Cyclometallation of Phenylphosphine and Neopentyl Ligands in Ruthenium(II) Complexes: Synthesis and Crystal Structure of the Orthometallated Complexes $[Ru(C_6H_4PR^1R^2)(CH_2CMe_3)(\eta^6\text{-}C_6Me_6)]$ ($R^1 = R^2 = Ph$; $R^1 = Me, R^2 = Ph$; $R^1 = R^2 = Me$) and of the Metallacyclobutanes $[Ru(CH_2CMe_2CH_2)(\eta\text{-}C_6Me_6)(PPhR^1R^2)]$ ($R^1 = R^2 = Ph$; $R^1 = Me, R^2 = Ph$) *

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The compounds $[RuCl_2(\eta^6\text{-}C_6Me_6)L]$ ($L = PPh_3$ **1**, or $PMePh_2$ **2**) react with an excess of $Mg(CH_2CMe_3)Cl$ to give the corresponding orthometallated complexes $[Ru(C_6H_4PR^1R^2)(CH_2CMe_3)(\eta^6\text{-}C_6Me_6)]$ [$R^1 = R^2 = Ph$, **4**; $R^1 = Me$, $R^2 = Ph$, **5**, only the diastereomer (*RS*:*SR*)], and the metallacyclobutanes $[Ru(CH_2CMe_2CH_2)(\eta^6\text{-}C_6Me_6)(PPhR^1R^2)]$ ($R^1 = R^2 = Ph$, **7**; $R^1 = Me$, $R^2 = Ph$, **8**). In contrast $[(RuCl_2(\eta^6\text{-}C_6Me_6)(PMe_2Ph)]$ **3** reacts to give only the orthometallated complex $[Ru(C_6H_4PMe_2)(CH_2CMe_3)(\eta^6\text{-}C_6Me_6)]$ **6**. The X-ray crystal structures of complexes **4**–**8** have been determined and their conformations are discussed. Crystal data are: **4**, $a = 10.483(2)$, $b = 16.050(10)$, $c = 18.451(9)$ Å, $\beta = 103.65(4)°$, $Z = 4$, space group $P2_1/c$, $R = 0.0548$; **5**, $a = 11.926(3)$, $b = 17.810(5)$, $c = 12.780(3)$ Å, $\beta = 99.37(1)°$, $Z = 4$, space group $P2_1/c$, $R = 0.0480$; **6**, $a = 16.762(21)$, $b = 10.116(10)$, $c = 14.874(15)$ Å, $\beta = 108.08(5)°$, $Z = 4$, space group $P2_1/n$, $R = 0.0441$; **7**, $a = 10.720(20)$, $b = 11.670(20)$, $c = 12.050(10)$ Å, $\alpha = 80.32(4)$, $\beta = 78.60(10)$, $\gamma = 87.88(3)°$, $Z = 2$, space group $P\bar{1}$, $R = 0.0232$; **8**, $a = 8.842(10)$, $b = 8.898(20)$, $c = 17.840(70)$ Å, $\alpha = 92.91(6)$, $\beta = 102.48(50)$, $\gamma = 103.12(9)°$, $Z = 2$, space group $P\bar{1}$, and $R = 0.0529$.

We have reported that by treating the complexes $[RuCl_2(\eta^6\text{-}C_6Me_6)(PPhR^1R^2)]$ ($R^1 = R^2 = Ph$; $R^1 = Me$, $R^2 = Ph$; $R^1 = R^2 = Me$) with $Mg(CH_2SiMe_3)Cl$ the corresponding orthometallated alkyl complexes $[Ru(C_6H_4PR^1R^2)(CH_2SiMe_3)(\eta^6\text{-}C_6Me_6)]$ are obtained.[1] These reactions are related to the alkylation of the isoelectronic systems $[MCl_2(\eta^5\text{-}C_5Me_5)(PPh_3)]$ (M = Rh or Ir) by $Mg(CH_2CMe_3)Cl$ or $Mg(CH_2SiMe_3)Cl$ where however dialkyl derivatives, or metallacyclobutanes, can be formed in addition to the orthometallated alkyl complexes, depending on the experimental conditions.[2]

We now report the results obtained from the reactions of the above ruthenium systems with $Mg(CH_2CMe_3)Cl$ in which, as in the case of the compounds of Rh and Ir cited above, the cyclometallation reaction involves both the phosphine and the alkyl group. A brief account of this research has been communicated.[3]

Results and Discussion

Chemical Studies.—The reaction of $[RuCl_2(\eta^6\text{-}C_6Me_6)(PPhR^1R^2)]$ ($R^1 = R^2 = Ph$, **1**; $R^1 = Me$, $R^2 = Ph$, **2**; $R^1 = R^2 = Me$, **3**) with $Mg(CH_2CMe_3)Cl$ in pentane is similar to that with $Mg(CH_2SiMe_3)Cl$,[1] giving in all cases alkyl derivatives of ruthenium(II), containing an orthometallated phosphine (see Scheme 1).

The orange-yellow compounds **4**–**6** have been isolated by column chromatography on neutral alumina of the hydrolysed reaction mixture, using pentane as the eluent, and crystallized from pentane to give crystals suitable for X-ray structure elucidation. In the case of complex **5**, where a pair of diastereomers can exist, only the (*RS*:*SR*) isomer has been obtained (see the crystallographic section), in contrast with what has been observed for the related $[Ru(C_6H_4PMePh)(CH_2SiMe_3)(\eta^6\text{-}C_6Me_6)]$, which was formed as a mixture of two diastereomers in different amounts (2:1).[1] The spatial arrangement of the substituents around the chiral centres in **5** is the same as that of the major isomer of the trimethylsilylmethyl analogue.

Since in principle the other diastereomer of compound **5** could have been lost during the purification procedures, we investigated the crude reaction mixture by ^1H NMR spectroscopy. No signals attributable to the missing diastereomer were found, but, in addition to **5**, a major product was present which was identified as the metallacyclobutane $[Ru(CH_2CMe_2CH_2)(\eta^6\text{-}C_6Me_6)(PMePh_2)]$ **8**.

The crude mixtures from the reaction of complexes **1** and **3** with $Mg(CH_2CMe_3)Cl$ were similarly examined and, while in the case of **3** we did not find any metallacyclobutane, in the case

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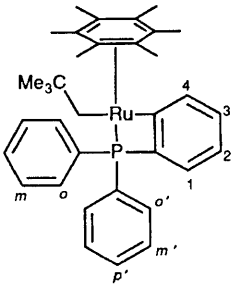
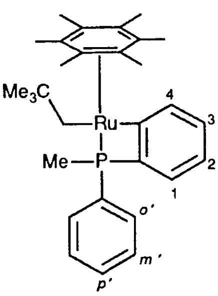
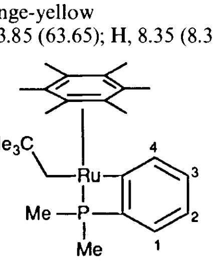
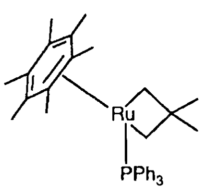
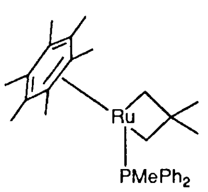
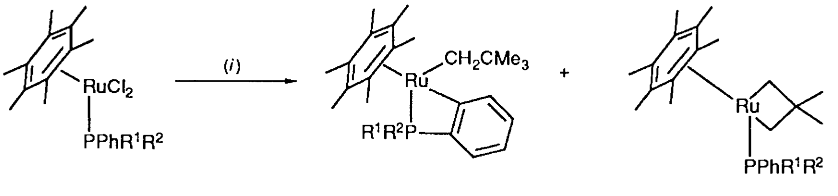
* (*o*-Diphenylphosphinophenyl-κ^2C^1,P)(η^6-hexamethylbenzene)(neopentyl)ruthenium(II), (*RS*:*SR*) (η^6-hexamethylbenzene)(*o*-methylphenylphosphinophenyl-κ^2C^1,P)(neopentyl)ruthenium(II), (*o*-dimethylphosphinophenyl-κ^2C^1,P)(η^6-hexamethylbenzene)(neopentyl)ruthenium(II), (2,2-dimethylpropane-1,3-diyl)(η^6-hexamethylbenzene)(triphenylphosphine)ruthenium(II), and (2,2-dimethylpropane-1,3-diyl)(η^6-hexamethylbenzene)(methyldiphenylphosphine)ruthenium(II).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 1 Analytical and spectroscopic data

Compound, colour and analysis[a]	^{1}H NMR data[b]
4 [Ru(*o*-C$_6$H$_4$PPh$_2$)(CH$_2$CMe$_3$)(η^6-C$_6$Me$_6$)] Orange-yellow C, 71.20 (70.55); H, 7.40 (7.25)  	0.73 (9 H, s, CMe$_3$), 1.35 [1 H, dd, *J*(H–H) 11.4, *J*(H–P) 18.4, C*H*CMe$_3$], 1.70 [18 H, d, *J*(H–P) 0.7, C$_6$Me$_6$], 1.95 [1 H, d, *J*(H–H) 11.4, C*H*CMe$_3$], 6.81 [1 H, ddd, *J*(H^1–H^2) 7.3, *J*(H^1–H^3) 1.4, *J*(H–P) 11.1, H^1], 6.84–6.91 (3 H, m, H$^{m'}$ + H$^{p'}$), 6.97 [1 H, ddt, *J*(H^2–H^1) ~ *J*(H^2–H^3) 7.4, *J*(H^2–H^4) 1.1, *J*(H–P) 3.2, H^2], 7.05–7.21 (5 H, m, H$^{o'}$ + H^m + H^p), 7.29 [1 H, dt, *J*(H^3–H^2) ~ *J*(H^3–H^4) 7.4, *J*(H^3–H^1) 1.4, H^3], 7.55 [1 H, dd, *J*(H^4–H^3) 7.4, *J*(H–P) 4.4, H^4], 7.62 [2 H, ddd, *J*(H^o–H^m) 9.4, *J*(H^o–H^p) 1.4, *J*(H–P) 8.0, H^o]
5 (*RS*:*SR*)[Ru(*o*-C$_6$H$_4$PMePh)(CH$_2$CMe$_3$)(η^6-C$_6$Me$_6$)][c] Orange-yellow C, 67.90 (67.50); H, 7.80 (7.75)  	1.00 (9 H, s, CMe$_3$), 1.64 [18 H, d, *J*(H–P) 0.8, C$_6$Me$_6$], 1.67 [3 H, d, *J*(H–P) 9.4, PMe], 1.75 [1 H, dd, *J*(H–H) 11.7, *J*(H–P) 18.9, C*H*CMe$_3$], 2.03 [1 H, d, *J*(H–H) 11.7, C*H*CMe$_3$], 6.51 [1 H, dddd, *J*(H^1–H^2) 7.3, *J*(H^1–H^3) 1.4, *J*(H^1–H^4) 0.7, *J*(H–P) 12.3, H^1], 6.95 [1 H, ddt, *J*(H^2–H^3) ~ *J*(H^2–H^1) 7.3, *J*(H^2–H^4) 1.1, *J*(H–P) 2.9, H^2], 6.98–7.12 (3 H, m, H$^{m'}$ + H$^{p'}$), 7.16–7.26 (2 H, m, H$^{o'}$), 7.29 [1 H, dt, *J*(H^3–H^2) ~ *J*(H^3–H^4) 7.4, *J*(H^3–H^1) 1.4, H^3], 7.54 [1 H, dddd, *J*(H^4–H^3) 7.4, *J*(H^4–H^2) 1.0, *J*(H^4–H^1) 0.8, *J*(H–P) 4.3, H^4]
6 [Ru(*o*-C$_6$H$_4$PMe$_2$)(CH$_2$CMe$_3$)(η^6-C$_6$Me$_6$)] Orange-yellow C, 63.85 (63.65); H, 8.35 (8.35)  	0.94 (9 H, s, CMe$_3$), 1.16 [3 H, d, *J*(H–P) 9.2, PMe], 1.30 [3 H, d, *J*(H–P) 9.3, PMe], 1.53 [1 H, dd, *J*(H–H) 11.6, *J*(H–P) 19.0, C*H*CMe$_3$], 1.80 [18 H, d, *J*(H–P) 0.7, C$_6$Me$_6$], 1.93 [1 H, d, *J*(H–H) 11.6, C*H*CMe$_3$], 6.48 [1 H, ddd, *J*(H^1–H^2) 7.2, *J*(H^1–H^3) 1.3, *J*(H–P) 12.5, H^1], 6.89 [1 H, ddt, *J*(H^2–H^3) ~ *J*(H^2–H^1) 7.3, *J*(H^2–H^4) 1.0, *J*(H–P) 2.9, H^2], 7.23 [1 H, dt, *J*(H^3–H^2) ~ *J*(H^3–H^4) 7.4, *J*(H^3–H^1) 1.3, H^3], 7.45 [1 H, dd, *J*(H^4–H^3) 7.3, *J*(H–P) 4.1, H^4]
7 [Ru(CH$_2$CMe$_2$CH$_2$)(η^6-C$_6$Me$_6$)(PPh$_3$)] Orange C, 71.00 (70.55); H, 7.35 (7.25)  	0.08 (3 H, s, CH$_2$C*Me*), 0.22 [2 H, dd, *J*(H–H) 7.3, *J*(H–P) 1.6, RuCH], 0.53 [2 H, dd, *J*(H–H) 7.3, *J*(H–P) 14.5, RuCH], 0.94 (3 H, s, CH$_2$C*Me*), 1.61 (18 H, s, C$_6$Me$_6$), 7.0–7.25 (9 H, m, H^m + H^p), 7.6–7.8 (6 H, m, H^o)
8 [Ru(CH$_2$CMe$_2$CH$_2$)(η^6-C$_6$Me$_6$)(PMePh$_2$)] Orange C, 67.65 (67.50); H, 7.80 (7.75)  	0.26 [2 H, dd, *J*(H–H) 7.7, *J*(H–P) 1.4, RuCH], 0.41 [2 H, dd, *J*(H–H) 7.7, *J*(H–P) 14.0, RuCH], 0.91 (3 H, s, CH$_2$C*Me*), 1.02 (3 H, s, CH$_2$C*Me*), 1.65 (18 H, s, C$_6$Me$_6$), 1.80 [3 H, d, *J*(H–P) 22.5, PMe], 7.0–7.2 (6 H, m, H^m + H^p), 7.43 [4 H, ddd, *J*(H^o–H^m) 9.3, *J*(H^o–H^p) 1.7, *J*(H–P) 7.7, H^o]

[a] Found (Calc.) (%). [b] Spectra recorded at 200 MHz; given as chemical shift (δ) [relative intensity, multiplicity, coupling (*J* in Hz), assignment]; in [^{2}H$_6$]benzene. [c] Fisher projection corresponding to the enantiomer shown in Fig. 1.



1 $R^1 = R^2 = Ph$ **4** (30%) **7** (45%)
2 $R^1 = Me, R^2 = Ph$ **5** (9%) **8** (70%)
3 $R^1 = R^2 = Me$ **6** (43%) –

Scheme 1 (*i*) $Mg(CH_2CMe_3)Cl$ in pentane, 20 °C

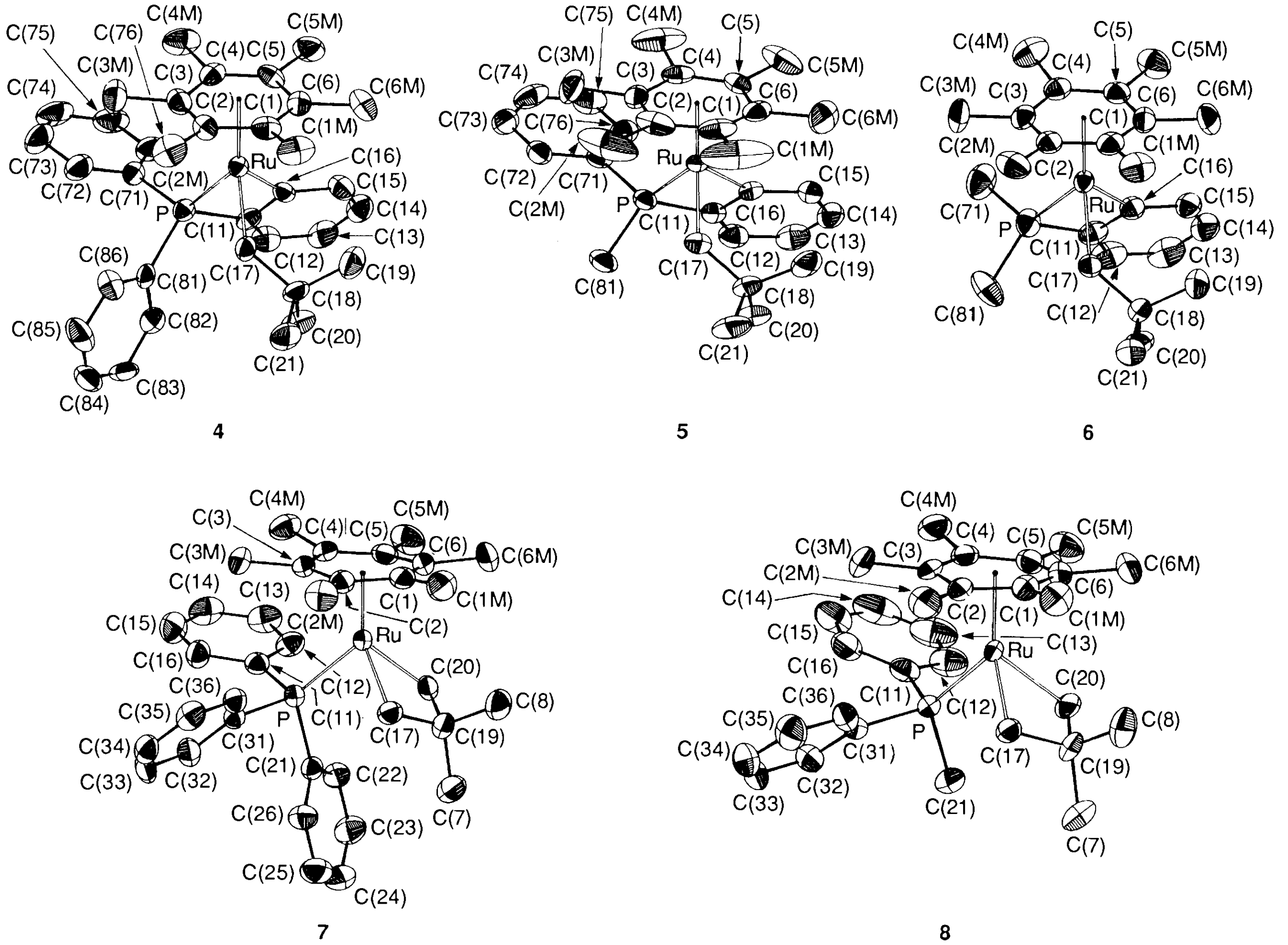


Fig. 1 ORTEP drawings of the complexes **4**–**8** showing the molecular structure and thermal motion. The hydrogen atoms are omitted for clarity. Thermal ellipsoids are at 50% probability.

of **1** we found the complex $[\overline{Ru(CH_2CMe_2}CH_2)(\eta^6\text{-}C_6Me_6)(PPh_3)]$ **7**, to be present in fairly high amounts. Compounds **7** and **8** are noticeably less soluble in pentane than the corresponding orthometallated compounds and can be isolated in a pure form by fractional crystallization. They do not survive chromatographic purification on neutral alumina: indeed no band was eluted by using pentane, diethyl ether, benzene or CH_2Cl_2 as eluent.

Finally the use of $Li(CH_2CMe_3)Cl$, instead of the Grignard reagent, in the alkylation of compounds **1**–**3** does not lead to the isolation of any product.

Analytical and ^1H NMR data are reported in Table 1. All the compounds **4**–**8** give well resolved ^1H NMR spectra; in the case of the orthometallated compounds **4**–**6** the main features are the non-equivalence of the methylene protons in the CH_2CMe_3 group and a characteristic pattern of four multiplets in the region δ 6.5–7.5, due to the aromatic protons of the orthometallated benzene ring. In the case of the ruthenacyclobutane complexes **7** and **8**, the protons of the metallacyclic moiety appear as two well separated singlets (two inequivalent methyl groups), and as two multiplets (the two protons of the same methylene group are different). The structures of complexes **4**–**8** have been determined by X-ray crystal analysis.

Crystal Structure Analysis of Compounds **4**–**8**.—The final atomic coordinates of the non-hydrogen atoms for the five compounds studied are given in Table 2 and the relevant structural parameters are compared in Table 3.

Thermal-motion analysis was carried out in Shomaker and Trueblood's[4] rigid-body approximation considering also the internal motions of some groups according to Dunitz and White's one-parameter model.[5,6] The results (deposited) correspond quite well to those found with the similar silyl derivatives we studied recently.[1] In particular the largest atomic

Table 2 Fractional coordinates (10^4) for compounds **4**–**8**

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Compound **4**							
Ru	2377.8(7)	1200.7(5)	2507.7(5)	C(16)	2535(9)	122(6)	1942(5)
P	4449(2)	967(2)	2327(1)	C(17)	1983(9)	1927(7)	1478(5)
C(1)	591(10)	1853(7)	2779(5)	C(18)	1260(10)	1646(7)	673(5)
C(2)	1761(10)	2291(6)	3142(5)	C(19)	-2(11)	1201(8)	684(6)
C(3)	2774(11)	1847(7)	3609(6)	C(20)	2098(12)	1058(7)	301(5)
C(4)	2645(10)	971(7)	3752(5)	C(21)	992(12)	2443(8)	193(6)
C(5)	1539(10)	539(7)	3379(5)	C(71)	5865(9)	683(7)	3067(5)
C(6)	488(9)	981(7)	2882(5)	C(72)	6657(10)	1276(8)	3458(5)
C(1M)	-574(11)	2323(8)	2326(6)	C(73)	7754(11)	1069(10)	4035(6)
C(2M)	1854(13)	3232(7)	3070(7)	C(74)	8020(13)	276(12)	4245(6)
C(3M)	3976(11)	2311(8)	4050(6)	C(75)	7243(13)	-347(9)	3841(7)
C(4M)	3737(12)	534(8)	4333(6)	C(76)	6157(10)	-136(7)	3273(5)
C(5M)	1330(12)	-383(8)	3494(6)	C(81)	5275(9)	1608(7)	1758(5)
C(6M)	-772(11)	545(7)	2484(6)	C(82)	5795(10)	1286(7)	1201(5)
C(11)	3809(9)	25(6)	1851(5)	C(83)	6393(11)	1786(10)	770(6)
C(12)	4261(11)	-670(7)	1522(6)	C(84)	6504(12)	2600(10)	887(7)
C(13)	3381(12)	-1294(7)	1249(6)	C(85)	5984(12)	2968(8)	1437(8)
C(14)	2125(11)	-1249(7)	1335(5)	C(86)	5367(10)	2441(7)	1845(6)
C(15)	1692(11)	-562(7)	1671(5)				
Compound **5**							
Ru	2254.3(3)	5484.3(2)	2931.6(3)	C(13)	3299(6)	5175(4)	-794(5)
P	3251.0(11)	4471.8(8)	2507.5(11)	C(14)	2673(5)	5793(4)	-693(5)
C(1)	1445(5)	6323(4)	3983(7)	C(15)	2305(4)	5960(3)	307(5)
C(2)	1638(5)	5630(5)	4591(5)	C(16)	2562(4)	5508(3)	1261(4)
C(3)	1244(5)	4957(4)	4073(6)	C(17)	3773(4)	6045(3)	3540(5)
C(4)	617(4)	4975(3)	2982(6)	C(18)	4372(5)	6636(4)	2949(5)
C(5)	499(4)	5651(3)	2384(5)	C(19)	3634(6)	7257(4)	2407(7)
C(6)	924(5)	6324(3)	2886(6)	C(20)	4942(5)	6296(4)	2030(6)
C(1M)	1822(8)	7053(6)	4600(11)	C(21)	5217(6)	6992(4)	3860(6)
C(2M)	2268(8)	5589(10)	5831(7)	C(71)	2694(4)	3522(3)	2339(4)
C(3M)	1370(8)	4211(6)	4706(10)	C(72)	2875(5)	3002(3)	3215(5)
C(4M)	59(7)	4275(5)	2450(10)	C(73)	2460(5)	2287(4)	3080(6)
C(5M)	-155(6)	5677(6)	1210(6)	C(74)	1864(6)	2082(4)	2067(7)
C(6M)	713(7)	7059(4)	2204(9)	C(75)	1676(5)	2580(4)	1193(6)
C(11)	3186(4)	4863(3)	1119(4)	C(76)	2087(5)	3301(4)	1322(5)
C(12)	3559(5)	4700(4)	126(5)	C(81)	4641(5)	4267(4)	3091(6)
Compound **6**							
Ru	7412.0(3)	-447.7(4)	-374.9(3)	C(11)	8300(4)	1331(5)	1046(4)
P	7854(1)	-199(2)	1247(1)	C(12)	8772(4)	2344(7)	1614(5)
C(1)	6727(4)	-1273(5)	-1852(4)	C(13)	9022(4)	3371(7)	1142(6)
C(2)	6726(4)	-2264(5)	-1163(4)	C(14)	8841(4)	3356(6)	175(5)
C(3)	7491(4)	-2636(5)	-495(4)	C(15)	8375(4)	2342(5)	-365(4)
C(4)	8266(4)	-2116(5)	-556(4)	C(16)	8081(3)	1297(5)	55(4)
C(5)	8255(4)	-1109(5)	-1203(4)	C(17)	6247(4)	516(5)	-377(4)
C(6)	7483(4)	-677(5)	-1864(4)	C(18)	5967(4)	1983(5)	-601(4)
C(1M)	5909(4)	-939(8)	-2587(4)	C(19)	6149(4)	2497(7)	-1456(5)
C(2M)	5911(4)	-2936(7)	-1190(5)	C(20)	6359(4)	2889(6)	239(5)
C(3M)	7496(5)	-3674(7)	234(5)	C(21)	5014(5)	2016(7)	-804(5)
C(4M)	9106(4)	-2693(7)	38(5)	C(71)	8719(5)	-1164(8)	2026(5)
C(5M)	9076(5)	-530(7)	-1259(6)	C(81)	7219(5)	28(9)	2030(5)
C(6M)	7493(5)	339(7)	-2620(5)				
Compound **7**							
Ru	1693.8(3)	1435.5(2)	1949.3(3)	C(11)	527(3)	3660(3)	3414(3)
P	2003.8(8)	3073.8(7)	2627.9(8)	C(12)	-192(4)	2925(3)	4334(3)
C(1)	1431(4)	305(3)	616(3)	C(13)	-1314(4)	3309(4)	4948(3)
C(2)	1322(4)	1507(3)	150(3)	C(14)	-1763(4)	4412(4)	4640(4)
C(3)	358(4)	2192(3)	708(3)	C(15)	-1090(4)	5124(4)	3708(4)
C(4)	-437(3)	1712(3)	1772(3)	C(16)	45(4)	4760(3)	3109(3)
C(5)	-223(4)	560(3)	2290(3)	C(21)	3110(3)	3108(3)	3634(3)
C(6)	665(4)	-163(3)	1672(4)	C(22)	2760(4)	2684(3)	4803(3)
C(1M)	2328(4)	-446(4)	-89(4)	C(23)	3614(4)	2702(4)	5523(4)
C(2M)	2153(4)	1963(4)	-998(3)	C(24)	4817(4)	3126(4)	5113(4)
C(3M)	65(4)	3409(3)	162(4)	C(25)	5177(4)	3539(4)	3954(4)
C(4M)	-1573(4)	2391(4)	2264(4)	C(26)	4337(4)	3520(4)	3238(3)
C(5M)	-1039(4)	56(4)	3433(4)	C(31)	2647(3)	4344(3)	1558(3)
C(6M)	721(5)	-1444(3)	2149(4)	C(32)	2871(4)	5416(3)	1852(3)
C(17)	3725(3)	1253(3)	1596(3)	C(33)	3377(4)	6327(3)	1018(4)
C(19)	3807(4)	293(3)	2617(3)	C(34)	3645(4)	6195(3)	-113(4)
C(20)	2448(4)	418(3)	3309(3)	C(35)	3443(4)	5152(4)	-418(3)
C(7)	4860(4)	464(4)	3264(4)	C(36)	2954(4)	4226(3)	423(3)
C(8)	4006(4)	-903(4)	2241(4)				

Table 2 (*continued*)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Compound **8**							
Ru	−852.3(6)	−1382.6(6)	−3076.2(3)	C(20)	−3308(9)	−2233(12)	−3021(6)
P	−175(2)	−1024(2)	−1774(1)	C(7)	−4138(13)	−5017(13)	−2611(7)
C(1)	−529(9)	−1742(9)	−4317(4)	C(8)	−4094(13)	−4649(14)	−3975(7)
C(2)	990(8)	−1340(9)	−3786(4)	C(11)	180(10)	993(9)	−1365(4)
C(3)	1482(9)	113(10)	−3324(5)	C(12)	−1125(13)	1656(11)	−1454(6)
C(4)	389(9)	1084(8)	−3334(4)	C(13)	−908(23)	3205(16)	−1187(9)
C(5)	−1200(9)	571(9)	−3798(4)	C(14)	565(21)	4113(13)	−851(6)
C(6)	−1609(9)	−814(9)	−4331(4)	C(15)	1840(19)	3472(11)	−758(6)
C(1M)	−907(13)	−3191(12)	−4902(6)	C(16)	1684(13)	1941(10)	−1017(5)
C(2M)	2126(14)	−2370(16)	−3805(7)	C(21)	−1518(11)	−1930(11)	−1173(5)
C(3M)	3161(12)	645(15)	−2856(8)	C(31)	1640(9)	−1598(9)	−1289(4)
C(4M)	946(18)	2691(12)	−2926(7)	C(32)	2246(11)	−1317(10)	−490(5)
C(5M)	−2364(14)	1581(13)	−3799(7)	C(33)	3609(12)	−1783(12)	−153(6)
C(6M)	−3183(13)	−1149(16)	−4921(6)	C(34)	4376(12)	−2497(14)	−594(7)
C(17)	−1479(9)	−3811(9)	−2973(5)	C(35)	3766(13)	−2808(15)	−1364(7)
C(19)	−3303(9)	−3962(9)	−3136(5)	C(36)	2404(11)	−2355(13)	−1700(7)

displacements are observed for the methyl groups of the hexamethylbenzene ligand, particularly in compound **5** (see the atomic ellipsoids in Fig. 1), and of the neopentyl moieties. In the following discussion all the conventions applied for averaging and comparing data in the previous papers of this series[1] are followed.

Discussion of the structures. All these molecules have the 'three-legged piano stool' type of structure observed for similar silyl derivatives, as can be seen from the structural parameters in Table 3. Nevertheless, considering the co-ordination spheres of the three orthometallated compounds, significant differences are observed between the distances and angles of **5** if compared with **4** and **6**. In particular the hexamethylbenzene in **5** is found nearer to the metal than in the other two compounds, and this produces a lengthening of 0.26 Å in the Ru–C(16) distance and a shortening of 0.08 and 0.03 Å in the Ru–C(17) and Ru–P distances, respectively, if compared with the other two orthometallated complexes. The bond angles at the metal which are particularly affected by this situation are Bz–Ru–C(17) (Bz is the centroid of hexamethylbenzene) which becomes narrower, and P–Ru–C(17) which becomes wider, the other angles remaining practically unchanged. Significant displacements from planarity of the benzene ring of the hexamethylbenzene ligand are observed for all five compounds as shown by the following parameters (Δ is the displacement of the ring atoms from the least-squares mean plane and Q is Cremer and Pople's total puckering amplitude).[7]

Compound	4	5	6	7	8
$\Sigma(\Delta/\sigma)^2$	16.6	113.4	112.4	218.1	51.6
Q/Å	0.042(9)	0.065(6)	0.063(6)	0.085(6)	0.098(14)

Considering the C–C distances in the benzene ring of hexamethylbenzene (Table 3), the same trend is observed as that found in the ruthenium orthometallated derivatives we recently studied,[1] *i.e.* the benzene ring shows a tendency to assume a C_{3v} instead of a D_{6h} symmetry, as the *cis* bonds (*i.e.* those intersecting the projections of the metal–other ligand bonds) are lengthened to 1.432(2) Å (av.) and the *trans* bonds (*i.e.* those that do not intersect the projections of the metal–other ligand bonds) are shortened to 1.410(3) Å (av.), as observed in benzenetricarbonylchromium.[8]

As observed for the other similar η^6-C_6Me_6 derivatives, the methyl groups are displaced [by 0.090(2) Å (av.)] from the plane of the ring in the opposite direction with respect to the metal [all methyls in compounds **4** and **5**, except C(3M) in compound **6**, and C(2M) and C(5M) in **7** and **8**], corresponding to an angle of 2.7(2)° (av.) formed by the C–CH_3 vector with the ring plane. This plane is perpendicular to the Ru–Bz direction with deviations from perpendicularity which do not exceed 0.9°, except for compound **5** that shows a higher deviation [6.3(2)°]. Probably this tilting is a consequence of the shorter approach of the η-ligand to the metal in this compound.

In compound **5** two chiral centres are present: Ru and P (see Fig. 1), so different diastereoisomers are possible, but only the *RS* and *SR* ones were obtained, both being present in the same crystal as the space group is centrosymmetric.

The Newman projections of Fig. 2 allow comparison of the conformations about the Ru–Bz and Ru–P directions in the two series of compounds. It appears that, while along Ru–Bz the only relevant difference involves C(16) (in orthometallates) and C(20) (in ruthenacyclobutanes) [Fig. 2(*a*) and (*c*)], along the Ru–P bond more drastic differences are present in the two conformations [Fig. 2(*b*) and (*d*)].

A deeper insight into the conformations of these molecules can be obtained by considering the van der Waals energy profiles calculated when fragments are rotated with respect to the rest of the molecule. Fig. 3 shows the energy profiles obtained by rotating the hexamethylbenzene ligand about the Ru–Bz direction. In the case of the orthometallates the maxima are due to the interactions involving the methyl groups of C_6Me_6 and the C(19) methyl, C(17) methylene, and the hydrogen bound to the C(15) carbon of the orthometallated phenyl ring and, for compound **6**, also the C(71) methyl (see Fig. 1). The energy barriers do not exceed 40 kJ mol^{-1} in the case of compounds **4** and **6**, while, with compound **5**, these barriers are in general much higher (the highest is about 200 kJ mol^{-1}). This has to be connected with the shorter Ru–Bz distance and the tilting of the benzene ligand found in this compound.

With metallacyclobutanes the interactions of the C_6Me_6 methyl groups involve the C(8) methyl, the C(20) methylene, and the phenyl hydrogen bound to C(36) in both compounds, and in addition the C(17) methylene and the phenyl hydrogen bound to C(12) in the case of compound **7**, for which the highest barriers are observed.

The energy profiles for rotation about C(17)–C(18) in the orthometallates (not shown in Fig. 3) are similar for the three compounds, but also in this case the highest barriers, which involve the interactions between the C(21) methyl with C(15) and C(16), are found for compound **5**, where interactions between the C(20) and C(21) methyls with the C(6M) methyls are also present (*ca.* 160 kJ mol^{-1} for **5**, *ca.* 70 kJ mol^{-1} for **4** and **6**). No other minimum was found besides that corresponding to the conformation of the molecule in the crystal when rotating all the neopentyl groups about Ru–C(17) in the orthometallated derivatives.

In the case of metallacyclobutanes, rotation about Ru–P shows very high energy barriers with two minima at 0 and 180° (the rotation is considered with respect to the position found

Table 3 Comparison of bond distances (Å) and angles (°) for complexes **4**–**8** with estimated standard deviations (e.s.d.s) in parentheses

	4	**5**	**6**	**7**	**8**	Average
(*a*) Co-ordination sphere						
Ru–P	2.304(3)	2.273(2)	2.307(3)	—	—	2.288(12)
	—	—	—	2.262(3)	2.257(10)	2.262(3)
Ru–C(C_6Me_6) (av.)	2.273(9)	2.213(41)	2.270(11)	—	—	2.270(7)
	—	—	—	2.298(12)	2.303(15)	2.300(9)
Ru–Bz	1.775(13)	1.712(7)	1.770(6)	—	—	1.749(20)
	—	—	—	1.810(5)	1.808(10)	1.810(4)
Ru–C(16)	2.038(9)	2.224(5)	2.083(5)	—	—	2.138(54)
Ru–C(17)	2.184(10)	2.104(5)	2.182(6)	—	—	2.142(28)
	—	—	—	2.144(5)	2.133(9)	2.141(4)
Ru–C(20)	—	—	—	2.133(4)	2.156(9)	2.137(8)
Bz–Ru–P	138.4(4)	137.0(2)	136.4(2)	—	—	136.9(4)
	—	—	—	133.2(3)	133.2(6)	133.2(3)
Bz–Ru–C(16)	131.2(5)	132.1(3)	131.2(3)	—	—	131.6(3)
Bz–Ru–C(17)	123.2(5)	119.5(3)	124.8(3)	—	—	122.3(17)
	—	—	—	130.1(2)	130.1(7)	130.1(2)
Bz–Ru–C(20)	—	—	—	128.1(3)	128.5(8)	128.1(3)
P–Ru–C(16)	66.3(3)	67.1(1)	67.6(2)	—	—	67.1(2)
P–Ru–C(17)	87.3(3)	90.7(2)	87.1(2)	—	—	88.6(12)
	—	—	—	86.7(2)	87.0(5)	86.7(2)
P–Ru–C(20)	—	—	—	90.2(2)	88.7(7)	90.1(4)
C(16)–Ru–C(17)	92.1(4)	94.5(2)	91.1(1)	—	—	91.8(9)
C(17)–Ru–C(20)	—	—	—	65.8(2)	66.8(7)	65.9(3)
[Ru–Bz] ∧ [C(1)–C(6)]	89.2(3)	83.7(2)	89.1(2)	89.3(2)	89.4(6)	87.7(12)
Ru–CH_2–C	128.4(7)	125.8(4)	129.4(4)	—	—	127.7(12)
(*b*) C_6Me_6 ligand						
C–C *cis** (av)	1.440(8)	1.443(18)	1.431(5)	1.430(3)	1.434(7)	1.432(2)
C–C *trans** (av.)	1.399(10)	1.424(7)	1.405(5)	1.412(3)	1.414(10)	1.410(3)
C–CH_3 (av.) 1.522(5) [minimum 1.494(14), maximum 1.642 (10)]						
C–C–C (endocyclic) (av.) 119.2(2) [minimum 117.3(6), maximum 121.7(6)]						
CH_3 · · · [C(1)–C(6)] (av.)	0.089(2)	0.060(31)	0.088(42)	0.120(55)	0.122(56)	0.086(16)
CH_3 ∧ [C(1)–C(6)] (av.)	3.4(8)	2.3(8)	3.5(13)	4.1(18)	3.9(16)	2.7(2)
C_6Me_6 Effective cone angle	156	166	159	157	158	159(2)
(*c*) Neopentyl ligand						
C–CH_2	1.565(13)	1.536(9)	1.562(8)	1.53 av.	1.54 av.	1.543(4)
C–CH_3 (av.)	1.536(14)	1.540(18)	1.517(12)	1.532(5)	1.540(11)	1.532(4)
CH_2–C–CH_3 minimum	106.7(8)	102.0(5)	106.8(5)	111.2(5)	110.1(15)	107.1(18)
maximum	113.4(8)	116.4(5)	112.7(5)	114.5(4)	115.4(12)	114.5(7)
CH_3–C–CH_3 minimum	107.1(8)	103.3(5)	107.6(5)	107.7(5)	107.2(11)	106.4(9)
maximum	111.0(9)	114.3(5)	109.8(5)	107.7(5)	107.2(11)	110.3(14)
(*d*) Metallaphosphacyclobutane ring						
P–C(11)	1.796(10)	1.896(6)	1.784(6)	—	—	1.836(38)
C(11)–C(16)	1.399(14)	1.396(8)	1.405(8)	—	—	1.400(5)
Ru · · · C(11)	2.852(10)	2.943(6)	2.822(6)	—	—	2.876(40)
P · · · C(16)	2.384(9)	2.487(5)	2.450(6)	—	—	2.457(26)
Ru–P–C(11)	87.2(3)	89.3(2)	86.3(2)	—	—	88.0(10)
P–C(11)–C(16)	95.7(7)	97.0(4)	99.7(4)	—	—	97.8(11)
Ru–C(16)–C(11)	110.8(7)	106.5(4)	106.4(4)	—	—	107.1(11)
Ru–C(16)–C(15)	136.0(7)	140.4(4)	137.5(4)	—	—	138.7(12)
P–C(11)–C(12)	138.9(8)	141.2(4)	136.0(5)	—	—	138.9(17)
Ru · · · [C(11)–C(16)]	0.072(1)	0.022(1)	0.035(3)	—	—	0.032(14)
P · · · [C(11)–C(16)]	0.095(3)	0.035(2)	0.081(3)	—	—	0.053(18)
(*e*) Orthometallated benzene						
C(11)–C(12)	1.406(16)	1.442(9)	1.406(8)	—	—	1.420(12)
C(12)–C(13)	1.373(16)	1.440(10)	1.389(11)	—	—	1.410(20)
C(13)–C(14)	1.365(18)	1.347(10)	1.376(12)	—	—	1.360(9)
C(14)–C(15)	1.392(16)	1.447(9)	1.385(9)	—	—	1.412(21)
C(15)–C(16)	1.429(13)	1.453(8)	1.392(8)	—	—	1.426(20)
C(12)–C(11)–C(16)	125.2(9)	121.8(5)	124.2(6)	—	—	123.2(10)
C(11)–C(12)–C(13)	118.1(11)	123.0(6)	116.4(6)	—	—	119.8(22)
C(12)–C(13)–C(14)	120.2(10)	116.8(6)	121.1(7)	—	—	119.0(14)
C(13)–C(14)–C(15)	121.2(10)	120.3(6)	121.1(7)	—	—	120.7(4)
C(14)–C(15)–C(16)	122.1(10)	125.0(5)	121.1(6)	—	—	123.1(13)
C(15)–C(16)–C(11)	113.2(9)	113.0(5)	116.1(5)	—	—	114.2(10)

Table 3 (*continued*)

	4	5	6	7	8	Average
(*f*) Metallacyclobutane						
Ru–CH_2–C	—	—	—	96.6(2) (av.)	95.4(7) (av.)	96.5(3)
CH_2–C	—	—	—	1.537(6) (av.)	1.546(9) (av.)	1.540(5)
(*g*) Phosphine ligand						
P–C(Ph) (av.) 1.844(6)	Ru–P–C(Ph) (av.) 120.5(16)					
P–C(Me) (av.) 1.791(26)	Ru–P–C(Me) (av.) 124.6(13)					
P–C–C (av.) 121.2(6)						

* See text.

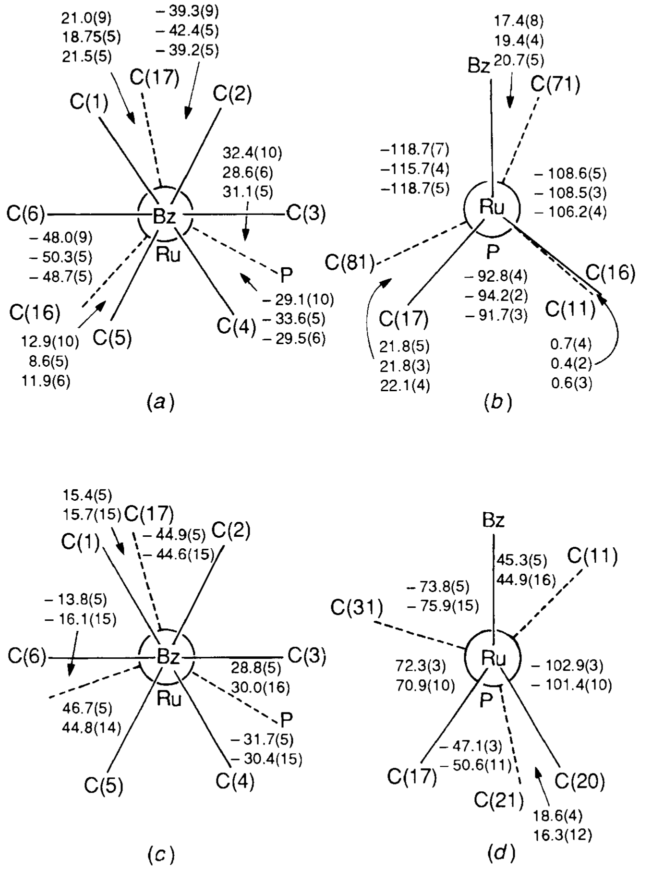


Fig. 2 Newman projections (angles in °) showing the conformations along Bz–Ru and Ru–P: (*a*) and (*b*) in orthometallates where the values of the torsion angles refer to the compounds **4**–**6** from the top to the bottom in each triplet of data; (*c*) and (*d*) in the ruthenacyclobutanes with the values of the angles for compound **7** above and for **8** below in each doublet

in the crystal), showing that there are only two possibilities for the orientation of the phosphine in these compounds.

The energy profiles for the rotation of the phosphine phenyl groups are similar in the two series of derivatives. Also in this case the energy barriers are lower for orthometallates than for metallacyclobutanes and with orthometallates the barriers for compound **5** are higher than for **4** and **6**.

The considerations of the deformation of the benzene ring involved in orthometallation and the conformation of the metallaphosphacyclobutane ring, developed in our previous paper on the similar silyl derivatives,[1] can also be applied to the neopentyl orthometallates, as shown by the data of Table 3. The metallacyclobutane rings are affected by a small but significant puckering: the total puckering amplitude *Q* is 0.052(2) Å in compound **7** and 0.053(4) Å in compound **8**. This conformation is essentially determined by the Ru–C bonds which are not significantly different from the corresponding ones in the orthometallates, and by the angles CH_2–Ru–CH_2 [96.5(3)° (av.)] and CH_2–C–CH_2 [98.1(4)° (av.)], the value of the latter being much less than the tetrahedral value.

Conclusion

Owing to the phenomenological analogy, we are inclined to rationalize the reactivity of [$RuCl_2(\eta^6$-$C_6Me_6)L$] with $Mg(CH_2EMe_3)Cl$ (E = C or Si), which is described in this paper and in a previous report,[1] adopting the same mechanistic scheme we have proposed[2] for the reactions of the analogous rhodium and iridium compounds with the same Grignard reagents (Scheme 2).

As had been demonstrated, metallacyclobutanes are formed from the decomposition of unstable dialkyl derivatives which relieve their steric congestion through cyclometallation of an alkyl group. In those cases, where the bulkiness of the alkyl groups was not so severe, dialkyl derivatives have been isolated, *e.g.* [$Ir(CH_2SiMe_3)_2(\eta^5$-$C_5Me_5)(PPh_3)$] or [$RhMe(CH_2CMe_3)(\eta^5$-$C_5Me_5)(PPh_3)$], and only after thermal decomposition do they transform into the corresponding metallacyclobutanes.

We had also demonstrated that the chloroalkyl intermediate **A** (Scheme 2) is a plausible precursor of the orthometallated derivative, since its reaction with the same alkylating agent used for its preparation gives the orthometallated alkyl derivative.

The ruthenium systems, although obeying this general scheme, have some peculiarities. For instance neither dialkyl derivatives nor the ruthenacyclobutanes are obtained in the case of the reactions with $Mg(CH_2SiMe_3)Cl$. Disregarding electronic effects, which however could be important, one would expect that, by analogy with Rh and Ir, at least the bis(trimethylsilylmethyl) derivatives (less bulky than the dineopentyl analogues) should be isolated. We explain the absence of the dialkyls in the reaction mixtures by the steric requirements of the C_6Me_6 ligand which are substantially higher than those of the C_5Me_5 ligand (cone angles: C_6Me_6–Ru, 157–166; C_5Me_5–Rh, 142; C_5Me_5–Ir, 146). It may also be that the unstable dialkyls decompose to give more stable compounds, but not ruthenacyclobutanes. It is interesting for instance that the thermal decomposition of [$RuMe(CH_2SiMe_3)(\eta^6$-$C_6Me_6)(PMe_2Ph)$] does not produce detectable amounts of the corresponding metallacyclobutane. Moreover the only observed dialkyl derivative, which is obtained[1] from the reaction of [$RuCl_2(\eta^6$-$C_6Me_6)(PMe_2Ph)$] with $Mg(CH_2SiMe_3)Cl$, is the dinuclear complex [$\{Ru(CH_2SiMe_3)_2(\mu$-σ,η^6-$PMe_2Ph)\}_2$], where the steric congestion has been relieved by the loss of the C_6Me_6 and its replacement with the phenyl group of the phosphine.

As for the orthometallated derivatives, the analogies with the rhodium and iridium cases are fewer: a chloroalkyl derivative, [$RuCl(CH_2SiMe_3)(\eta^6$-$C_6Me_6)(PMe_2Ph)$], has been isolated and converted into the corresponding orthometallated derivative by reaction with the chloro(trimethylsilylmethyl) Grignard reagent.[1]

Although the detailed mechanism by which the chloroalkyl intermediate **A** transforms into the orthometallated compound

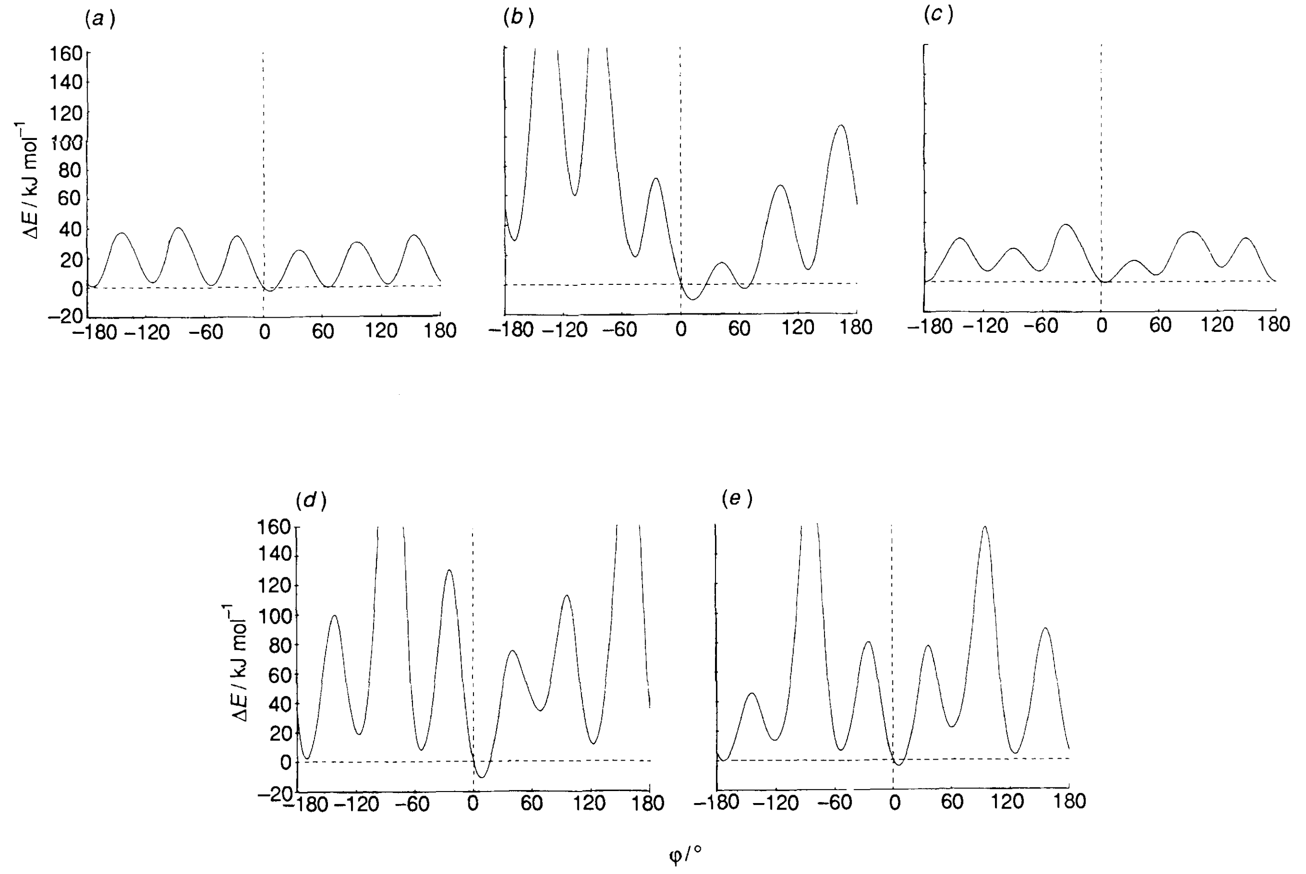
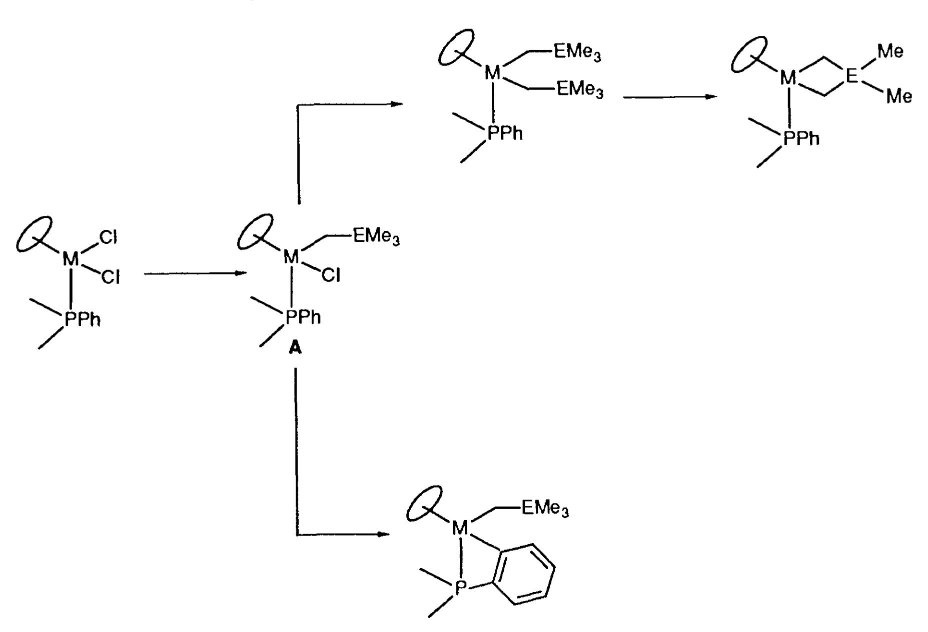
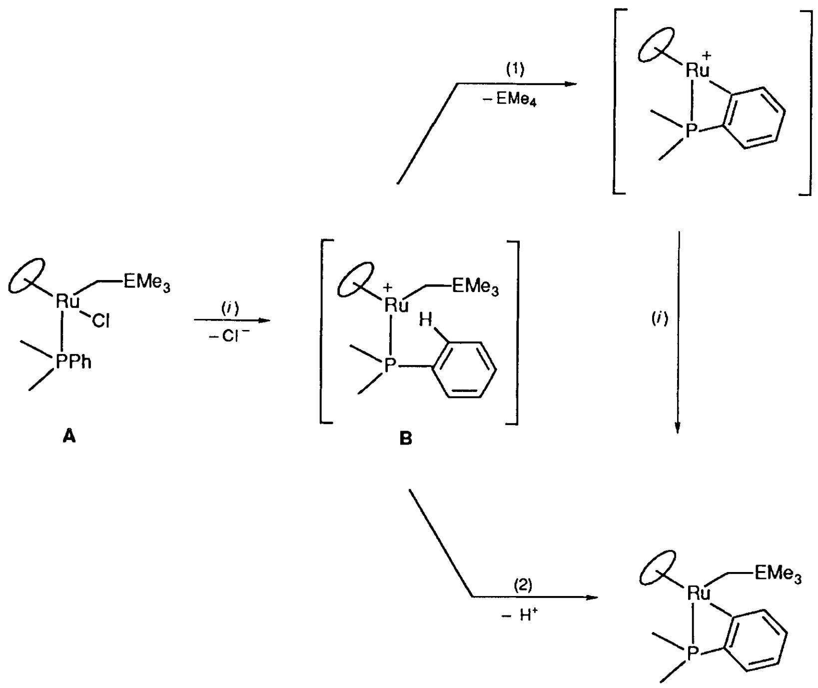


Fig. 3 Calculated difference potential-energy profiles (*a*)–(*e*) for the rotation of hexamethylbenzene about the Ru–Bz direction (φ/°) in the free molecule, for compounds **4**–**8**. The zero of the energy is assumed for the conformation in the crystals.



Scheme 2 E = C or Si

is still to be clarified, we tentatively propose, as shown in Scheme 3, that the crucial intermediate is a co-ordinatively unsaturated metal centre, **B**, obtained by removal of the chloride ion from the chloroalkyl derivative by the alkylating agent. Such a co-ordinative unsaturation could be necessary in order to favour an agostic interaction between the metal centre and an *ortho*-hydrogen of the phosphine, which presumably is a pre-requisite for the formation of the orthometallated derivative. According to Scheme 3, the different pathways that link the 16-electron species and the orthometallated product differ in the destiny of the alkyl group, which is present in the 16-electron intermediate. In fact this CH_2EMe_3 group is retained in the co-ordination sphere of the metal according to path (1), while it is replaced by a new CH_2EMe_3 group according to path (2). In order to discriminate between these two alternatives we have treated $[RuCl(CH_2SiMe_3)(\eta^6\text{-}C_6Me_6)(PMe_2Ph)]$ **9** with $Mg(CH_2CMe_3)Cl$ and obtained only the orthometallated neopentyl complex $[\overline{Ru(C_6H_4P}Me_2)(CH_2CMe_3)(\eta^6\text{-}C_6Me_6)]$ **6** without the presence of the trimethylsilylmethyl analogue, a finding strongly consistent



Scheme 3 E = C or Si. (*i*) $Mg(CH_2EMe_3)Cl$

with path (1). However, further experimental evidence is needed to support this interpretation.

A final comment is needed on the formation of only one diastereomer of the orthometallated complex **5**. This diastereomer is the (*RS*:*SR*) isomer: we recall that in the analogous reaction of $[RuCl_2(\eta^6\text{-}C_6Me_6)(PMe_2Ph)]$ with $Mg(CH_2SiMe_3)Cl$ both the (*RR*:*SS*) and (*RS*:*SR*) diastereomers (2:1 molar ratio) were formed.[1] It is perhaps of some interest that the minor isomer is the one which suffers greater steric constraints (as indicated by the van der Waals potential-energy calculations). Then, by considering the substitution of the CH_2SiMe_3 group by the bulkier CH_2CMe_3 group, which involves a formal inversion of the configuration at the ruthenium centre according to the IUPAC priority rules, one could explain why the (*RR*:*SS*) isomer of **5** is not formed.

Experimental

The reactions and manipulations of organometallics were carried out under dinitrogen or argon, using standard techniques. The solvents were dried and distilled prior to use. The compounds $[RuCl_2(\eta^6\text{-}C_6Me_6)L]$ (L = PPh_3, **1**; $PMePh_2$, **2**; or PMe_2Ph, **3**),[9,10] $[RuCl(CH_2SiMe_3)(\eta^6\text{-}C_6Me_6)(PMe_2Ph)]$ **9**,[1] $[RuMe(CH_2SiMe_3)(\eta^6\text{-}C_6Me_6)(PMe_2Ph)]$,[1] $Mg(CH_2CMe_3)Cl$[11] and $Li(CH_2CMe_3)$[12] were prepared as described. Nuclear magnetic resonance spectra were recorded on Varian Gemini 200 and VXR 300 instruments. Microanalyses were performed by the Laboratorio di Microanalisi of the Istituto di Chimica Organica, Facoltà di Farmacia, University of Pisa.

Reaction of $[RuCl_2(\eta^6\text{-}C_6Me_6)(PPh_3)]$ **1** *with* $Mg(CH_2CMe_3)Cl$: *Formation of* $[Ru(C_6H_4PPh_2)(CH_2CMe_3)(\eta^6\text{-}C_6Me_6)]$ **4** *and* $[Ru(CH_2CMe_2CH_2)(\eta^6\text{-}C_6Me_6)(PPh_3)]$ **7**.—To a stirred suspension of compound **1** (0.226 g, 0.379 mmol) in pentane (30 cm^3) was added $Mg(CH_2CMe_3)Cl$ (2.9 cm^3 of a 0.8 mol dm^{-3} solution in diethyl ether, 2.28 mmol) at room temperature over a period of 15 min. The reaction mixture was stirred for 18 h, then the orange-yellow mixture was hydrolysed at 0 °C with water (4 cm^3). The organic layer was dried over sodium sulphate and then evaporated to dryness. After three crystallizations at −20 °C from pentane, yellow crystals of compound **7** were obtained (0.102 g, 45%). The mother-liquors of the above crystallizations were collected, concentrated to *ca.* 5 cm^3, and chromatographed through a column of neutral alumina (Merck). Elution with pentane gave an orange-yellow band. Evaporation of the solvent gave compound **4**, as an orange-yellow solid (0.068 g, 30%), which was crystallized from pentane at −20 °C.

Reaction of $[RuCl_2(\eta^6\text{-}C_6Me_6)(PMePh_2)]$ **2** *with* $Mg(CH_2CMe_3)Cl$: *Formation of* $[Ru(C_6H_4PMePh)(CH_2CMe_3)(\eta^6\text{-}C_6Me_6)]$ **5** and $[Ru(CH_2CMe_2CH_2)(\eta^6\text{-}C_6Me_6)(PMePh_2)]$ **8**.—To a stirred suspension of compound **2** (0.25 g, 0.47 mmol) in pentane (50 cm^3) was added $Mg(CH_2CMe_3)Cl$ (9.4 cm^3 of a 0.5 mol dm^{-3} solution in diethyl ether, 4.7 mmol) at room temperature over a period of 30 min. The reaction mixture was stirred for 5 h, then hydrolysed with water (4 cm^3). The organic layer was dried over Na_2SO_4 and evaporated to dryness to give a solid residue which was crystallized from pentane at −20 °C to give yellow crystals of compound **8** (0.170 g, 70% yield). The mother-liquor was concentrated to *ca.* 5 cm^3 and chromatographed through a column of neutral alumina (Merck). Elution with pentane gave a yellow band; evaporation of the solvent, followed by crystallization from pentane, gave yellow-orange crystals of (*RS*:*SR*) **5** (0.022 g, 9% yield).

Reaction of $[RuCl_2(\eta^6\text{-}C_6Me_6)(PMe_2Ph)]$ **3** *with* $Mg(CH_2CMe_3)Cl$: *Formation of* $[Ru(C_6H_4PMe_2)(CH_2CMe_3)(\eta^6\text{-}C_6Me_6)]$ **6**.—To a stirred suspension of compound **3** (0.25 g, 0.53 mmol) in pentane (50 cm^3) was added $Mg(CH_2CMe_3)Cl$ (10.6 cm^3 of a 0.5 mol dm^{-3} solution in diethyl ether, 5.3 mmol) at room temperature over a period of 30 min. The reaction mixture was stirred for 4 h and then, following the same procedure as for **4**, 0.108 g (43% yield) of yellow crystals of compound **6** was obtained.

Reaction of $[RuCl(CH_2SiMe_3)(\eta^6\text{-}C_6Me_6)(PMe_2Ph)]$ **9** *with* $Mg(CH_2CMe_3)Cl$: *Formation of Compound* **6**.—To a solution of compound **9** (0.060 g, 0.12 mmol) in pentane (10 cm^3) was added $Mg(CH_2CMe_3)Cl$ (0.3 cm^3 of a 0.62 mol dm^{-3} solution in diethyl ether, 0.19 mmol) at room temperature and

Table 4 Experimental data for the crystallographic analyses[a]

Compound	**4**	**5**	**6**	**7**	**8**
Formula	$C_{35}H_{43}PRu$	$C_{30}H_{41}PRu$	$C_{25}H_{39}PRu$	$C_{35}H_{43}PRu$	$C_{30}H_{41}PRu$
M	595.77	533.70	471.63	595.80	533.70
Space group	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a/Å	10.483(2)	11.926(3)	16.762(21)	10.720(20)	8.842(10)
b/Å	16.050(10)	17.810(5)	10.116(10)	11.670(20)	8.898(20)
c/Å	18.451(9)	12.780(3)	14.874(15)	12.050(10)	17.840(70)
α/°	—	—	—	80.32(4)	92.91(6)
β/°	103.65(4)	99.37(1)	108.08(5)	78.6(1)	102.48(50)
γ/°	—	—	—	87.88(3)	103.12(9)
U/Å^3	3017(2)	2678(1)	2398(4)	1457(4)	1327(7)
Z	4	4	4	2	2
D_c/Mg m^{-3}	1.312	1.324	1.307	1.358	1.335
Diffractometer	Philips PW1100	Philips PW1100	Philips PW1100	CAD4	CAD4
Reflections for lattice parameters: number	21	29	30	20	20
θ range/°	12–18	19–24	19–25	10–13	10–14
F(000)	1248	1120	992	624	560
Crystal size/mm	0.26 × 0.48 × 0.54	0.32 × 0.34 × 0.40	0.23 × 0.42 × 0.72	0.10 × 0.20 × 0.24	0.22 × 0.26 × 0.40
μ/mm^{-1}	0.582	0.647	0.714	0.602	0.653
Absorption correction (min., max.)	0.9758–1.0569	—	—	—	—
Extinction correction (min., max.)	0.9544–1.0307	—	—	—	—
Scan speed/° min^{-1}	0.075	0.10	0.10	0.66	0.75
Scan width/°	1.20	1.40	1.60	1.20 + 0.35 tanθ	1.20 + 0.35 tanθ
θ range/°	3–25	3–26	3–25	3–24	3–24
h range	−12 to 12	−15 to 15	−19 to 18	−11 to 12	−10 to 9
k range	0–19	0–21	0–12	−13 to 13	−10 to 10
l range	0–21	0–11	0–17	0–13	0–20
Standard reflection	$\bar{4}\,0\,6$	$\bar{5}\,4\,3$	$1\,0\,5$	$6\,\bar{2}\,2$	$0\,\bar{2}\,9$
No. of measured reflections	5693	5678	4651	4811	4290
No. of reflections used in refinement	2494	3640	3022	2991	3490
$R(\text{int}) = \Sigma\lvert I - (I)\rvert/\Sigma I$	0.0418	0.0314	0.0294	0.0304	0.011
Max. least squares shift-to-error ratio	0.66	0.41	0.63	0.15	0.28
Min., max. height in final difference map, $\Delta\rho$/e Å^{-3}	−0.26, 0.23	−0.12, 0.25	−0.12, 0.42	−0.15, 0.13	−0.78, 0.63
No. of refined parameters	506	453	401	506	453
$R = \Sigma\lvert\Delta F\rvert/\Sigma\lvert F_o\rvert$	0.0548	0.0480	0.0441	0.0232	0.0529
$R' = [\Sigma w(\Delta F)^2/\Sigma wF_o^2]^{\frac{1}{2}}$	0.0619	0.0572	0.0638	—	0.0820
$S = [\Sigma w(\Delta F)^2/(N - P)]^{\frac{1}{2}}$[b]	1.4227	1.1841	0.8766	1.0713	0.8434
k, g in ($w = k/[\sigma^2(F_o) + gF_o^2]$)	1.402, 0.000 482	1.258, 0.000 758	0.9003, 0.002 404	Unit weights[c]	0.7729, 0.005 000

[a] Details in common: Mo-$K\alpha$ radiation (λ = 0.709 30 Å); no intensity variation; scan mode, θ–2θ; condition for observed reflections $I \geqslant 2\sigma(I)$. [b] P = Number of parameters, N = number of observations. [c] Using the SHELX 76 weighting scheme values too small for goodness of fit are obtained, indicating that such weights are not reliable, so unit weights were considered. No significant differences were observed for the atomic positional and thermal parameters and standard deviations at the end of the weighted and unweighted refinements.

the reaction mixture was stirred for 4 h. Pentane (30 cm^3) was added to the orange-red mixture, which was then hydrolysed at 0 °C with water (3 cm^3) and the organic layer dried over sodium sulphate. The pentane solution was concentrated to *ca.* 4 cm^3 and chromatographed through a column of neutral alumina. Elution with pentane gave a yellow band (A), and 50% diethyl ether in pentane eluted a second orange band (B). Evaporation of the solvent from band A gave compound **6** as a yellow solid (0.012 g, 20% yield), and from band B gave unreacted **9** as an orange-red solid (0.045 g).

Thermal Decomposition of [RuMe(CH$_2$SiMe$_3$)(η^6-C$_6$Me$_6$)(PMe$_2$Ph)].—A solution of freshly crystallized [RuMe(CH$_2$SiMe$_3$)(η^6-C$_6$Me$_6$)(PMe$_2$Ph)] in cyclohexane was kept at 45 °C for 70 h. The solution darkened and a black precipitate was formed, which was insoluble in pentane.

Crystal Structure Analyses.—Relevant data for the crystal structure analyses are given in Table 4. The lattice parameters were refined by a least-squares procedure[13] using the Nelson and Riley[14] extrapolation function. All reflections were corrected for Lorentz and polarization effects, while absorption was corrected only for compound **4** using the empirical method of Walker and Stuart.[15] The structures were solved by Patterson (using the SHELX 86 program[16]) and Fourier techniques and refined on F by blocked least squares (one block for the non-hydrogen atom parameters, the other for hydrogens), using the SHELX 76 program.[17]

The atom–atom non-bonded potential-energy calculations were carried out with the ROTENER[18] program which makes use of a function of the type $E_{ij} = B_{ij}\exp(-C_{ij}r_{ij}) - A_{ij}r_{ij}^{-6}$, disregarding the coulombic energy and assuming the H atoms to be in calculated positions (C–H 1.07 Å).

Atomic scattering factors and anomalous scattering coefficients were taken from the literature.[19] The calculations were carried out on the ENCORE POWERNODE 6040 computer of the Centro di Studio per la Strutturistica Diffrattometrica del CNR (Parma). In addition to the quoted programs, PARST,[20] THMV[21] and ORTEP[22] were used.

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

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