.m.r., and fast atom bombardment mass spectrometry.

By virtue of their structure metallacycloalkanes offer the opportunity to study how the chemical behaviour of hydrocarbon chains alters when they are constrained around a transition metal atom. The results reported to date<sup>1</sup> suggest that marked electronic modifications may occur at the carbon chains within the metallacyclic moieties<sup>2-5</sup> that make such chains capable of exhibiting a reactivity which has no parallel in the conventional chemistry of hydrocarbon skeletons.

In this connection, the reaction of metallacycles with Lewis acids is enlightening. Depending upon both the nature of the acid and the structure of the metallacycle, several types of reactions may occur,<sup>1</sup> including the unusually mild aluminium(III)-promoted carbon-carbon cleavage of four-membered titanium(IV) metallacycles,<sup>6,7</sup> the  $\text{AlEt}_3$ - and  $\text{BF}_3$ -promoted displacements of the metal from nickelacyclopentanes,<sup>8</sup> and the conversion of palladium(II),<sup>9</sup> rhodium(III),<sup>10</sup> and iridium(III)<sup>10</sup> metallacyclopentanes to cationic  $\eta^3$ -butenyl complexes via the abstraction of a  $\beta$ -hydrogen atom by the trityl cation.

The reasons why metallacyclic C–C and C–H bonds can undergo reactions with Lewis acids are not obvious. However, at least in some cases, X-ray diffraction studies have shown some structural features within the metallacyclic moieties which suggest possible explanations for some aspects of the above reactivity. This is the case for some molybdenum,<sup>3</sup> cobalt,<sup>2</sup> rhodium,<sup>2</sup> and iridium<sup>2</sup> metallacyclopentanes which exhibit two interesting structural features, namely the presence of some C–C bond distances which remain shorter than the standard  $\text{C}(sp^3)\text{-C}(sp^3)$ , even after correction for thermal motion effects and the puckering of the ring, so that one  $\beta$ -carbon atom is closer to the metal than the other, which may resemble an early transition state for facile  $\beta$ -hydrogen release. These data suggest some questions. Are the above shortenings real and of some generality? What is the correlation, if any, between the observation of short endocyclic C–C distances and the facile  $\beta$ -hydrogen release? How does the presence of groups at the ring carbon atoms influence the ring conformation?

This paper is an attempt to provide some answers, through the X-ray diffraction study of some new alkyl-substituted rhoda- and irida-cyclopentanes, and by examining the reactions of these metallacycles with Lewis acids. We have found that a variety of rhoda- and irida-cyclopentanes lose easily a  $\beta$ -hydro-

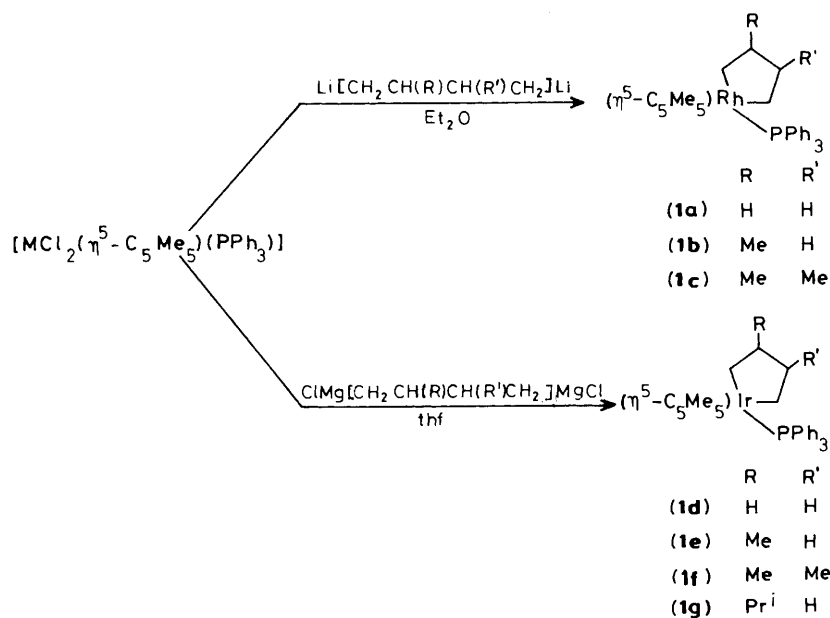
† Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii–xx.

Non-S.I. unit employed: mmHg  $\approx$  133 Pa.

**Table 1.** Analytical and spectroscopic data for the metallacyclopentane derivatives (**1b**), (**1c**), and (**1e**)–(**1g**)

Compound	Colour	Analysis <sup>a</sup> (%)			<i>m/z</i> <sup>b</sup>	<sup>1</sup> H N.m.r. data <sup>c</sup>
		C	H	F		
( <b>1b</b> ) [Rh{CH <sub>2</sub> CH(Me)CH <sub>2</sub> CH <sub>2</sub> }(η <sup>5</sup> -C <sub>5</sub> Me <sub>5</sub> )(PPh <sub>3</sub> )]	Orange-yellow	69.50 (69.45)	7.10 (7.65)	5.50 (5.45)	570	0.53–0.80 (5, br m, CH <sub>2</sub> CH <sub>2</sub> -CHMe), 1.10–1.39 (4, br m, Rh-CH <sub>2</sub> ), 1.40 (15, d, <i>J</i> 2 Hz, C <sub>5</sub> Me <sub>5</sub> ), 1.60–2.00 (1, br m, CHMe), 7.26 (15, m, Ph)
( <b>1c</b> ) [Rh{CH <sub>2</sub> CH(Me)CH(Me)CH <sub>2</sub> }(η <sup>5</sup> -C <sub>5</sub> Me <sub>5</sub> )(PPh <sub>3</sub> )]	Orange-yellow	70.00 (69.85)	7.30 (7.25)	5.20 (5.30)	584	0.4–0.6 (6, m, CHMe), 0.70–1.33 (4, br m, Rh-CH <sub>2</sub> ), 1.43 (15, d, <i>J</i> 2 Hz, C <sub>5</sub> Me <sub>5</sub> ), 1.60–2.20 (2, br m, CH), 7.30 (15, m, Ph)
( <b>1e</b> ) [Ir{CH <sub>2</sub> CH(Me)CH <sub>2</sub> CH <sub>2</sub> }(η <sup>5</sup> -C <sub>5</sub> Me <sub>5</sub> )(PPh <sub>3</sub> )]	Yellow	60.05 (60.00)	6.10 (6.15)	4.70 (4.75)	660 <sup>d</sup>	0.63–0.86 (3, m, CHMe), 0.93–1.36 (4, br m, Ir-CH <sub>2</sub> ), 1.43 (15, d, <i>J</i> 2 Hz, C <sub>5</sub> Me <sub>5</sub> ), 1.57–2.10 (3, br m, CH <sub>2</sub> CH-Me), 7.25 (15, m, Ph)
( <b>1f</b> ) [Ir{CH <sub>2</sub> CH(Me)CH(Me)CH <sub>2</sub> }(η <sup>5</sup> -C <sub>5</sub> Me <sub>5</sub> )(PPh <sub>3</sub> )]	Yellow	60.65 (60.60)	6.30 (6.30)	4.65 (4.60)	674 <sup>d</sup>	0.43–0.73 (6, m, CHMe), 0.90–1.40 (4, br m, Ir-CH <sub>2</sub> ), 1.40 (15, d, <i>J</i> 2 Hz, C <sub>5</sub> Me <sub>5</sub> ), 1.60–2.16 (2, br m, CHMe), 7.30 (15, m, Ph)
( <b>1g</b> ) [Ir{CH <sub>2</sub> CH(Pr <sup>i</sup> )CH <sub>2</sub> CH <sub>2</sub> }(η <sup>5</sup> -C <sub>5</sub> Me <sub>5</sub> )(PPh <sub>3</sub> )]	Yellow	61.05 (61.10)	6.50 (6.45)	4.60 (4.50)	688 <sup>d</sup>	0.70 (6, m, CHMe <sub>2</sub> ), 0.80–1.25 (4, m, Ir-CH <sub>2</sub> CH <sub>2</sub> ), 1.33 (2, d, <i>J</i> 6 Hz, Ir-CH <sub>2</sub> CH), 1.43 (15, d, <i>J</i> 2 Hz, C <sub>5</sub> Me <sub>5</sub> ), 1.70–2.50 (2, br m, CHCHMe <sub>2</sub> ), 7.3 (15, m, Ph)

<sup>a</sup> Calculated values are given in parentheses. <sup>b</sup> Mass spectra: molecular ions only are given. <sup>c</sup> Measured in CDCl<sub>3</sub> solution at 37 °C, and referenced to SiMe<sub>4</sub> as internal standard. Given as chemical shift (δ), relative intensity, multiplicity, coupling constant, assignment; br = broad, d = doublet, m = multiplet. <sup>d</sup> Given for <sup>193</sup>Ir.

**Scheme 1.**

gen and transform into cationic η<sup>3</sup>-allyl complexes by reacting with BF<sub>3</sub>·Bu<sup>n</sup><sub>2</sub>O, this being, to our knowledge, the first example of boron trifluoride-promoted C–H bond activation in transition metal alkyls.

## Results

*Synthesis of Rhoda- and Irida-cyclopentanes.*—Scheme 1 outlines the reactions employed for the preparation of the metallacyclopentane derivatives (**1**). Complexes (**1a**) and (**1d**)

**Table 2.** Fractional atomic co-ordinates ( $\times 10^4$ ) with estimated standard deviations (e.s.d.s) in parentheses

Atom	Complex (1c) (M = Rh)			Complex (1e) (M = Ir)			Complex (1f) (M = Ir)		
	X/a	Y/b	Z/c	X/a	Y/b	Z/c	X/a	Y/b	Z/c
M	2 252.9(2)	731.5(3)	2 574.8(2)	1 468.6(1)	-227.2(4)	-1 581.7(2)	2 251.6(2)	727.0(2)	2 568.2(1)
P	2 363(1)	1 269(1)	3 759(1)	1 250(1)	-68(3)	-2 773(1)	2 367(1)	1 273(2)	3 750(1)
C(1)	1 355(4)	2 266(5)	1 986(3)	1 715(4)	-2 566(12)	-1 367(7)	1 362(4)	2 232(7)	1 993(3)
C(2)	1 047(3)	1 152(5)	1 652(3)	1 437(4)	-2 282(12)	-1 014(6)	1 054(5)	1 123(7)	1 651(4)
C(3)	1 777(3)	660(5)	1 339(3)	1 647(4)	-1 180(12)	-490(6)	1 788(4)	634(6)	1 335(3)
C(4)	2 517(3)	1 495(5)	1 481(3)	2 050(4)	-826(12)	-508(6)	2 525(4)	1 489(6)	1 472(3)
C(5)	2 267(3)	2 478(4)	1 885(3)	2 086(4)	-1 650(12)	-1 049(6)	2 284(4)	2 469(6)	1 877(4)
C(6)	777(5)	3 165(6)	2 313(3)	1 612(5)	-3 743(12)	-1 939(7)	806(6)	3 175(7)	2 323(4)
C(7)	100(4)	647(7)	1 545(3)	1 025(5)	-3 111(14)	-1 124(8)	102(5)	619(8)	1 542(4)
C(8)	1 712(5)	-430(5)	846(3)	1 506(5)	-730(15)	63(8)	1 709(6)	-446(7)	847(4)
C(9)	3 396(4)	1 379(6)	1 203(3)	2 404(5)	153(15)	11(7)	3 410(5)	1 349(8)	1 197(4)
C(10)	2 791(4)	3 625(5)	2 059(3)	2 504(5)	-1 783(15)	-1 153(8)	2 799(6)	3 620(7)	2 042(5)
C(11)	2 958(3)	315(5)	4 526(3)	1 108(4)	1 698(11)	-3 229(6)	2 966(4)	317(7)	4 519(3)
C(12)	3 747(4)	638(6)	5 010(3)	1 399(4)	2 519(13)	-3 378(7)	3 757(5)	642(7)	4 999(4)
C(13)	4 119(4)	-130(8)	5 599(4)	1 285(5)	3 882(14)	-3 684(8)	4 132(6)	-100(10)	5 589(5)
C(14)	3 718(5)	-1 196(8)	5 702(4)	874(5)	4 411(11)	-3 847(7)	3 724(6)	-1 157(9)	5 703(5)
C(15)	2 933(5)	-1 540(7)	5 231(4)	586(5)	3 614(13)	-3 697(8)	2 933(6)	-1 520(8)	5 227(5)
C(16)	2 555(4)	-779(6)	4 654(3)	691(4)	2 294(12)	-3 398(7)	2 561(5)	-762(8)	4 640(4)
C(17)	1 876(4)	-1 075(4)	1 724(3)	859(4)	646(13)	-1 714(7)	1 869(5)	-1 081(6)	2 725(4)
C(18)	2 687(4)	-1 943(5)	2 849(4)	903(5)	2 245(16)	-1 464(11)	2 667(5)	-1 963(7)	2 856(5)
C(19)	3 468(4)	-1 365(6)	2 565(4)	1 321(7)	2 754(17)	-1 181(13)	3 470(5)	-1 416(8)	2 580(5)
C(20)	3 534(3)	-81(5)	2 839(3)	1 653(4)	2 007(12)	-1 380(6)	3 553(4)	-78(7)	2 825(4)
C(21)	2 929(4)	2 733(5)	3 946(3)	1 664(4)	-781(11)	-3 043(6)	2 927(5)	2 736(7)	3 931(4)
C(22)	3 834(4)	2 816(5)	3 842(3)	2 087(4)	-196(13)	-2 715(7)	3 835(5)	2 824(7)	3 827(4)
C(23)	4 286(5)	3 901(7)	3 965(4)	2 422(5)	-706(19)	-2 868(9)	4 302(7)	3 907(9)	3 953(5)
C(24)	3 879(7)	4 918(7)	4 144(4)	2 340(6)	-1 797(21)	-3 347(10)	3 875(10)	4 933(10)	4 141(6)
C(25)	2 985(7)	4 851(6)	4 227(4)	1 934(6)	-2 409(15)	-3 657(8)	2 990(9)	4 870(8)	4 220(5)
C(26)	2 508(4)	3 773(5)	4 118(3)	1 590(5)	-1 910(12)	-3 514(7)	2 513(6)	3 780(7)	4 121(4)
C(27)	2 436(5)	-3 205(6)	2 592(4)	544(7)	2 764(18)	-1 315(12)	2 401(6)	-3 231(8)	2 608(5)
C(28)	4 370(4)	-2 065(6)	2 773(4)				4 356(6)	-2 142(8)	2 788(5)
C(31)	1 294(3)	1 433(4)	4 094(3)	743(4)	-1 069(11)	-3 377(6)	1 299(4)	1 425(6)	4 094(3)
C(32)	1 283(4)	1 833(5)	4 815(3)	560(4)	-964(13)	-4 120(7)	1 283(5)	1 844(7)	4 814(4)
C(33)	477(4)	1 875(6)	5 072(3)	179(5)	-1 736(16)	-4 548(7)	469(6)	1 892(8)	5 080(4)
C(34)	-326(4)	1 543(6)	4 615(3)	-1(5)	-2 647(15)	-4 237(9)	-325(5)	1 539(8)	4 641(5)
C(35)	-320(4)	1 139(6)	3 910(3)	175(5)	-2 756(14)	-3 502(9)	-326(5)	1 117(8)	3 937(5)
C(36)	487(4)	1 087(5)	3 658(3)	542(4)	-1 970(12)	-3 059(7)	485(5)	1 078(6)	3 670(4)

have already been described elsewhere;<sup>2,11,12</sup> all the others are new compounds. The employment of 1,4-dilithiobutane and 1,4-dihalogenomagnesium butanes for the cyclodialkylation of the starting rhodium and iridium dichlorides, respectively, was dictated by our previous studies which demonstrated the critical dependence of metallacycle yields upon the nature of the alkylating reagent.<sup>11</sup> In Table 1 we report the analytical, <sup>1</sup>H n.m.r., and mass spectral data for the new complexes. The resonances of metallacyclic protons give broad signals which cover relatively large ranges of frequency. However, comparison of the spectra of the complexes (1b)–(1g) with those of the unsubstituted<sup>2</sup> and partially or fully<sup>10</sup> deuteriated isostructural rhoda- and irida-cyclopentanes leaves no ambiguity about the structural assignment.

The electron impact (e.i.) mass spectra of the rhodium complexes (1b) and (1c) show weak molecular ions [relative intensity (r.i.) < 1%] at  $m/z$  570 and 584, respectively. On the contrary, in the iridium derivatives (1e)–(1g), the molecular ion peaks are intense (r.i. 15–30%). The rhodium and the iridium complexes all exhibit similar fragmentation patterns including the formation of the following ions:  $[M(C_5Me_5)(PPh_3)]^+$ ,  $[M(C_5Me_5)_2CH_2CH(R)CH(R)CH_2]^+$ , and  $[M(C_5Me_5)]^+$ , which are of diagnostic importance.

*Crystal Structure Analysis of Metallacyclopentanes.*—This study was limited to complexes (1c), (1e), and (1f), since we failed to obtain crystals suitable for X-ray diffraction by

crystallization of the other metallacycles. Atomic co-ordinates of the non-hydrogen atoms are given in Table 2 and Table 3 shows the relevant structural parameters for the three complexes giving also the interatomic distances corrected for thermal motion. This correction was carried out using the rigid-body approximation of Schomaker and Trueblood<sup>13</sup> taking into account the libration of the  $C_5Me_5$  ligand, the phenyl groups, and the metallacycle carbon atoms relative to the rigid-body core of the molecule according to the one-parameter model of Dunitz and White.<sup>14</sup> From the relevant data of this analysis (see supplementary data) it appears that the motions do not change markedly in the three compounds and are similar to those found in some isostructural metallacyclobutane derivatives of rhodium and iridium we have studied recently.<sup>15</sup>

*Co-ordination polyhedra.* As it can be deduced from the data quoted in Table 3, and as shown in Figure 1, the co-ordination polyhedra of the three complexes are quite similar to those already described from some analogous metallacyclobutane derivatives,<sup>15</sup> the most relevant differences involving the C–M–C angles formed by the M–C 'legs' of the 'piano stool' co-ordination polyhedron which are now more open as a consequence of the increased ring size. The same considerations about the mutual orientation of the bulky  $C_5Me_5$  and  $PPh_3$  ligand already developed in a previous paper<sup>15</sup> apply to the compounds (1c), (1e), and (1f), as shown by the Newman projections in Figure 2, which illustrates that the ligands are arranged essentially in the same manner in the three

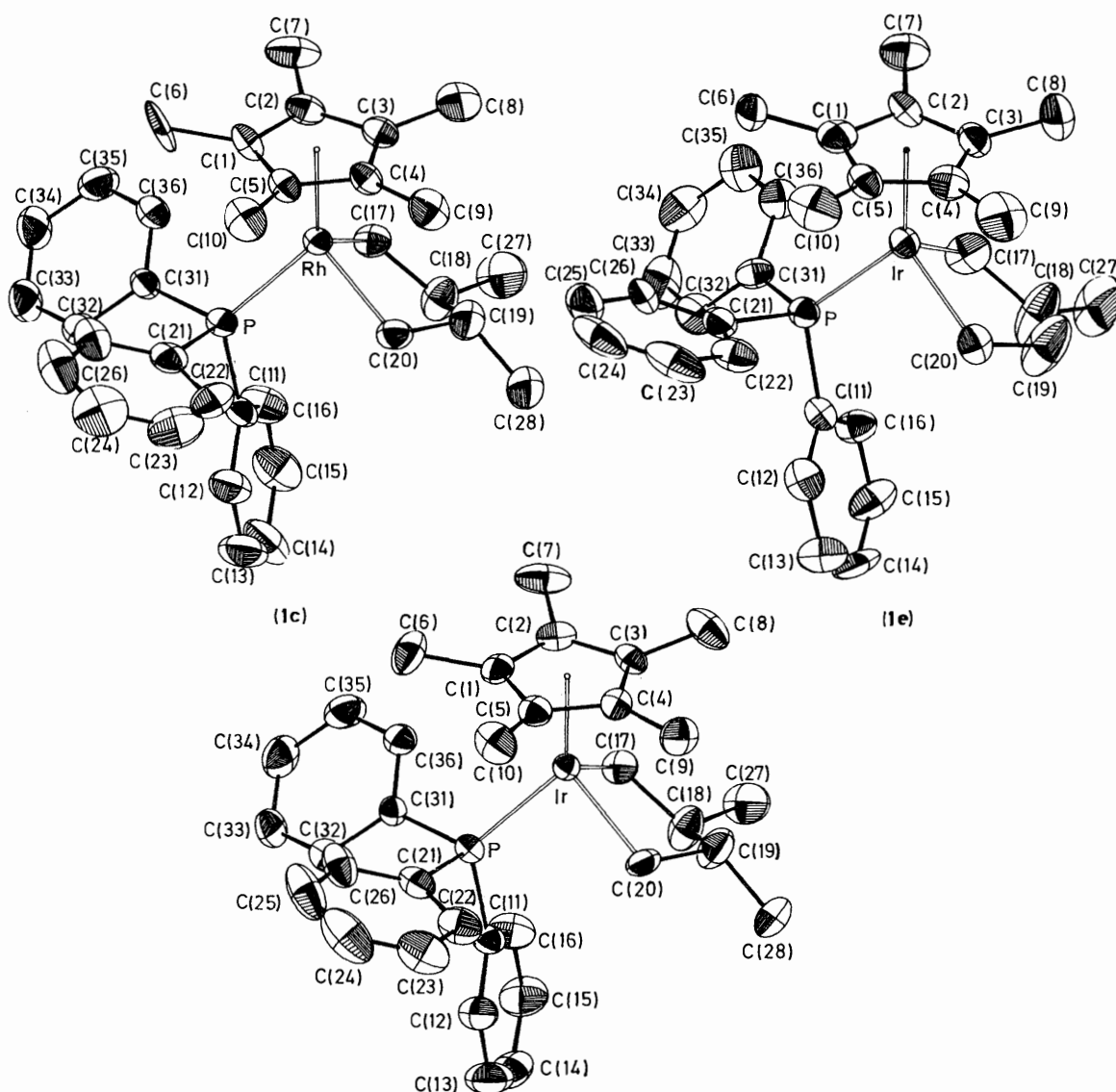


Figure 1. ORTEP Drawings of (1c), (1e), and (1f) showing thermal ellipsoids at 40% probability

compounds. In particular, the  $C_5Me_5$  ligand is oriented in such a way as to have a  $cp$ -(pentagon vertex) direction ( $cp$  = centroid of  $C_5Me_5$ ) nearly eclipsed by the  $M-C(20)$  bond [Figure 2(a)], and the triphenylphosphine  $P-C$  bonds are staggered with respect to the  $M-C$  bonds [Figure 2(b)].

**Metallacyclopentane ring.** The metallacyclopentane ring is puckered, this depending upon the nature of the substituents at the carbon atoms of the rings (see Table 4, where relevant parameters defining several metallacyclopentane rings are compared). Considering the puckering parameters of Cromer and Pople<sup>16</sup> it appears that the largest puckering is observed either when both  $\beta$ - and  $\beta'$ -carbon atoms are not methylated or when they are both mono-methylated, while puckering is reduced in the case of 3,4-dimethylenemetallacyclopentane moieties or, alternatively, when the ring is mono-methylated.

From the asymmetry parameters<sup>17</sup> it appears that the most commonly adopted conformation is of the 'half-chair' type with the pseudo-two-fold axis along the  $\alpha$ -carbon, while the

envelope conformation is observed with the pseudo-mirror along the  $\alpha$ - or the  $\beta$ -carbon, or the metal itself.

As a consequence of the ring puckering the distance of C(18) from the plane through C(17), C(19), and C(27) is 0.408(7) Å in (1c), 0.402(9) Å in (1f), and much less, 0.178(19) Å in (1e); furthermore, the distance of C(19) from the plane through C(18), C(20), and C(28) is 0.461(7) Å in (1e) and 0.440(9) Å in (1f). As shown in Figure 2, projections (c) and (d), the C(17)-C(18) bond tends to eclipse the  $M-C(20)$  bond, while the C(20)-C(19) bond shows the tendency to assume a staggered conformation with respect to the  $M-C(17)$  bond.

No particular shortening of the ring bond distances are observed with the exception of C(18)-C(19) and C(18)-C(27) of (1e), which are, respectively, *ca.*  $6\sigma$  and  $2.5\sigma$  shorter than the expected  $C(sp^3)-C(sp^3)$  bond distance. Moreover, a flattening of the bonds formed by C(19) in (1e) and a relevant widening of the C(18)-C(19)-C(20) angle with respect to the expected tetrahedral value are observed. Even though the above

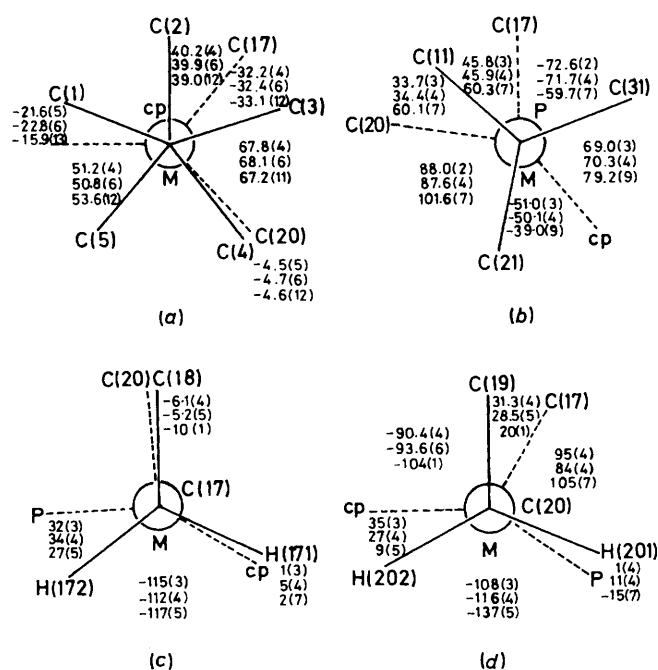
**Table 3.** Relevant structural parameters [distances (Å) and angles (°)] for complexes (1c), (1e), and (1f). Values corrected for thermal motion are given in square brackets; the weighted averages of these values are calculated by assigning them the e.s.d.s of the corresponding uncorrected values

	(1c)	(1e)	(1f)
Co-ordination sphere			
M-C(1)	2.302(5) [2.309]	2.297(11) [2.302]	2.272(7) [2.280]
M-C(2)	2.276(5) [2.282]	2.264(12) [2.269]	2.266(7) [2.274]
M-C(3)	2.251(5) [2.255]	2.231(12) [2.236]	2.252(6) [2.256]
M-C(4)	2.289(5) [2.292]	2.267(12) [2.273]	2.298(7) [2.302]
M-C(5)	2.315(5) [2.320]	2.286(12) [2.292]	2.322(7) [2.328]
Average M-C(1-5)	2.287(11) [2.292]	2.270(11) [2.276]	2.280(13) [2.286]
M-cp	1.939(5) [1.944]	1.923(11) [1.927]	1.928(7) [1.932]
M-P	2.237(2) [2.240]	2.224(4) [2.229]	2.237(3) [2.241]
M-C(17)	2.108(5) [2.114]	2.107(14) [2.113]	2.122(7) [2.129]
M-C(20)	2.089(5) [2.096]	2.153(11) [2.158]	2.118(7) [2.124]
Average M-C(17,20)	2.098(10) [2.105]	2.135(22) [2.141]	2.120(5) [2.126]
cp-M-P	130.8(2)	131.8(4)	131.0(2)
cp-M-C(17)	121.8(2)	123.8(7)	121.8(3)
cp-M-C(20)	125.0(2)	121.8(5)	124.0(3)
P-M-C(17)	95.5(2)	90.5(5)	95.6(2)
P-M-C(20)	89.8(2)	94.2(4)	89.9(2)
C(17)-M-C(20)	79.6(2)	80.4(5)	80.4(3)
(M-cp)-[C(1)···C(5)]	88.2(2)	88.2(6)	88.1(2)
C <sub>5</sub> Me <sub>5</sub> ligand			
Average C-C (ring)	1.424(6) [1.427]	1.416(8) [1.420]	1.436(10) [1.441]
Average C-CH <sub>3</sub>	1.504(4) [1.507]	1.508(9) [1.512]	1.508(8) [1.513]
Average C-C-C (ring)	108.0(4)	108.0(5)	108.0(6)
Average CH <sub>3</sub> ···(ring)	0.157(16)	0.159(27)	0.158(28)
Metallacyclic moiety			
C(17)-C(18)	1.531(8) [1.535]	1.557(20) [1.561]	1.531(10) [1.535]
C(19)-C(20)	1.503(9) [1.508]	1.518(30) [1.522]	1.551(11) [1.554]
Average	1.519(14) [1.523]	1.545(18) [1.549]	1.540(10) [1.544]
C(18)-C(19)	1.512(10) [1.515]	1.344(27) [1.347]	1.521(12) [1.523]
C(18)-C(27)	1.498(9) [1.502]	1.456(34) [1.460]	1.510(11) [1.512]
C(19)-C(28)	1.541(9) [1.546]		1.540(12) [1.544]
Average	1.520(22) [1.524]		1.524(15) [1.527]
M-C(17)-C(18)	112.9(4)	112.4(12)	113.7(5)
M-C(20)-C(19)	109.3(4)	108.0(11)	108.6(5)
Average	111.1(18)	110.0(22)	111.2(26)
C(17)-C(18)-C(19)	109.1(5)	114.0(15)	109.7(6)
C(17)-C(18)-C(27)	113.2(5)	114.8(14)	113.2(7)
C(19)-C(18)-C(27)	116.7(6)	126.7(17)	116.9(7)
Sum	339.0(9)	355.5(27)	339.8(12)
C(18)-C(19)-C(20)	106.8(5)	118.4(16)	108.1(7)
C(18)-C(19)-C(28)	113.7(5)		114.1(7)
C(20)-C(19)-C(28)	113.1(5)		114.2(7)
Triphenylphosphine ligand			
Average P-C	1.837(6) [1.842]	1.844(7) [1.849]	1.844(9) [1.850]
Average M-P-C	116.6(31)	117.3(22)	116.6(29)
Average C-P-C	101.6(23)	101.3(12)	101.3(26)
PPh <sub>3</sub> Cone angle	139	147	140
Phenyl rings			
Average C-C	1.383(3) [1.386]	1.375(5) [1.378]	1.390(4) [1.394]
Average C-C( <i>ipso</i> )-C	117.9(3)	118.1(7)	117.5(4)
Average C-C( <i>ortho</i> )-C	120.7(4)	120.2(6)	121.2(3)
Average C-C( <i>meta</i> )-C	120.4(4)	120.6(6)	119.9(3)
Average C-C( <i>para</i> )-C	119.6(5)	119.9(8)	120.0(5)
Sum	719.7(10)	719.6(16)	719.7(9)
M-P-C(11)-C(12)	69.5(5)	96.6(12)	114.7(6)
M-P-C(11)-C(16)	-114.5(5)	-79.3(12)	-69.0(7)
Sum	184.0(7)	175.9(17)	183.7(9)

**Table 4.** Comparison of the parameters of some metallacyclopentane rings

Compound	C-M-C/ $^{\circ}$	C-M (av.)/ $\text{\AA}$	C $_{\alpha}$ ...C $_{\alpha}$ / $\text{\AA}$	Q/ $\text{\AA}$	$\varphi$ / $^{\circ}$	Minimum asymmetry parameters <sup>b</sup>	Conformation	Ref.
(1c) [Rh{CH <sub>2</sub> CH(Me)CH(Me)CH <sub>2</sub> }( $\eta^5$ -C <sub>5</sub> Me <sub>5</sub> )-(PPh <sub>3</sub> )]	79.6(2)	2.098(10)	2.687(7)	0.471(6)	55.4(7)	$\Delta_2(C_{\alpha}) = 0.023\ 2(23)$	Half-chair	c
(1f) [Ir{CH <sub>2</sub> CH(Me)CH(Me)CH <sub>2</sub> }( $\eta^5$ -C <sub>5</sub> Me <sub>5</sub> )-(PPh <sub>3</sub> )]	80.4(3)	2.120(5)	2.736(10)	0.449(8)	56.1(9)	$\Delta_2(C_{\alpha}) = 0.024\ 7(33)$	Half-chair	c
(1e) [Ir{CH <sub>2</sub> CH(Me)CH <sub>2</sub> CH <sub>2</sub> }( $\eta^5$ -C <sub>5</sub> Me <sub>5</sub> )-(PPh <sub>3</sub> )]	80.4(5)	2.135(22)	2.751(18)	0.281(16)	145(4)	$\Delta_2(C_{\alpha}) = 0.021\ 7(77)$	Envelope	c
[Rh(CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> )( $\eta^5$ -C <sub>5</sub> Me <sub>5</sub> )(PPh <sub>3</sub> )]	80.2(4)	2.101(6)	2.707(6)	0.406(13)	52(2)	$\Delta_2(C_{\alpha}) = 0.012\ 3(44)$	Half-chair	d
[Ir(CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> )( $\eta^5$ -C <sub>5</sub> Me <sub>5</sub> )(PPh <sub>3</sub> )]	80.1(10)	2.118(17)	2.725(17)	0.360(34)	41(6)	$\Delta_2(C_{\alpha}) = 0.026\ 3(106)$	Half-chair	d
[Co(CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> )( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> )(PPh <sub>3</sub> )]	84.0(2)	2.025(3)	2.708(3)	0.454(6)	60.6(7)	$\Delta_2(C_{\alpha}) = 0.043\ 3(22)$	Half-chair	d
[Ir{CH <sub>2</sub> C(=CH <sub>2</sub> )C(=CH <sub>2</sub> )CH <sub>2</sub> }(C <sub>5</sub> H <sub>4</sub> -(acac)(py)] <sup>e</sup>	84.0(9)	2.091(19)	2.800(19)	0.301(29)	87(4)	$\Delta_2(\text{Ir}) = 0.007\ 3(85)$	Half-chair	f
[Rh{CH <sub>2</sub> C(=CH <sub>2</sub> )C(=CH <sub>2</sub> )CH <sub>2</sub> }(acac)(py) <sub>2</sub> ]	84.0(2)	2.044(4)	-2.735(4)	0.347(5)	66.9(8)	$\Delta_2(C_{\beta}) = 0.012\ 4(21)$	Envelope	g
[(PPh <sub>3</sub> )(acac)Rh-CH <sub>2</sub> C(=CH <sub>2</sub> )C(=CH <sub>2</sub> )CH <sub>2</sub> ]Rh(acac)(PPh <sub>3</sub> )]	83.7(4)	2.085(7)	2.784(7)	0.289(10)	-0.2(22)	$\Delta_5(\text{Rh}) = 0.000\ 5(53)$	Envelope	g

<sup>a</sup> Q and  $\varphi$  are the puckering parameters of Cromer and Pople.<sup>16</sup> The asymmetry parameters are calculated according to Nardelli.<sup>17</sup> <sup>b</sup> C $_{\alpha}$  and C $_{\beta}$  indicate the positions of the carbons in the ring with respect to the metal. <sup>c</sup> This work. <sup>d</sup> Ref. 2. <sup>e</sup> acac = Acetylacetonate, py = pyridine. <sup>f</sup> P. Diversi, G. Ingrassio, A. Immirzi, W. Porzio, and M. Zocchi, *J. Organomet. Chem.*, 1977, **81**, 217. <sup>g</sup> A. Immirzi, *J. Organomet. Chem.*, 1974, **81**, 217.



**Figure 2.** Newman projections along M-cp (a), P-M (b), C(17)-M (c), and C(20)-M directions (d). Each triplet of angle values refers to complexes (1c), (1f), and (1e), respectively, from top to bottom. The geometries of the projections themselves refer to complex (1f)

shortenings are substantially maintained after correction of the experimental data using a plausible thermal motion model (Table 3), the possibility that they arise from disorder of the carbon atoms involved cannot be rejected.

It should be noted that once again it is observed that in the metallacyclic moiety of derivatives of the cobalt group metals some C-C single bonds are shorter than the expected C(sp<sup>3</sup>)-C(sp<sup>3</sup>) distance. Indeed, for the complexes of formula [M(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)( $\eta^5$ -C<sub>5</sub>R<sub>5</sub>)(PPh<sub>3</sub>)] (M = Co, R = H;

M = Rh or Ir, R = Me),<sup>2</sup> the rhodium derivative has two C-C bonds, *i.e.* C $_{\alpha}$ -C $_{\beta}$  and C $_{\beta}$ -C $_{\beta}$ , which are shorter than the normal distance, while in the case of the cobalt and iridium complexes C $_{\beta}$ -C $_{\beta}$  is the short one.

The metallacyclopentane rings of the compounds quoted in Table 4 can be subdivided into two groups depending upon the value of the C-M-C angle which is *ca.* 80 $^{\circ}$  in the first five compounds and *ca.* 84 $^{\circ}$  in the others. The observation is systematic and is related to the C $_{\alpha}$ ...C $_{\alpha}$  distances that increase as the M-C bond lengths increase so as to maintain the C-M-C angle constant within each group.

Finally, there are two asymmetric centres of the same chirality, C(18) and C(19), in (1c) and (1f), while in (1e) there is only one asymmetric carbon atom, C(18). Both enantiomers of each species are present in the crystals, the space groups of the three compounds being centrosymmetric.

**Pentamethylcyclopentadienyl ligand.** As observed recently<sup>13</sup> for some metallacyclobutane derivatives similar to (1c), (1e), and (1f), no significant distortion from planarity of the C<sub>5</sub> ring nor from the five-fold symmetry has been found, as indicated by the values of the  $\Sigma(\Delta/\sigma)^2$  parameter which are 3.5, 2.0, and 6.1 for (1c), (1e), and (1f), respectively, and by the values of the C-C distances (Table 3). As usually found for this bulky ligand, the five methyl groups deviate significantly from the ring plane, with mean displacements of 0.16(3)  $\text{\AA}$  in the three complexes, in a direction opposite to the metal atom so as to reduce the effective cone angle of the C<sub>5</sub>Me<sub>5</sub> ligand.

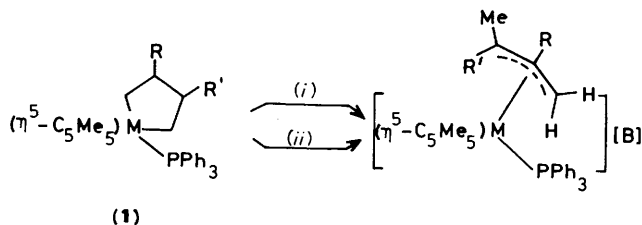
**Triphenylphosphine.** The data (Table 3) agree quite well with those found in similar metallacyclobutane derivatives described previously;<sup>15</sup> therefore the same considerations developed in the previous work apply here. In particular, the same steric effects determining the orientation of the phenyl rings have been observed.

**Reaction of Rhoda- and Irida-cyclopentanes with Boron Trifluoride and with the Trityl Cation.**—The metallacycles (1a)—(1f) react rapidly with BF<sub>3</sub>·Bu<sup>n</sup>O in Bu<sup>n</sup>O under very mild conditions, undergoing a hydrogen abstraction reaction with the formation of the tetrafluoroborate salts of the  $\eta^3$ -allyl cations (2a)—(2f) (Scheme 2). The yields were not high (*ca.* 50%), with the exception of (2a) which was obtained in *ca.* 80%

**Table 5.** Analytical and spectroscopic data for the  $\eta^3$ -allyl complexes (2a)—(2f) and (3a)—(3f)

Compound	Colour	Analysis <sup>a</sup> (%)			<sup>1</sup> H N.m.r. data <sup>b</sup>
		C	H	P	
(2a) [Rh( $\eta^3$ -CH <sub>2</sub> CHCHMe)( $\eta^5$ -C <sub>5</sub> Me <sub>5</sub> )(PPh <sub>3</sub> )] [BF <sub>4</sub> ]	Pale yellow	59.90 (59.85)	5.85 (5.80)	4.90 (4.80)	1.50 (15, d, <i>J</i> 3 Hz, C <sub>5</sub> Me <sub>5</sub> ), 1.53 (3, d, <i>J</i> 3 Hz, Me), 1.75 (1, m, H <sub>b</sub> ), 2.45 (1, m, H <sub>b</sub> ), 3.06 (1 d, <i>J</i> 7 Hz, H <sub>c</sub> ), 3.94 (1, m, H <sub>c</sub> ), 7.5 (15, m, Ph) <sup>c</sup>
(2b) [Rh( $\eta^3$ -CH <sub>2</sub> C(Me)CHMe)( $\eta^5$ -C <sub>5</sub> Me <sub>5</sub> )(PPh <sub>3</sub> )] [BF <sub>4</sub> ]	Orange-yellow	60.45 (60.40)	6.00 (6.00)	4.90 (4.70)	1.43 (3, d, <i>J</i> 2.5 Hz, Me <sub>c</sub> ), 1.52 (15, d, <i>J</i> 2.5 Hz, C <sub>5</sub> Me <sub>5</sub> ), 1.60 (3, br d, <i>J</i> ca. 6 Hz, Me <sub>c</sub> ), 1.96 (1, br m, H <sub>a</sub> ), 2.53 (1, m, CHMe), 3.08 (1, br m, H <sub>c</sub> ), 7.5 (15, m, Ph) <sup>d</sup>
(2c) [Rh( $\eta^3$ -CH <sub>2</sub> C(Me)CMe <sub>2</sub> )( $\eta^5$ -C <sub>5</sub> Me <sub>5</sub> )(PPh <sub>3</sub> )] [BF <sub>4</sub> ]	Orange	60.95 (60.90)	6.20 (6.15)	4.70 (4.60)	1.2 (3, s, Me <sub>a</sub> ), 1.35 (3, s, Me <sub>c</sub> ), 1.38 (15, d, <i>J</i> 3 Hz, C <sub>5</sub> Me <sub>5</sub> ), 1.54 (3, s, Me <sub>c</sub> ), 1.85 (1, m, H <sub>a</sub> ), 3.0 (1, m, H <sub>c</sub> ), 7.45 (15, m, Ph) <sup>d</sup>
(2d) [Ir( $\eta^3$ -CH <sub>2</sub> CHCHMe)( $\eta^5$ -C <sub>5</sub> Me <sub>5</sub> )(PPh <sub>3</sub> )] [BF <sub>4</sub> ]	Pale yellow	52.60 (52.55)	5.15 (5.10)	4.30 (4.25)	1.55 (3, m, Me), 1.57 (15, d, <i>J</i> 2 Hz, C <sub>5</sub> Me <sub>5</sub> ), 1.6 (1, br d, <i>J</i> 9 Hz, H <sub>a</sub> ), 2.25 (1, m, H <sub>b</sub> ), 2.85 (1, d, <i>J</i> 7 Hz, H <sub>c</sub> ), 3.65 (1, m, H <sub>c</sub> ), 7.4 (15, m, Ph) <sup>c</sup>
(2e) [Ir( $\eta^3$ -CH <sub>2</sub> C(Me)CHMe)( $\eta^5$ -C <sub>5</sub> Me <sub>5</sub> )(PPh <sub>3</sub> )] [BF <sub>4</sub> ] <sup>e</sup>	Yellow	53.20 (53.15)	5.30 (5.25)	4.20 (4.15)	0.90 (3, d, <i>J</i> 7 Hz, Me <sub>a</sub> ), 1.57 (15, d, <i>J</i> 2 Hz, C <sub>5</sub> Me <sub>5</sub> , <i>syn</i> isomer), 1.60 (3, d, <i>J</i> 8 Hz, Me <sub>c</sub> ), 1.65 (15, d, <i>J</i> 2 Hz, C <sub>5</sub> Me <sub>5</sub> , <i>anti</i> isomer), 1.69 (3 br s, Me <sub>c</sub> , <i>syn</i> and <i>anti</i> isomers), 1.8—2.05 (1, br m, H <sub>a</sub> , <i>syn</i> and <i>anti</i> isomers), 2.0—2.4 (1, br m, CHMe, <i>syn</i> and <i>anti</i> isomers), 2.5—2.9 (1, br m, H <sub>c</sub> , <i>syn</i> and <i>anti</i> isomers), 7.4 (15, br m, Ph) <sup>d</sup>
(2f) [Ir( $\eta^3$ -CH <sub>2</sub> C(Me)CMe <sub>2</sub> )( $\eta^5$ -C <sub>5</sub> Me <sub>5</sub> )(PPh <sub>3</sub> )] [BF <sub>4</sub> ]	Yellow	53.80 (53.75)	5.45 (5.45)	4.15 (4.05)	0.96 (3, d, <i>J</i> 2 Hz, Me <sub>a</sub> ), 1.43 (3, d, <i>J</i> 2 Hz, Me <sub>c</sub> ), 1.60 (15, d, <i>J</i> 2 Hz, C <sub>5</sub> Me <sub>5</sub> ), 1.75 (3, d, <i>J</i> 2 Hz, Me <sub>c</sub> ), 2.1 (1, m, H <sub>a</sub> ), 3.03 (1, m, H <sub>c</sub> ), 7.5 (15, m, Ph) <sup>d</sup>
(3a) [Rh( $\eta^3$ -CH <sub>2</sub> CHCHMe)( $\eta^5$ -C <sub>5</sub> Me <sub>5</sub> )(PPh <sub>3</sub> )] [PF <sub>6</sub> ]	Yellow	54.80 (54.75)	5.35 (5.30)	8.90 (8.85)	1.50 (15, d, <i>J</i> 3 Hz, C <sub>5</sub> Me <sub>5</sub> ), 1.55 (3, d, <i>J</i> 3 Hz, Me), 1.8 (1, m, H <sub>a</sub> ), 2.45 (1, m, H <sub>b</sub> ), 3.0 (1, d, <i>J</i> 7 Hz, H <sub>c</sub> ), 3.95 (1, m, H <sub>c</sub> ), 7.5 (15, m, Ph) <sup>c</sup>
(3b) [Rh( $\eta^3$ -CH <sub>2</sub> C(Me)CHMe)( $\eta^5$ -C <sub>5</sub> Me <sub>5</sub> )(PPh <sub>3</sub> )] [PF <sub>6</sub> ]	Orange-yellow	55.45 (55.50)	5.50 (5.55)	8.65 (8.75)	1.43 (3, d, <i>J</i> 2.5 Hz, Me <sub>c</sub> ), 1.5 (15, d, <i>J</i> 2.5 Hz, C <sub>5</sub> Me <sub>5</sub> ), 1.63 (3, br d, <i>J</i> ca. 6 Hz, Me <sub>c</sub> ), 1.95 (1, br m, H <sub>a</sub> ), 2.53 (1, m, CHMe), 3.05 (1, br m, H <sub>c</sub> ), 7.5 (15, m, Ph) <sup>d</sup>
(3c) [Rh( $\eta^3$ -CH <sub>2</sub> C(Me)CMe <sub>2</sub> )( $\eta^5$ -C <sub>5</sub> Me <sub>5</sub> )(PPh <sub>3</sub> )] [PF <sub>6</sub> ]	Orange	56.10 (56.05)	5.70 (5.65)	8.60 (8.50)	1.17 (3, s, Me <sub>a</sub> ), 1.33 (3, s, Me <sub>c</sub> ), 1.38 (15, d, <i>J</i> 3 Hz, C <sub>5</sub> Me <sub>5</sub> ), 1.50 (3, s, Me <sub>c</sub> ), 1.83 (1, m, H <sub>a</sub> ), 2.9 (1, m, H <sub>c</sub> ), 7.45 (15, m, Ph) <sup>d</sup>
(3d) [Ir( $\eta^3$ -CH <sub>2</sub> CHCHMe)( $\eta^5$ -C <sub>5</sub> Me <sub>5</sub> )(PPh <sub>3</sub> )] [PF <sub>6</sub> ]	Pale yellow	48.70 (48.65)	4.75 (4.70)	7.90 (7.85)	1.55 (3, m, Me), 1.57 (15, d, <i>J</i> 2 Hz, C <sub>5</sub> Me <sub>5</sub> ), 1.6 (1, br d, <i>J</i> 9 Hz, H <sub>a</sub> ), 2.20 (1, m, H <sub>b</sub> ), 2.9 (1, d, <i>J</i> 7 Hz, H <sub>c</sub> ), 3.6 (1, m, H <sub>c</sub> ), 7.4 (15, m, Ph) <sup>c</sup>
(3e) [Ir( $\eta^3$ -CH <sub>2</sub> C(Me)CHMe)( $\eta^5$ -C <sub>5</sub> Me <sub>5</sub> )(PPh <sub>3</sub> )] [PF <sub>6</sub> ] <sup>e</sup>	Pale yellow	49.35 (49.30)	4.90 (4.95)	7.70 (7.80)	0.96 (3, d, <i>J</i> 7 Hz, Me <sub>a</sub> ), 1.57 (15, d, <i>J</i> 2 Hz, C <sub>5</sub> Me <sub>5</sub> , <i>syn</i> isomer), 1.60 (3, d, <i>J</i> 8 Hz, Me <sub>c</sub> ), 1.63 (15, d, <i>J</i> 2 Hz, C <sub>5</sub> Me <sub>5</sub> , <i>anti</i> isomer), 1.67 (3, br s, Me <sub>c</sub> , <i>syn</i> and <i>anti</i> isomers), 1.80—2.05 (1, br m, H <sub>a</sub> , <i>syn</i> and <i>anti</i> isomers), 2.0—2.4 (1, m, CHMe, <i>syn</i> and <i>anti</i> isomers), 2.5—2.9 (1, br m, H <sub>c</sub> , <i>syn</i> and <i>anti</i> isomers), 7.4 (15, br m, Ph) <sup>d</sup>
(3f) [Ir( $\eta^3$ -CH <sub>2</sub> C(Me)CMe <sub>2</sub> )( $\eta^5$ -C <sub>5</sub> Me <sub>5</sub> )(PPh <sub>3</sub> )] [PF <sub>6</sub> ]	Yellow	50.00 (49.95)	5.10 (5.05)	7.65 (7.55)	0.96 (3, d, <i>J</i> 2 Hz, Me <sub>a</sub> ), 1.5 (3, d, <i>J</i> 2.5 Hz, Me <sub>c</sub> ), 1.60 (15, d, <i>J</i> 2 Hz, C <sub>5</sub> Me <sub>5</sub> ), 1.76 (3, d, <i>J</i> 2 Hz, Me <sub>c</sub> ), 2.10 (1, m, H <sub>a</sub> ), 3.0 (1, m, H <sub>c</sub> ), 7.45 (15, m, Ph) <sup>d</sup>

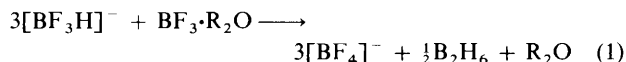
<sup>a</sup> Calculated values given in parentheses. <sup>b</sup> Measured in CDCl<sub>3</sub> solution, at 37 °C, and referenced to SiMe<sub>4</sub> as internal standard. Given as chemical shift ( $\delta$ ), relative intensity, multiplicity, coupling constant, assignment; br = broad, d = doublet, m = multiplet, s = singlet. <sup>c</sup> H<sub>a</sub> = *anti*-H, H<sub>b</sub> = CHMe, H<sub>c</sub> = *syn*-H, H<sub>c</sub> = central H. <sup>d</sup> Me<sub>s</sub> = *syn*-Me, Me<sub>a</sub> = *anti*-Me, Me<sub>c</sub> = central Me, H<sub>a</sub> = *anti*-H, H<sub>s</sub> = *syn*-H. <sup>e</sup> Mixture of *syn* and *anti* isomers.



	M	R	R'	B <sup>-</sup>
(2a)	Rh	H	H	BF <sub>4</sub> <sup>-</sup>
(2b)	Rh	Me	H	BF <sub>4</sub> <sup>-</sup>
(2c)	Rh	Me	Me	BF <sub>4</sub> <sup>-</sup>
(2d)	Ir	H	H	BF <sub>4</sub> <sup>-</sup>
(2e)	Ir	Me	H	BF <sub>4</sub> <sup>-</sup>
(2f)	Ir	Me	Me	BF <sub>4</sub> <sup>-</sup>
(3a)	Rh	H	H	PF <sub>6</sub> <sup>-</sup>
(3b)	Rh	Me	H	PF <sub>6</sub> <sup>-</sup>
(3c)	Rh	Me	Me	PF <sub>6</sub> <sup>-</sup>
(3d)	Ir	H	H	PF <sub>6</sub> <sup>-</sup>
(3e)	Ir	Me	H	PF <sub>6</sub> <sup>-</sup>
(3f)	Ir	Me	Me	PF <sub>6</sub> <sup>-</sup>

Scheme 2. (i)  $\text{BF}_3 \cdot \text{Bu}^n_2\text{O}$ , in  $\text{Bu}^n_2\text{O}$ ,  $-78$  to  $+20$  °C; (ii)  $[\text{CPh}_3][\text{PF}_6]$ , in  $\text{CH}_2\text{Cl}_2$ , at room temperature

yield, and were markedly lowered when substrate to boron trifluoride molar ratios lower than 1:2 were employed, or, alternatively, when the reactions were carried out in the presence of free triphenylphosphine, the effect being proportional to the amount of added ligand. While the latter effect is easily understood in terms of a lowered concentration of boron trifluoride as a consequence of the formation of the stable adduct  $\text{BF}_3 \cdot \text{PPh}_3$ ,<sup>18</sup> the explanation of the influence exerted by the substrate to boron trifluoride ratio on the reaction course requires the assumption of the occurrence of the  $[\text{BF}_3\text{H}]^-$  species resulting from hydride abstraction from the metallacyclic moiety, which should react rapidly with  $\text{BF}_3 \cdot \text{Bu}^n_2\text{O}$  to give  $[\text{BF}_4]^-$  and  $\text{B}_2\text{H}_6$  [equation (1)].<sup>19</sup> Indeed, the presence of



$\text{B}_2\text{H}_6$  in the mixtures coming from the reactions of complexes (1a)–(1f) with boron trifluoride was confirmed by g.l.c. analysis of the volatile reaction products collected in a trap cooled at  $-180$  °C. Furthermore, the nature of  $[\text{BF}_4]^-$  as the counter ion was unambiguously determined by fast atom bombardment (f.a.b.) mass spectrometry (see below).

The conversion of metallacyclopentanes into  $\eta^3$ -allyl complexes by reaction with the trityl cation has been recently discovered.<sup>9,10</sup> Thus the above results illustrate the analogy between the reactions of metallacycles with boron trifluoride and with the trityl cation. Indeed, we have observed that complexes (1a)–(1f) react with  $[\text{CPh}_3]^+$  at room temperature to give the same organometallic cations that are produced from the corresponding reactions with boron trifluoride (Scheme 2). Either  $[\text{CPh}_3][\text{BF}_4]$  or  $[\text{CPh}_3][\text{PF}_6]$  were used, and both gave the same results.

The analytical and  $^1\text{H}$  n.m.r. data for complexes (2a)–(2f) and (3a)–(3f), deriving from the reactions of compounds (1a)–(1f) with  $\text{BF}_3 \cdot \text{Bu}^n_2\text{O}$  and  $[\text{CPh}_3][\text{PF}_6]$ , respectively, are reported in Table 5. Owing to the molecular complexity as well as to the coalescence of some signals, the interpretation of the  $^1\text{H}$  n.m.r. spectra was not easy in some cases. However, the

assignments given in Table 5, which are based also upon the analysis of the spectra of neutral<sup>20</sup> and cationic<sup>10</sup> complexes containing the same  $\eta^3$ -allyl ligands as those in complexes (2a)–(2f) and (3a)–(3f) leave no doubts about the characterization of these compounds which were studied also by f.a.b. mass spectrometry. This technique has been successfully employed for structural studies of ionic organometallic compounds.<sup>21</sup>

We have obtained excellent f.a.b. mass spectra of the complexes (2a)–(2f) and (3a)–(3f) employing a 1:1 mixture of glycerol and thioglycerol as the 'matrix'. The positive ion mass spectra of the rhodium complexes (2a)–(2c) and (3a)–(3c) show molecular peaks at  $m/z$  555, 569, and 583, respectively. Parent peaks are observed in all the spectra corresponding to the fragments  $[M - \text{CH}_2\text{C}(\text{R})\text{C}(\text{R}')\text{CH}_3]^+$ ,  $[M - \text{PPh}_3]^+$  and  $[M - \text{C}_5\text{Me}_5]^+$ . Furthermore, all the spectra show a very intense (r.i. > 60%) peak at  $m/z$  499, in addition to the base peak at  $m/z$  500,  $[M - \text{CH}_2\text{C}(\text{R})\text{C}(\text{R}')\text{CH}_3]^+$ . This signal, which corresponds to a fragment deriving from the molecular ions by the loss of the allyl moiety and of a hydrogen atom, could be associated with a relatively stable ion bearing an ortho-metallated triphenylphosphine. Finally all the spectra show peaks at  $m/z$  higher than the molecular ion value which are attributable to ions arising from the interaction of the complexes with the 'matrix'.

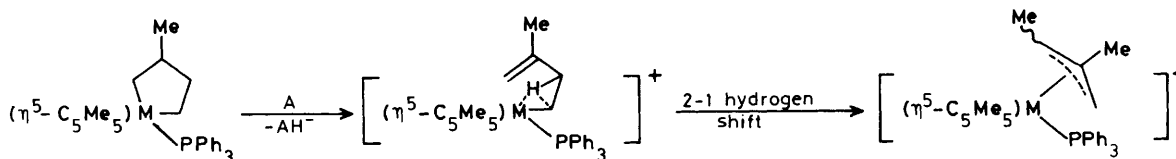
Under the same experimental conditions, the iridium complexes (2d)–(2f) and (3d)–(3f) exhibit fragmentation patterns strictly similar to those observed in the case of the rhodium compounds. The positive ion mass spectra show molecular peaks at  $m/z$  645, 659, and 673, respectively, for the couples (2d) and (3d), (2e) and (3e), and (2f) and (3f), in addition to peaks due to fragments arising from the loss of the allyl moiety, or triphenylphosphine, or pentamethylcyclopentadienyl ligand from the molecular ions. As observed in the case of the rhodium complexes, also in all the spectra of the iridium compounds a peak ( $m/z$  589) is present which is attributable to a fragment deriving from the molecular ions by the loss of the allyl moiety and of a hydrogen atom, this being now the main fragmentation process; while the loss of the  $\text{CH}_2\text{C}(\text{R})\text{C}(\text{R}')\text{CH}_3$  ligand alone from the molecular ions is scarcely operative. Finally, the negative ion spectra of all complexes (2a)–(2f) and (3a)–(3f) confirm the presence of  $[\text{BF}_4]^-$  and  $[\text{PF}_6]^-$  as counter ions, respectively.

Regarding the mechanism of the reaction of metallacyclopentanes with boron trifluoride, we strongly suspect that it involves initial  $\beta$ -hydride abstraction by boron trifluoride followed by rapid isomerization of the resulting 3-butenyl intermediate to the  $\eta^3$ -allyl complex, as has been demonstrated for reactions with the trityl cation.<sup>10</sup> Indeed, the analogy between these two reactions is great: both occur under mild conditions, both are fast, both generate the same organometallic cation, the starting metallacycle being the same, and both exhibit the same regiospecificity, *i.e.* when one of the ring  $\beta$  positions is alkyl substituted the only observed product is derived from regiospecific hydrogen abstraction from the substituted carbon atom (Scheme 3), as observed in the case of (1b) and (1e).

## Conclusions

On the basis of the X-ray data, an indication emerges of the relation between metallacyclopentane constitution and structure in the crystalline state, for the cobalt triad metals studied. The lack or presence of alkyl substituents at the metallacyclic carbon atoms influences markedly the ring conformation, the M–C distances, and the non-bonding C...C distances. The puckering of the metallacyclic moiety, which is large when both the  $\beta$  and  $\beta'$  carbon atoms bear an alkyl group,



Scheme 3.  $\text{A} = \text{BF}_3$  or  $[\text{CPh}_3]^+$ 

makes one  $\beta$  carbon atom closer to the metal than the other. On the other hand, a shortening of some endocyclic C-C bond distances is observed when the ring puckering is small. Therefore, if these C-C shortenings are real and are not due to thermal motion (or disorder), the findings are consistent with the change in conformation on going from cyclopentane to cyclopentene, regarding these molecules as stressed models of metallacyclopentanes having the conformational features described above.

We cannot definitely exclude disorder as an explanation of the endocyclic C-C shortenings discussed above as well as those reported in the literature in other metallacyclopentane derivatives.<sup>2,3</sup> However, further evidence is provided by the ring conformation and some metallacyclic C-C distances; the findings are of general interest and are not confined to the chemistry of metallacycles.<sup>22</sup>

Turning to the reactions of rhoda- and irida-cyclopentanes with boron trifluoride and with the trityl cation, a first comment is that such reactions occur easily, under very mild experimental conditions, whatever the structure of the reacting metallacycle. It is then difficult to rationalize these results in terms of the X-ray structure of the starting metallacycles; furthermore, we do not know whether the  $\beta$ -hydrogen abstraction by Lewis acids takes place with or without the assistance of the transition metal. If the shortening of the  $\text{C}_\beta\text{-C}_\beta$  bond distance is real and is to be associated to an increased electron density between these carbon atoms, this could offer the prerequisite for facile  $\text{H}^-$  release. On the other hand, the ring puckering suggests the possibility that a transition state could be operative in the  $\beta$ -hydrogen abstraction step in which the hydrogen atom to be released is interacting simultaneously with the transition metal and with the acid, as well as with the  $\beta$ -carbon atom.

## Experimental

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  $[\text{MCl}_2(\eta^5\text{-C}_5\text{Me}_5)(\text{PPh}_3)]$  ( $\text{M} = \text{Rh}$  or  $\text{Ir}$ ),<sup>23</sup>  $[\text{M}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)(\eta^5\text{-C}_5\text{Me}_5)(\text{PPh}_3)]$  [ $\text{M} = \text{Rh}$ , (**1a**);  $\text{M} = \text{Ir}$ , (**1d**)],<sup>12</sup>  $\text{ClCH}_2\text{CH}(\text{Me})\text{CH}(\text{Me})\text{CH}_2\text{Cl}$ ,<sup>3</sup>  $\text{Li}[\text{CH}_2\text{CH}(\text{Me})\text{CH}(\text{Me})\text{CH}_2]\text{Li}$ ,<sup>3</sup>  $\text{HOCH}_2\text{CH}(\text{Me})\text{CH}(\text{Me})\text{CH}_2\text{OH}$ ,<sup>24</sup> and  $\text{EtOOCCH}(\text{Pr}^i)\text{CH}_2\text{COOEt}$ <sup>25</sup> were prepared according to the literature.  $\text{ClMg}[\text{CH}_2\text{CH}(\text{Me})\text{CH}(\text{Me})\text{CH}_2]\text{MgCl}$  was prepared (yield, 45%) from  $\text{ClCH}_2\text{CH}(\text{Me})\text{CH}(\text{Me})\text{CH}_2\text{Cl}$  following standard procedures.<sup>26</sup>  $[\text{CPh}_3][\text{PF}_6]$  (Aldrich Chemie) was used as received.  $\text{BF}_3 \cdot \text{Bu}^n_2\text{O}$  was prepared from  $\text{BF}_3 \cdot \text{OEt}_2$  (Carlo Erba) and  $\text{Bu}^n_2\text{O}$  by distillation of diethyl ether. 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. Mass spectra were obtained with a VG Analytical 7070E apparatus. Microanalyses were performed by the Laboratorio di Microanalisi of the Istituto di Chimica Organica, Facoltà di Farmacia, University of Pisa. G.l.c. analyses were performed on a Perkin-Elmer Sigma 3B instrument equipped with flame ionization detectors.

(*R*)(*S*)-1,4-Dichloro-2-methylbutane.—This compound [b.p. 65 °C (20 mmHg)] was isolated in 60% yield after treatment of the corresponding alcohol with  $\text{SOCl}_2$  and pyridine, using the procedure described by Vogel<sup>27a</sup> (Found: C, 56.85; H, 9.50; Cl, 33.50.  $\text{C}_5\text{H}_{10}\text{Cl}_2$  requires C, 56.85; H, 9.45; Cl, 33.55%). <sup>1</sup>H N.m.r. (pure liquid):  $\delta$  1.0 (d, 3 H,  $J$  6 Hz, Me), 1.9 (m, 3 H,  $-\text{CH}_2\text{CHMe}$ ), 3.5 (m, 4 H,  $\text{CH}_2\text{Cl}$ ).

(*R*)(*S*)-1,4-Dilithio-2-methylbutane.—This compound was obtained in 51% yield by reacting  $\text{ClCH}_2\text{CH}(\text{Me})\text{CH}_2\text{CH}_2\text{Cl}$  with lithium in diethyl ether at 0 °C using the procedure described for the corresponding unmethylated compound.<sup>28</sup>

(*R*)(*S*)-1,4-Bis(chloromagnesio)-2-methylbutane.—This compound was prepared in 55% yield by reacting  $\text{ClCH}_2\text{CH}(\text{Me})\text{CH}_2\text{CH}_2\text{Cl}$  with magnesium turnings in tetrahydrofuran (thf) following the procedure described for the corresponding unmethylated compound.<sup>26</sup>

(*R*)(*S*)-1,4-Bis(chloromagnesio)-2-isopropylbutane.—(*R*)(*S*)-2-Isopropyl-1,4-butanediol [b.p. 138 °C (23 mmHg)] was isolated in 98% yield after treatment of (*R*)(*S*)-diethyl 2-isopropylsuccinate with  $\text{LiAlH}_4$  in diethyl ether,<sup>27b</sup> followed by basic hydrolysis<sup>29</sup> of the reaction mixture (Found: C, 63.6; H, 12.2.  $\text{C}_7\text{H}_{16}\text{O}_2$  requires C, 63.6; H, 12.2%). <sup>1</sup>H N.m.r. ( $\text{CDCl}_3$ ):  $\delta$  0.9 (d, 6 H,  $J$  6 Hz,  $\text{Me}_2\text{CH}-$ ), 1.6 (m, 2 H,  $-\text{CH}-\text{CH}-$ ), 3.6 (br m, 4 H,  $\text{CH}_2\text{OH}$ ), 5.0 (br s, 2 H,  $-\text{OH}$ ).  $\text{ClCH}_2\text{CH}(\text{Pr}^i)\text{CH}_2\text{CH}_2\text{Cl}$  [b.p. 88 °C (23 mmHg)] was isolated in 83% yield after treatment of the diol with  $\text{SOCl}_2$  and pyridine.<sup>27a</sup> <sup>1</sup>H N.m.r. (pure liquid):  $\delta$  0.9 (d, 6 H,  $J$  7 Hz,  $\text{Me}_2\text{CH}-$ ), 1.9 (m, 4 H,  $-\text{CHCHCH}_2-$ ), 3.6 (m, 4 H,  $-\text{CH}_2\text{Cl}$ ). Reaction of the dichloride with magnesium turnings in thf yielded the desired product (40% yield).

(2-Methylbutane-1,4-diyl)( $\eta^5$ -pentamethylcyclopentadienyl)-(triphenylphosphine)rhodium(III), (**1b**).—Following already published procedures,<sup>12</sup>  $[\text{RhCl}_2(\eta^5\text{-C}_5\text{Me}_5)(\text{PPh}_3)]$  (0.3 g, 0.525 mmol) was reacted with (*R*)(*S*)-1,4-dilithio-2-methylbutane (4 cm<sup>3</sup> of a 0.405 mol dm<sup>-3</sup> diethyl ether solution, 1.62 mmol) to give the product (0.04 g, 15% yield) as orange-yellow crystals.

(2,3-Dimethylbutane-1,4-diyl)( $\eta^5$ -pentamethylcyclopentadienyl)-(triphenylphosphine)rhodium(III), (**1c**).—Following the usual procedure,<sup>12</sup>  $[\text{RhCl}_2(\eta^5\text{-C}_5\text{Me}_5)(\text{PPh}_3)]$  (0.3 g, 0.525 mmol) was reacted at 0 °C, with 1,4-dilithio-2,3-dimethylbutane (mixture of *threo* and *erythro* forms) (2.6 cm<sup>3</sup> of a 0.61 mol dm<sup>-3</sup> diethyl ether solution, 1.59 mmol) to give 0.065 g of the product (22% yield) as orange-yellow crystals.

(2-Methylbutane-1,4-diyl)( $\eta^5$ -pentamethylcyclopentadienyl)-(triphenylphosphine)iridium(III), (**1e**).—Following the usual procedure,<sup>12</sup>  $[\text{IrCl}_2(\eta^5\text{-C}_5\text{Me}_5)(\text{PPh}_3)]$  (0.3 g, 0.455 mmol), suspended in thf (70 cm<sup>3</sup>), was reacted with (*R*)(*S*)-1,4-bis(chloromagnesio)-2-methylbutane (10 cm<sup>3</sup> of a 0.144 mol dm<sup>-3</sup> thf solution, 1.44 mmol) to give the product (0.06 g, 20% yield) as yellow crystals.

(2,3-Dimethylbutane-1,4-diyl)( $\eta^5$ -pentamethylcyclopentadienyl)(triphenylphosphine)iridium(III), (**1f**).—Following the usual procedure,<sup>12</sup>  $[\text{IrCl}_2(\eta^5\text{-C}_5\text{Me}_5)(\text{PPh}_3)]$  (0.32 g, 0.482 mmol), suspended in thf (70 cm<sup>3</sup>) was reacted at room temperature with 1,4-bis(chloromagnesio)-2,3-dimethylbutane (mixture of the *threo* and *erythro* forms, 7.7 cm<sup>3</sup> of a 0.113 mol dm<sup>-3</sup> thf solution, 0.87 mmol) to give the product (0.146 g, 45% yield) as yellow crystals.

(2-Isopropylbutane-1,4-diyl)( $\eta^5$ -pentamethylcyclopentadienyl)(triphenylphosphine)iridium(III), (**1g**).—Following the usual procedure,<sup>12</sup>  $[\text{IrCl}_2(\eta^5\text{-C}_5\text{Me}_5)(\text{PPh}_3)]$  (0.19 g, 0.294 mmol), suspended in thf (40 cm<sup>3</sup>), was reacted at room temperature with (*R*)(*S*)-1,4-bis(chloromagnesio)-2-isopropylbutane (5.8 cm<sup>3</sup> of a 0.102 mol dm<sup>-3</sup> thf solution, 0.589 mmol) to give, after crystallization from ethanol, the product (0.01 g, 5% yield) as yellow crystals.

Reaction of (**1a**) with  $\text{BF}_3 \cdot \text{Bu}^n_2\text{O}$ : Formation of ( $\eta^3$ -1-Methylallyl)( $\eta^5$ -pentamethylcyclopentadienyl)(triphenylphosphine)rhodium(III) Tetrafluoroborate, (**2a**).—To a mixture of (**1a**) (0.171 g, 0.308 mmol) and  $\text{Bu}^n_2\text{O}$  (4 cm<sup>3</sup>),  $\text{BF}_3 \cdot \text{Bu}^n_2\text{O}$  (0.116 cm<sup>3</sup>, 0.616 mmol) was added by a microsyringe, at  $-78^\circ\text{C}$ . The reaction mixture was kept at  $-78^\circ\text{C}$  for 2 min, the temperature was slowly raised to  $20^\circ\text{C}$ , and the reaction mixture stirred for 2 h. An orange-red suspension was obtained that was evaporated to dryness under vacuum. The residue was dissolved in  $\text{CH}_2\text{Cl}_2$  (1 cm<sup>3</sup>) and the resulting solution was added dropwise to diethyl ether (60 cm<sup>3</sup>) while stirring. A pale yellow microcrystalline solid precipitated which was separated by filtration, washed repeatedly with diethyl ether and dried, yield 0.5 g (75%).

Reaction of (**1b**) with  $\text{BF}_3 \cdot \text{Bu}^n_2\text{O}$ : Formation of ( $\eta^3$ -1,2-Dimethylallyl)( $\eta^5$ -pentamethylcyclopentadienyl)(triphenylphosphine)rhodium(III) Tetrafluoroborate, (**2b**).—A similar reaction between (**1b**) (0.104 g, 0.183 mmol) in  $\text{Bu}^n_2\text{O}$  (2.5 cm<sup>3</sup>) and  $\text{BF}_3 \cdot \text{Bu}^n_2\text{O}$  (0.077 cm<sup>3</sup> of a 4.787 mol dm<sup>-3</sup>  $\text{Bu}^n_2\text{O}$  solution, 0.368 mmol) gave orange microcrystals of the title compound, yield 0.05 g (45%).

Reaction of (**1c**) with  $\text{BF}_3 \cdot \text{Bu}^n_2\text{O}$ : Formation of ( $\eta^5$ -Pentamethylcyclopentadienyl)( $\eta^3$ -1,1,2-trimethylallyl)(triphenylphosphine)rhodium(III) Tetrafluoroborate (**2c**).—A similar reaction between (**1c**) (0.153 g, 0.276 mmol) in  $\text{Bu}^n_2\text{O}$  (3 cm<sup>3</sup>) and  $\text{BF}_3 \cdot \text{Bu}^n_2\text{O}$  (0.12 cm<sup>3</sup> of a 4.662 mol dm<sup>-3</sup>  $\text{Bu}^n_2\text{O}$  solution, 0.56 mmol) gave orange microcrystals of (**2c**), yield 0.105 g (60%).

Reaction of (**1d**) with  $\text{BF}_3 \cdot \text{Bu}^n_2\text{O}$ : Formation of ( $\eta^3$ -1-methylallyl)( $\eta^5$ -pentamethylcyclopentadienyl)(triphenylphosphine)iridium(III) Tetrafluoroborate, (**2d**).—A similar reaction between (**1d**) (0.1 g, 0.155 mmol) in  $\text{Bu}^n_2\text{O}$  (2.5 cm<sup>3</sup>) and  $\text{BF}_3 \cdot \text{Bu}^n_2\text{O}$  (0.067 cm<sup>3</sup> of a 4.662 mol dm<sup>-3</sup>  $\text{Bu}^n_2\text{O}$  solution, 0.312 mmol) gave pink-yellow microcrystals of (**2d**), yield 0.06 g (55%).

Reaction of (**1e**) with  $\text{BF}_3 \cdot \text{Bu}^n_2\text{O}$ : Formation of ( $\eta^3$ -1,2-Dimethylallyl)( $\eta^5$ -pentamethylcyclopentadienyl)(triphenylphosphine)iridium(III) Tetrafluoroborate, (**2e**).—A similar reaction between (**1e**) (0.097 g, 0.148 mmol) in  $\text{Bu}^n_2\text{O}$  (2.5 cm<sup>3</sup>) and  $\text{BF}_3 \cdot \text{Bu}^n_2\text{O}$  (0.062 cm<sup>3</sup> of a 4.782 mol dm<sup>-3</sup>  $\text{Bu}^n_2\text{O}$  solution, 0.295 mmol) gave yellow microcrystals of (**2e**), yield 0.04 g (40%).

Reaction of (**1f**) with  $\text{BF}_3 \cdot \text{Bu}^n_2\text{O}$ : Formation of ( $\eta^5$ -Pentamethylcyclopentadienyl)( $\eta^3$ -1,1,2-trimethylallyl)(triphenylphosphine)iridium(III) Tetrafluoroborate, (**2f**).—A similar

Table 6. Experimental data\* for the crystallographic analyses of (**1c**), (**1e**), and (**1f**)

	(1c)	(1e)	(1f)
Formula	$\text{C}_{34}\text{H}_{42}\text{PRh}$	$\text{C}_{33}\text{H}_{40}\text{IrP}$	$\text{C}_{14}\text{H}_{42}\text{IrP}$
<i>M</i>	584.6	659.9	673.9
Space group	$P2_1/c$	$C2/c$	$P2_1/c$
<i>a</i> /Å	14.982(9)	33.63(4)	15.01(2)
<i>b</i> /Å	11.058(6)	9.29(1)	11.10(1)
<i>c</i> /Å	18.421(10)	20.56(2)	18.44(2)
$\beta$ /°	101.13(2)	116.6(2)	100.90(4)
<i>U</i> /Å <sup>3</sup>	2 994(3)	5 744(15)	3 017(6)
<i>Z</i>	4	8	4
<i>D<sub>c</sub></i> /Mg m <sup>-3</sup>	1.297	1.526	1.484
Reflections for lattice parameters			
Number	20	20	20
θ Range (°)	17.6–24.1	16.7–22.2	20.2–25.6
<i>F</i> (000)	1 224	2 640	1 352
Crystal size (mm)	0.19 × 0.27 × 0.69	0.23 × 0.32 × 0.51	0.26 × 0.45 × 0.82
$\mu$ /nm <sup>-1</sup>	0.632	4.704	4.479
Absorption corrections (min., max.)		1.002–1.286	1.000–1.531
Scan speed/s <sup>-1</sup>	0.075	0.10	0.20
Scan width/°	1.10	1.60	1.60
θ Range (°)	3–25	3–25	3–27
<i>h</i> Range	$\overline{17}$ –17	$\overline{39}$ –34	$\overline{18}$ –18
<i>k</i> Range	0–13	0–10	0–13
<i>l</i> Range	0–21	$\overline{24}$ –24	0–22
Standard reflection	$\overline{7}02$	426	043
Scan mode	0/20	$\omega$	$\omega$
No. of measured reflections	5 752	10 023	6 367
Conditions for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 3\sigma(I)$
No. of observed reflections	3 964	6 301	4 503
No. of reflections used in the refinement	3 964	3 196	4 136
$R_{\text{int}} = \Sigma(I - \langle I \rangle) / \Sigma(I)$	0.0289	0.0441	0.0347
Max. least-squares shift-to-error ratio	0.24	0.41	0.19
Min., max. height in final Fourier map (e Å <sup>-3</sup> )	–0.30, 0.23	–1.15, 1.07	–0.85, 1.01
No. of refined parameters	493	476	446
$R = \Sigma \Delta F / \Sigma  F_o $	0.0443	0.0472	0.0334
$R' = [\Sigma w(\Delta F)^2 / \Sigma w F_o^2]^{1/2}$	0.0482	0.0484	0.0373
$S = [\Sigma w(\Delta F)^2 / (N - P)]^{1/2}$	1.541	1.946	1.290
$k, g \{w = k / [\sigma^2(F_o) + g F_o^{-1}]\}$	1.0, $8.5 \times 10^{-6}$	2.2589, $1.76 \times 10^{-4}$	1.0

\* Data common to all three determinations: Mo- $K_{\alpha 1}$  radiation ( $\lambda = 0.709 30$  Å), Philips PW1100 diffractometer,  $T = 294$  K, data intensity variation  $< 0.2\%$ , block-diagonal least-squares refinement on *F*. *N* = Number of observations, *P* = number of parameters.

reaction between (**1f**) (0.093 g, 0.138 mmol) in  $\text{Bu}^n_2\text{O}$  (2.5 cm<sup>3</sup>) and  $\text{BF}_3 \cdot \text{Bu}^n_2\text{O}$  (0.058 cm<sup>3</sup> of a 4.782 mol dm<sup>-3</sup>  $\text{Bu}^n_2\text{O}$  solution, 0.277 mmol) gave yellow microcrystals of (**2f**), yield 0.05 g (50%).

Reaction of (**1a**) with  $[\text{CPh}_3][\text{PF}_6]$ : Formation of ( $\eta^3$ -1-Methylallyl)( $\eta^5$ -pentamethylcyclopentadienyl)(triphenylphosphine)rhodium(III) Hexafluorophosphate, (**3a**).—According to the already reported procedure,<sup>10</sup> a solution of  $[\text{CPh}_3][\text{PF}_6]$  (0.081 g, 0.21 mmol) in  $\text{CH}_2\text{Cl}_2$  (2 cm<sup>3</sup>) was added dropwise to a solution of (**1a**) (0.12 g, 0.216 mmol) in  $\text{CH}_2\text{Cl}_2$  (2 cm<sup>3</sup>), with stirring at room temperature. The resulting red-orange solution was added to diethyl ether (30 cm<sup>3</sup>) and a yellow microcrystalline solid precipitated. The precipitate was collected, washed repeatedly with diethyl ether and dried, yield 0.128 g (85%).

Reaction of (**1b**) with  $[\text{CPh}_3][\text{PF}_6]$ : Formation of  $(\eta^3\text{-1,2-Dimethylallyl})(\eta^5\text{-pentamethylcyclopentadienyl})(\text{triphenylphosphine})\text{rhodium(III) Hexafluorophosphate}$ , (**3b**).—A similar reaction between (**1b**) (0.056 g, 0.098 mmol) and  $[\text{CPh}_3][\text{PF}_6]$  (0.095 mmol) in  $\text{CH}_2\text{Cl}_2$  (4  $\text{cm}^3$ ) gave orange-yellow microcrystals of (**3b**), yield 0.04 g (60%).

Reaction of (**1c**) with  $[\text{CPh}_3][\text{PF}_6]$ : Formation of  $(\eta^5\text{-Pentamethylcyclopentadienyl})(\eta^3\text{-1,1,2-trimethylallyl})(\text{triphenylphosphine})\text{rhodium(III) Hexafluorophosphate}$ , (**3c**).—A similar reaction between (**1c**) (0.126 g, 0.197 mmol) and  $[\text{CPh}_3][\text{PF}_6]$  (0.058 g, 0.149 mmol) in  $\text{CH}_2\text{Cl}_2$  (4  $\text{cm}^3$ ) gave orange microcrystals of (**3c**), yield 0.02 g (20%).

Reaction of (**1d**) with  $[\text{CPh}_3][\text{PF}_6]$ : Formation of  $(\eta^3\text{-1-Methylallyl})(\eta^5\text{-pentamethylcyclopentadienyl})(\text{triphenylphosphine})\text{iridium(III) Hexafluorophosphate}$ , (**3d**).—A similar reaction between (**1d**) (0.126 g, 0.197 mmol) and  $[\text{CPh}_3][\text{PF}_6]$  (0.074 g, 0.192 mmol) in  $\text{CH}_2\text{Cl}_2$  (4  $\text{cm}^3$ ) gave pale yellow microcrystals of (**3d**), yield 0.133 g (86%).

Reaction of (**1e**) with  $[\text{CPh}_3][\text{PF}_6]$ : Formation of  $(\eta^3\text{-1,2-Dimethylallyl})(\eta^5\text{-pentamethylcyclopentadienyl})(\text{triphenylphosphine})\text{iridium(III) Hexafluorophosphate}$ , (**3e**).—A similar reaction between (**1e**) (0.126 g, 0.197 mmol) and  $[\text{CPh}_3][\text{PF}_6]$  (2.3  $\text{cm}^3$  of a 0.0485  $\text{mol dm}^{-3}$   $\text{CH}_2\text{Cl}_2$  solution, 0.111 mmol) in  $\text{CH}_2\text{Cl}_2$  (2  $\text{cm}^3$ ) gave pale yellow microcrystals of (**3e**), yield 0.025 g (30%).

Reaction of (**1f**) with  $[\text{CPh}_3][\text{PF}_6]$ : Formation of  $(\eta^5\text{-Pentamethylcyclopentadienyl})(\eta^3\text{-1,1,2-trimethylallyl})(\text{triphenylphosphine})\text{iridium(III) Hexafluorophosphate}$ , (**3f**).—Reaction of (**1f**) (0.098 g, 0.146 mmol) with  $[\text{CPh}_3][\text{PF}_6]$  (0.14 mmol) in  $\text{CH}_2\text{Cl}_2$  (4  $\text{cm}^3$ ), at 0°C, gave (**3f**) as a yellow microcrystalline solid, yield 0.04 g (40%).

*Crystal Structure Analysis.*—The relevant data concerning the crystal structure analyses are summarized in Table 6. The lattice parameters were refined by a least-squares procedure<sup>30</sup> using the Nelson and Riley extrapolation function.<sup>31</sup> All reflections were corrected for Lorentz and polarization effects, while absorption effects were corrected only for (**1e**) and (**1f**) using the azimuthal scan method.<sup>32</sup> The structures were solved by Patterson and Fourier techniques and refined by block-diagonal least-squares methods (one block for the non-hydrogen atoms parameters, the other for hydrogens when these were refined), using the SHELX 76 program.<sup>33</sup> The hydrogen atoms were partly located from Fourier difference syntheses and partly put in calculated positions and refined isotropically only in the case of (**1c**) and (**1e**), and, for a number of hydrogens, in the case of (**1f**). Compound (**1e**) was at first treated as triclinic  $P\bar{1}$  with cell constants  $a = 17.439(44)$ ,  $b = 20.428(49)$ ,  $c = 9.292(10)$  Å,  $\alpha = 103.1(1)$ ,  $\beta = 105.4(3)$ ,  $\gamma = 107.4(1)^\circ$ ,  $Z = 4$ , and refined down to  $R = 0.0413$ ,  $R' = 0.0443$ ,  $S = 1.11$ , then transformed to  $C2/c$  by using the matrix  $(2\ 0\ 0\ -1; -1\ -1\ -1)$  deduced from the inspection of the Niggli matrix: (86.34 304.12 417.30; -106.35 -43.15 -43.00). The triclinic refinement gave two pseudo-independent molecules whose averaged parameters did not differ significantly from those found from the monoclinic refinement, except for the e.s.d.s which were larger in the case of the triclinic treatment. Atomic scattering factors and anomalous scattering coefficients were taken from the literature.<sup>34</sup> The calculations were carried out on the GOULD-SELL 32/77 computer of the 'Centro di Studio per la Strutturistica Diffattometrica del C.N.E.' (Parma). In addition to the quoted program, PARST,<sup>35</sup> THMV,<sup>36</sup> and ORTEP<sup>37</sup> programs were used.

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

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