Alumina/Chloroform-promoted Conversion of the Ruthenacycles $[\mathrm{Ru(CH_2CMe_2CH_2)(\eta^6\text{-}C_6Me_6)(PRPh_2)}]$ (R = Me or Ph) into the Chloro Orthometallated Derivatives $[\mathrm{Ru(C_6H_4PRPh)Cl(\eta^6\text{-}C_6Me_6)}]$ *

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Interaction of the ruthenacyclobutanes $[\mathrm{Ru(CH_2CMe_2CH_2)(\eta^6\text{-}C_6Me_6)(PRPh_2)}]$ (R = Me **1** or Ph **3**) with neutral alumina causes the decomposition of the metallacyclic moiety, with the formation of 1,1-dimethylcyclopropane, neopentane and alumina-adsorbed metal complexes which lead to the corresponding chloro orthometallated compounds $[\mathrm{Ru(C_6H_4PRPh)Cl(\eta^6\text{-}C_6Me_6)}]$ (R = Me **2** or Ph **4**) by reaction with $\mathrm{CHCl_3}$. The X-ray crystal structure of complex **2** reveals the presence of clathrated benzene. Crystal data: space group $P2_1/c$, $a = 14.068(14)$, $b = 15.392(13)$, $c = 13.064(14)$ Å, $\beta = 116.38(6)°$, $Z = 4$, $R = 0.0510$.

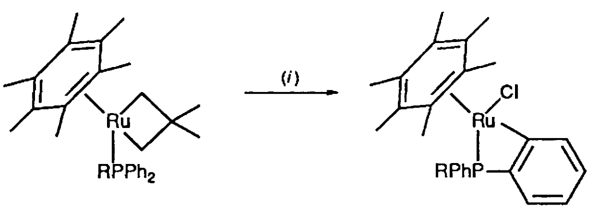
We have recently reported that the ruthenacyclobutanes prepared by alkylation of the dichloro compounds $[\mathrm{RuCl_2(\eta^6\text{-}C_6Me_6)(PRPh_2)}]$ (R = Me or Ph) with neopentylmagnesium chloride do not survive attempted chromatographic purification on neutral alumina.[1] During examination of the crude reaction mixture we noticed spectroscopically that two major compounds were formed. While one of these, *i.e.* the orthometallated complex $[\mathrm{Ru(C_6H_4PRPh)(CH_2CMe_3)(\eta^6\text{-}C_6Me_6)}]$ (R = Me or Ph), was obtained in a pure form by column chromatography on neutral alumina, the other product was not recovered from the column. This compound was purified by fractional crystallization of the crude products and found to be the ruthenacyclobutane derivative $[\mathrm{Ru(CH_2CMe_2CH_2)(\eta^6\text{-}C_6Me_6)(PRPh_2)}]$ (R = Me **1** or Ph **3**).

The reactivity of these ruthenacycles towards alumina seems to be peculiar to the four-membered moiety, since ruthenacyclopentanes carrying the same ancillary ligands have been chromatographed unchanged on alumina.[2]

The interaction of compounds **1** and **3** with neutral alumina has now been studied in order to understand the destiny of such compounds during column chromatography. The results are reported in this paper.

Results and Discussion

Chemical Studies.—Pure samples of the ruthenacyclobutanes $[\mathrm{Ru(CH_2CMe_2CH_2)(\eta^6\text{-}C_6Me_6)(PRPh_2)}]$ (R = Me **1** or Ph **3**) were dissolved in pentane and chromatographed on a column of neutral alumina. Pentane, diethyl ether, or benzene eluted only traces of starting material. Methylene chloride did not move any band along the column. Finally elution with chloroform (Scheme 1) gave a yellow band, from which the complexes $[\mathrm{Ru(C_6H_4PRPh)Cl(\eta^6\text{-}C_6Me_6)}]$ (R = Me **2** or Ph **4**) were obtained by evaporation of the solvent. Analytical and



	R	
1	Me	**2**
3	Ph	**4**

Scheme 1 (*i*) Column chromatography on alumina, elution with $\mathrm{CHCl_3}$

^{1}H NMR data are reported in Table 1. Complexes **2** and **4** showed ^{1}H NMR signals due to the hexamethylbenzene ligand and the typical pattern[1,3] of the orthometallated phosphine in the aromatic region. No signal due to aliphatic protons was present. In the case of **2** a pair of diastereomers can exist, but only one isomer was detected by ^{1}H NMR spectroscopy, thus showing that the conversion of **1** into **2** is diastereoselective.

Well formed crystals of complex **2** were obtained from pentane–benzene, and X-ray single-crystal analysis showed the structure to be that of a chloro orthometallated ruthenium(II) derivative with the (*RR*:*SS*) configuration and containing a clathrate benzene molecule (see crystallographic section). It is of some importance to recall that the orthometallated complex $[\mathrm{Ru(C_6H_4PMePh)(CH_2CMe_3)(\eta^6\text{-}C_6Me_6)}]$, having the same spatial arrangement of the substituents around the chiral centres, is the only diastereoisomer which is formed in the alkylation reaction of the corresponding dichloro compound with $\mathrm{Mg(CH_2CMe_3)Cl}$.[1] It is probable that this diastereoselectivity is due to steric effects as previous results seem to indicate.[3]

This surprising one-step conversion of ruthenacyclobutanes into chloro orthometallated derivatives can be of some synthetic utility since **2** and **4** cannot easily be prepared by alternative

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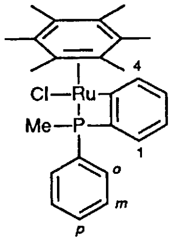
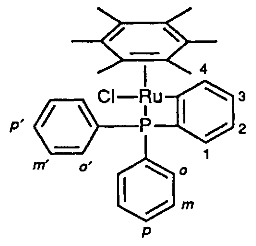
* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Table 1 Analytical and spectroscopic data

Compound, colour, analysis[a]	^{1}H NMR data[b]
2 (*RR*:*SS*)-[$Ru(C_6H_4PMePh)Cl(\eta^6-C_6Me_6)$][c] Orange-red C, 60.0 (60.3); H, 6.0 (6.1); Cl, 6.5 (7.1) 	(C_6D_6): 1.66 [18 H, d, *J*(H–P) 1.0, C_6Me_6], 1.86 [3 H, d, *J*(H–P) 11.4, PMe], 6.66 [1 H, dd, *J*(H^1–H^2) 7.40, *J*(H–P) 12.4, H^1], 6.93–7.13 (4 H, m, H^2 + H^m + H^p), 7.18–7.30 (2 H, m, H^o), 7.37 [1 H, dt, *J*(H^3–H^2) ≈ *J*(H^3–H^4) 7.5, *J*(H^3–H^1) 1.4, H^3], 7.73 [1 H, dd, *J*(H^4–H^3) 7.5, *J*(H–P) 4.1, H^4] ($CDCl_3$): 1.85 [18 H, d, *J*(H–P) 1.0, C_6Me_6], 1.88 [3 H, d, *J*(H–P) 11.4, PMe], 6.72 [1 H, dd, *J*(H^1–H^2) 7.4, *J*(H–P) 12.4, H^1], 6.91 [1 H, ddt, *J*(H^2–H^1) ≈ *J*(H^2–H^3) 7.4, *J*(H^2–H^4) 1.0, *J*(H–P) 3.0, H^2], 7.25 [1 H, dt, *J*(H^3–H^2) ≈ *J*(H^3–H^4) 7.5, *J*(H^3–H^1) 1.4, H^3], 7.3–7.4 (5 H, m, Ph), 7.57 [1 H, dd, *J*(H^4–H^3) 7.5, *J*(H–P) 4.1, H^4]
4 [$Ru(C_6H_4PPh_2)Cl(\eta^6-C_6Me_6)$] Orange-red C, 64.2 (64.3); H, 5.6 (5.8); Cl, 5.8 (6.3) 	(C_6D_6): 1.71 [18 H, d, *J*(H–P) 0.94, C_6Me_6], 6.8–7.2 (10 H, m, $H^{o'}$ + $H^{m'}$ + $H^{p'}$ + H^m + H^p + H^1 + H^2), 7.37 (1 H, m, H^3), 7.76 [1 H, dddd, *J*(H^4–H^3) 7.4, *J*(H^4–H^2) 0.9, *J*(H^4–H^1) 0.9, *J*(H–P) 4.3, H^4], 7.95 [2 H, ddd, *J*(H^o–H^m) 10.6, *J*(H^o–H^p) 1.6, *J*(H–P) 8.0, H^o]

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

Table 2 Fractional coordinates (× 10^4) for compound **2**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Ru	3852.2(7)	684.8(5)	1968.4(6)
Cl	5009(2)	1533(2)	1425(2)
P	2917(2)	330(2)	23(2)
C(1)	4846(12)	928(8)	3856(9)
C(2)	5318(9)	203(9)	3528(9)
C(3)	4734(10)	−509(7)	2997(8)
C(4)	3656(11)	−542(8)	2721(9)
C(5)	3142(10)	142(12)	3031(11)
C(6)	3801(14)	898(10)	3642(10)
C(1M)	5497(20)	1728(12)	4451(15)
C(2M)	6444(12)	301(14)	3783(14)
C(3M)	5268(19)	−1250(9)	2692(17)
C(4M)	3062(16)	−1391(11)	2168(14)
C(5M)	2004(14)	22(21)	2780(16)
C(6M)	3203(26)	1529(14)	4029(20)
C(11)	2144(8)	1294(6)	−113(8)
C(12)	1339(10)	1746(9)	−980(11)
C(13)	1038(10)	2513(10)	−700(12)
C(14)	1496(10)	2815(9)	424(12)
C(15)	2316(9)	2366(7)	1281(9)
C(16)	2656(8)	1569(6)	1040(8)
C(71)	2025(8)	−586(7)	−483(8)
C(72)	2340(11)	−1357(9)	−827(11)
C(73)	1662(15)	−2080(9)	−1142(14)
C(74)	717(13)	−2052(10)	−1099(13)
C(75)	406(12)	−1302(9)	−754(11)
C(76)	1062(10)	−597(9)	−474(10)
C(81)	3492(10)	415(9)	−985(10)
C(91)	−790(21)	4409(20)	−791(34)
C(92)	−632(22)	4500(16)	317(45)
C(93)	181(32)	5071(27)	1097(18)

routes. We have in fact failed to prepare them by reaction of the dichloro compounds [$RuCl_2(\eta^6-C_6Me_6)(PRPh_2)$] with bases[4] or by protonolysis of the orthometallated complexes [$Ru(C_6H_4PRPh)(CH_2CMe_3)(\eta^6-C_6Me_6)$] with HCl.

We then made some efforts in order to understand how the ruthenacyclobutanes are transformed into the chloro orthometallated compounds during chromatography. First, to rule out the possibility that chloroform is the only reagent responsible for this transformation, the ruthenacyclobutanes **1** and **3** were dissolved in $CDCl_3$ and, although immediate decomposition was observed, no evidence for the presence of the chloro orthometallated complexes **2** and **4** was found by ^{1}H NMR analysis. Then, a solution of **1** or **3** in C_6D_6 was stirred in the presence of alumina and examined by ^{1}H NMR spectroscopy. After 1 h **1** or **3** was found to have almost completely disappeared, the only signals being those of 1,1-dimethylcyclopropane and neopentane (1:1 ratio). Extraction of Al_2O_3 with benzene or CH_2Cl_2 did not bring into solution any metallorganic species, while chloroform extracted the chloro orthometallated derivative.

As for the decomposition of the ruthenacyclobutanes on alumina, a someway related alumina-promoted reductive elimination of alkane from [$IrH(CH_2CMe_3)(\eta^5-C_5Me_5)(PPh_3)$] has been reported by Janowicz and Bergman[5] and attributed to a possible electrophilic interaction. More recently Marks[6] has described some O-bound organometallics resulting from the interaction of actinide dimethyl derivatives with the acidic centres of alumina. Although we have no direct evidence, we suggest that the ruthenacyclobutanes **1** and **3** could interact analogously with alumina giving up the metallacyclic moiety and forming Ru–O bonds, from which the organometallic fragment is released by reacting with $CHCl_3$ and giving the chloro orthometallated compound **2** or **4**.

Crystal Structure Analysis of Compound **2**.—The final atomic coordinates of the non-hydrogen atoms are in Table 2, and relevant structural parameters are in Table 3. Thermal motion analysis was carried out in Schomaker and Trueblood's[7] rigid-body approximation considering also the internal motions of some groups according to the Dunitz and White one-parameter model.[8,9] The results correspond quite well to those found with similar ruthenium complexes we studied recently,[1,2] in

Table 3 Bond distances (Å) and angles (°) for compound **2** with estimated standard deviations in parentheses

Ru–Bz	1.745(12)	Ru–C(1)	2.26(1)	C(1)–C(2)	1.46(2)	C(1)–C(1M)	1.52(2)
Ru–Cl	2.425(4)	Ru–C(2)	2.28(1)	C(2)–C(3)	1.36(2)	C(2)–C(2M)	1.48(2)
Ru–P	2.349(4)	Ru–C(3)	2.29(1)	C(3)–C(4)	1.40(2)	C(3)–C(3M)	1.51(2)
Ru–C(16)	2.084(9)	Ru–C(4)	2.20(1)	C(4)–C(5)	1.43(2)	C(4)–C(4M)	1.55(2)
		Ru–C(5)	2.20(2)	C(5)–C(6)	1.48(2)	C(5)–C(5M)	1.50(2)
P–C(11)	1.80(1)	Ru–C(6)	2.24(2)	C(6)–C(1)	1.37(3)	C(6)–C(6M)	1.51(4)
P–C(71)	1.81(1)		av. 2.25(2)		av. 1.42(2)		av. 1.51(1)
P–C(81)	1.83(2)						
C(11)–C(12)	1.38(1)	C(71)–C(72)	1.41(2)	C(91)–C(92)	1.37(7)		
C(12)–C(13)	1.36(2)	C(72)–C(73)	1.40(2)	C(91)–C(93′)	1.36(6)		
C(13)–C(14)	1.39(2)	C(73)–C(74)	1.36(3)	C(92)–C(93)	1.44(4)		
C(14)–C(15)	1.38(2)	C(74)–C(75)	1.38(2)		av. 1.41(3)		
C(15)–C(16)	1.40(2)	C(75)–C(76)	1.36(2)				
C(16)–C(11)	1.42(1)	C(76)–C(71)	1.36(2)				
	av. 1.39(1)		av. 1.38(1)				
Bz–Ru–C(16)	133.2(6)	P–Ru–C(16)	66.6(3)	Ru–C(16)–C(15)	135.1(8)	Ru–C(16)–C(11)	108.7(7)
Bz–Ru–P	138.7(5)	P–Ru–Cl	86.3(2)				
Bz–Ru–Cl	124.6(5)	Cl–Ru–C(16)	87.2(3)	Ru–Bz–C(6)	89.2(8)	P–C(11)–C(16)	98.2(7)
				Ru–Bz–C(5)	87.0(8)	P–C(11)–C(12)	137.3(9)
Ru–P–C(81)	123.2(2)	C(71)–P–C(81)	104.4(5)	Ru–Bz–C(4)	88.2(8)	P–C(71)–C(76)	122.6(9)
Ru–P–C(71)	122.8(4)	C(11)–P–C(81)	108.1(5)	Ru–Bz–C(3)	92.2(8)	P–C(71)–C(72)	120.6(11)
Ru–P–C(11)	86.5(3)	C(11)–P–C(71)	108.4(6)	Ru–Bz–C(2)	92.7(8)		
				Ru–Bz–C(1)	90.8(8)		
					av. 90.0(9)		
C(2)–C(1)–C(6)	120(1)	C(6)–C(1)–C(1M)	119(2)	C(72)–C(71)–C(76)	117(1)	C(92)–C(91)–C(93′)	115(3)
C(1)–C(2)–C(3)	121(1)	C(2)–C(1)–C(1M)	121(2)	C(71)–C(72)–C(73)	120(2)	C(91)–C(92)–C(93)	121(4)
C(2)–C(3)–C(4)	120(1)	C(1)–C(2)–C(2M)	116(1)	C(72)–C(73)–C(74)	121(1)	C(92)–C(93)–C(91′)	124(3)
C(3)–C(4)–C(5)	122(1)	C(3)–C(2)–C(2M)	123(1)	C(73)–C(74)–C(75)	120(2)		av. 120(3)
C(4)–C(5)–C(6)	117(1)	C(2)–C(3)–C(3M)	119(2)	C(74)–C(75)–C(76)	119(2)		
C(1)–C(6)–C(5)	120(2)	C(4)–C(3)–C(3M)	121(1)	C(75)–C(76)–C(71)	124(1)		
	av. 120(7)	C(3)–C(4)–C(4M)	117(1)		av. 120(1)		
C(12)–C(11)–C(16)	124(1)	C(5)–C(4)–C(4M)	121(2)				
C(11)–C(12)–C(13)	117(1)	C(4)–C(5)–C(5M)	118(2)	C_6Me_6 effective cone angle*	159°		
C(12)–C(13)–C(14)	121(1)	C(6)–C(5)–C(5M)	125(2)				
C(13)–C(14)–C(15)	121(1)	C(5)–C(6)–C(6M)	112(2)				
C(14)–C(15)–C(16)	120(1)	C(1)–C(6)–C(6M)	128(2)				
C(15)–C(16)–C(11)	116.0(9)		av. 120(1)				
	av. 120(1)						

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

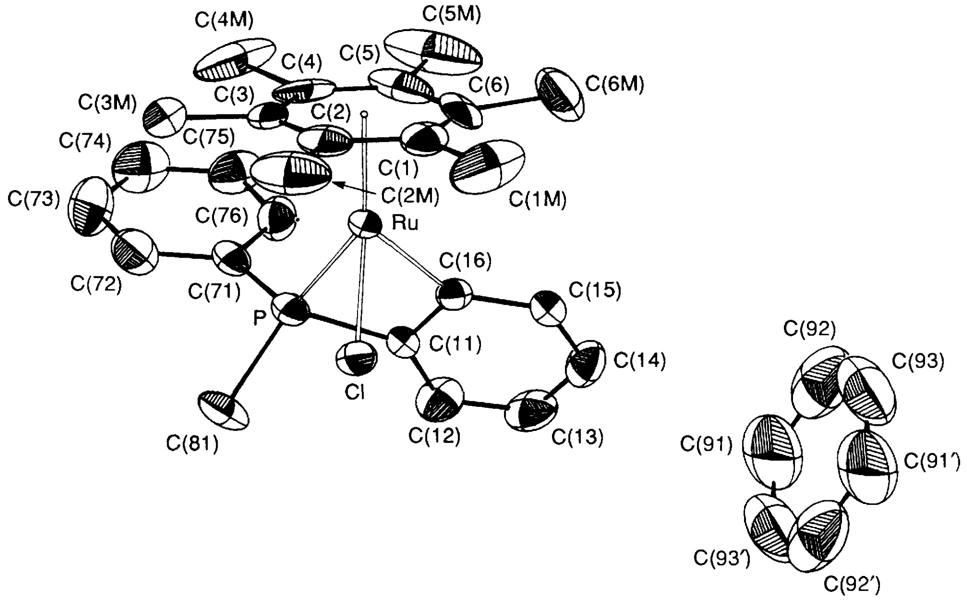


Fig. 1 An ORTEP[10] drawing of complex **2** showing the molecular structure and thermal motion. The hydrogen atoms are omitted for clarity. Thermal ellipsoids are at 40% probability

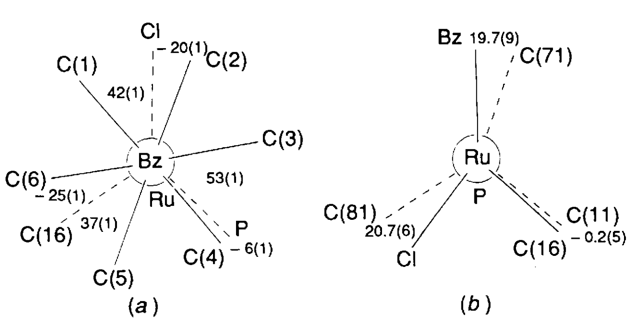


Fig. 2 Newman projections (angles in °) showing the conformations along (*a*) Bz–Ru and (*b*) Ru–P

particular the largest atomic displacements are observed for the methyl groups of the hexamethylbenzene ligand, as shown by the atomic ellipsoids in Fig. 1.

The rigid-body treatment gave a value of 0.162 for the index $R_{wU} = [\Sigma w(\Delta U)^2/\Sigma w(U_o)^2]^{\frac{1}{2}}$ where $\Delta U = U_{ij}(\text{obs.}) - U_{ij}(\text{calc.})$ which improved to 0.093 on considering the libration of hexamethylbenzene about the normal to the plane of the ring at its centroid, and the libration of the phenyls about the normals to their planes at the carbons bound to P.

In the following discussion all the conventions applied for averaging and comparing data in the previous papers of this series[1,2] are followed.

The molecule has the 'three-legged piano-stool' type of structure observed for the similar orthometallated complexes, as can be seen from the structural parameters in Table 3. In particular, similarity is observed with the related complex $[Ru(C_6H_4PMePh)(CH_2CMe_3)(\eta^6\text{-}C_6Me_6)]$ (compound **5** in ref. 1). Unfortunately the accuracy of the analysis is not such as to allow detailed comparison, nevertheless it can be seen that substitution of the neopentyl ligand with chlorine causes some significant changes, like that in the orientation of the hexamethylbenzene ligand about the Bz–Ru direction (Bz is the centroid of the hexamethylbenzene), while the conformation about the Ru–P bond does not seem significantly influenced, as shown by the Newman projections of Fig. 2. Also some distances seem to be influenced, like that of hexamethylbenzene from ruthenium and that of the Ru–P bond which are slightly increased (by 0.03 and 0.08 Å, respectively), while the Ru–C(16) distance is shortened by 0.14 Å.

As observed for other η^6-C_6Me_6 metal complexes, the methyl groups of the hexamethylbenzene ligand tend to be displaced from the plane of the ring in an opposite direction with respect to metal; in the present compound this kind of displacement is found for all methyls except C(1M) and C(2M) which are displaced towards the metal by 0.04 and 0.05 Å respectively, while the displacements of the other methyls are in the 0.04–0.17 Å range.

The most relevant changes are observed in the packing of the molecules that now is such as to create holes in which occluded benzene molecules can be located, as shown in the PLUTO[11] projection of Fig. 3. The benzene molecules are on the symmetry centres at 0,½,0, surrounded by phenyls of adjacent complex molecules.

It is interesting to determine the freedom of these clathrate molecules in the holes, so the van der Waals energy profiles were calculated for rotation of a benzene molecule with respect to the environment in the hole. The curves in Fig. 4 (*i*), which refer to rotations about the ring diagonals, all show a well defined minimum corresponding to the position assumed by the molecule in the crystal ($\varphi = 0°$) and two energy barriers ranging from 515 to 830 kJ mol^{-1} mainly due to the steric hindrance between the benzene hydrogens and the hydrogens bound to C(14) and, to a lesser extent, to C(12), C(13), C(74) and C(5M). The curve in Fig. 4 (*ii*), which refers to the rotation of benzene about a direction perpendicular to its plane through the centre of the ring, shows only small energy barriers ranging from 4 to 6 kJ mol^{-1}, due to steric hindrance between the benzene hydrogens and the hydrogens of the C(2M) and C(5M) methyls. This finding is in agreement with the shapes of the benzene atomic ellipsoids (Fig. 1) which indicate a preferential librational motion (or static disorder) of the molecule about the normal to the molecular plane.

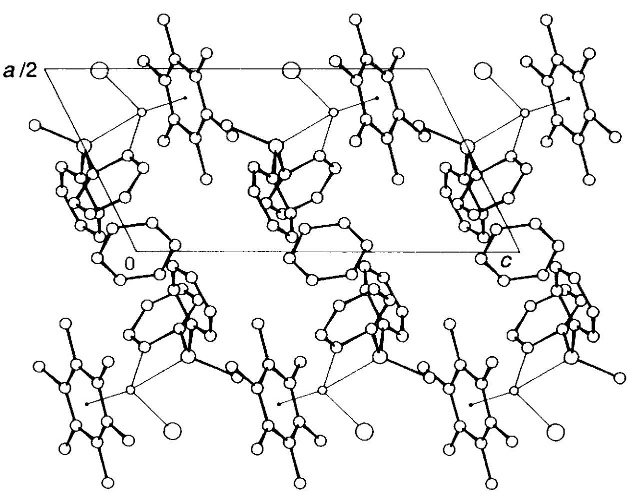


Fig. 3 A PLUTO[11] projection of the structure of compound **2** showing the occlusion of benzene

Experimental

The reactions and manipulation of organometallics were carried out under dinitrogen or argon, using standard techniques. The solvents were dried and distilled prior to use. The compounds $[Ru(CH_2CMe_2CH_2)(\eta^6\text{-}C_6Me_6)(PRPh_2)]$ (R = Me or Ph) were prepared as described.[1] Nuclear magnetic resonance spectra were recorded on a Varian Gemini 200 instrument. Microanalyses were performed by the Laboratorio di Microanalisi of the Istituto di Chimica Organica, Facoltà di Farmacia, University of Pisa.

Preparation of $[Ru(C_6H_4PMePh)Cl(\eta^6\text{-}C_6Me_6)]$ **2**.—The compound $[Ru(CH_2CMe_2CH_2)(\eta^6\text{-}C_6Me_6)(PMePh_2)]$ **1** (0.098 g) was dissolved in pentane and applied at the top of a chromatographic column containing alumina (Merck, Aktivitätsstufe II–III, 70–230 mesh ASTM, height 8 cm). Chloroform eluted a fast-running yellow band. Evaporation of the solvent gave $[Ru(C_6H_4PMePh)Cl(\eta^6\text{-}C_6Me_6)]$ **2** (80%). Crystallization from benzene–pentane at room temperature gave orange-red crystals of (*RR*:*SS*)-**2** containing a clathrate benzene molecule.

Preparation of $[Ru(C_6H_4PPh_2)Cl(\eta^6\text{-}C_6Me_6)]$ **4**.—In a similar way $[Ru(CH_2CMe_2CH_2)(\eta^6\text{-}C_6Me_6)(PPh_3)]$ **3** (0.125 g) in pentane was chromatographed using $CHCl_3$ as the eluent to give $[Ru(C_6H_4PPh_2)Cl(\eta^6\text{-}C_6Me_6)]$ **4** (85%) after evaporation of the solvent.

Reaction of the Ruthenacyclobutanes **1** *and* **3** *with Alumina*.—The ruthenacyclobutane (*ca.* 0.2 mmol) was dissolved in C_6D_6 (3 cm^3) and stirred with Al_2O_3 (0.250 g) for 3–4 h at room temperature. The C_6D_6 solution was decanted and analysis by ^1H NMR spectroscopy revealed the presence of 1,1-dimethylcyclopropane [δ 0.97 (6 H, s, Me) and 0.21 (4 H, s, CH_2)] and neopentane [δ 0.899 (12 H, s, Me)] in addition to minor amounts of starting ruthenacycle. The alumina was dried and extracted with CH_2Cl_2 (no significant amount of material was detected), and then with $CHCl_3$, which extracted a yellow

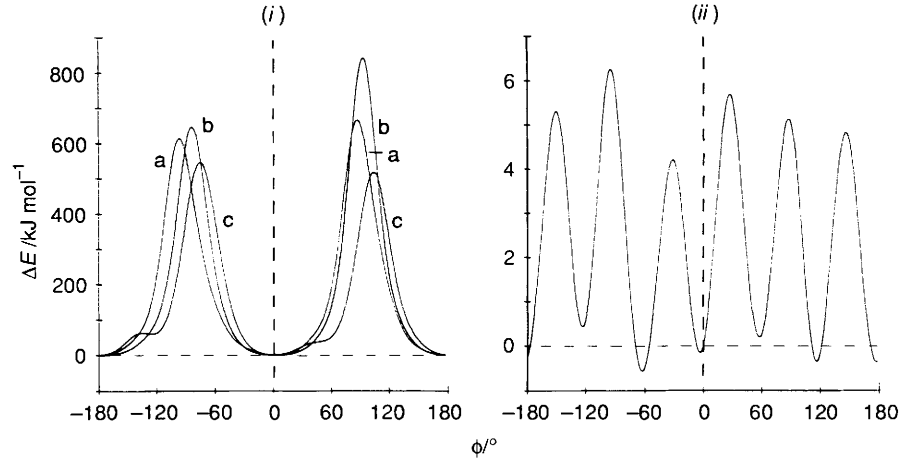


Fig. 4 Calculated difference potential-energy profiles for (*i*) the rotation of benzene about (*a*) C(91)···C(91′), (*b*) C(92)···C(92′), (*c*) C(93)···C(93′); (*ii*) the normal to the benzene plane at the centroid of the ring. Positive values of φ are for counterclockwise rotations. The zero of the energy is assumed for the conformation found in the crystals

Table 4 Experimental data for the crystal structure analysis of compound **2**

Formula	$C_{25}H_{30}ClPRu\cdot 0.5C_6H_6$
M	537.07
Space group	$P2_1/c$
Crystal symmetry	Monoclinic
a/Å	14.068(14)
b/Å	15.392(13)
c/Å	13.064(14)
β/°	116.38(6)
U/Å^3	2534(4)
Z	4
D_c/Mg m^{-3}	1.408
No. of reflections for lattice parameters (θ range/°)	26 (9–14)
Radiation for lattice parameters (λ/Å)	Mo-Kα1 (0.709 300)
F(000)	1108
T/K	293(2)
Crystal size/mm	0.16 × 0.18 × 0.39
Diffractometer	Siemens AED
μ/mm^{-1}	0.788
Scan speed/° min^{-1}	2.5–12
Scan width/°	1.20 + 0.142 tan θ
Radiation for intensity measurement	Mo-Kα (mean)
θ range/°	3–25
h,k,l ranges	−16 to 16, 0–17, 0–15
Standard reflection	2 2 4
Intensity variation	None
No. of measured reflections	4832
Condition for observed reflections	$I > 2\sigma(I)$
No. of reflections used in refinement (N)	2115
R(int.)	0.0497
Maximum shift to error ratio	0.62
Minimum, maximum height in final difference map, Δρ/e Å^{-3}	−0.57, 0.34
No. of refined parameters (P)	358
$R = \Sigma\lvert\Delta F\rvert/\Sigma\lvert F_o\rvert$	0.0510
$R' = [\Sigma w(\Delta F)^2/\Sigma wF_o^2]^{\frac{1}{2}}$	0.0610
$S = [\Sigma w(\Delta F)^2/(N - P)]^{\frac{1}{2}}$	0.6214
k, g in $w = k/[\sigma^2(F_o) + gF_o^2]$	1, 0.0005

compound identified as the chloro orthometallated compounds **2** and **4** respectively.

Crystal Structure Determination of $[\overline{\mathrm{Ru}(\mathrm{C_6H_4}\mathrm{P}}\mathrm{Ph_2})\mathrm{Cl}(\eta^6\text{-}\mathrm{C_6Me_6})]\cdot 0.5\mathrm{C_6H_6}$.—The relevant data for the crystal structure analysis are in Table 4. The lattice parameters were refined by a least-squares procedure[12] using the Nelson and Riley[13] extrapolation function. All reflections were corrected for Lorentz and polarization effects; no correction for absorption nor for extinction was considered. The structure was solved by Patterson (using the SHELX 86 program[14]) and Fourier techniques and refined on F by full-matrix least squares using the SHELX 76 program.[15] The hydrogen atoms were put in calculated positions.

The atom–atom non-bonded potential-energy calculations were carried out with the ROTENER[16] program which makes use of a function of the 'exp-6-1' type: $E_{ij} = B_{ij}\exp(-C_{ij}r_{ij}) - A_{ij}r_{ij}^{-6}$, where the A,B,C parameters were taken from Mirsky[17] disregarding the Coulombic energy.

Atomic scattering factors and anomalous scattering coefficients were taken from ref. 18. 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 cited programs, PARST,[19] THMV,[20] ORTEP[10] and PLUTO[11] 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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