η^6-Arene-stabilized Ruthenacyclopentanes: Synthesis, *X*-Ray Structures, and Reaction with the Trityl Cation†

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The ruthenacyclopentane complexes $[\overline{\text{Ru}(\text{CH}_2\text{CH}_2\text{CH}_2\text{C}}\text{H}_2)(\eta^6\text{-C}_6\text{Me}_6)\text{L}]$ [L = PPh_3 (**2a**), $PMePh_2$ (**2b**), or PMe_2Ph (**2c**)] have been prepared by reacting the corresponding dichlororuthenium derivatives with an excess of 1,4-dilithiobutane. Their crystal structures have been determined: (**2a**) and (**2b**) have space group $P2_1/n$ crystals, while (**2c**) crystallizes in space group $P2_1/c$. Cell constants: (**2a**), a = 9.249(3), b = 16.160(7), c = 19.094(21) Å, β = 90.70(1)°, Z = 4, and R (3 203 reflections, 453 parameters) = 0.0425; (**2b**), a = 17.463(13), b = 8.708(6), c = 17.749(13) Å, β = 109.15(4)°, Z = 4, and R(3 412, 436) = 0.0395; (**2c**), a = 9.575(6), b = 11.899(8), c = 19.494(12) Å, β = 97.96(2)°, Z = 4, and R(3 080, 383) = 0.0330. All compounds possess structures of the 'three-legged piano stool' type, and the metallacyclopentane ring is puckered having a twisted conformation which is intermediate between the envelope and half-chair forms. The orientations of the hexamethylbenzene and phosphine ligands are considered with respect to the minima of the van der Waals conformation energies of the free molecules. The ruthenacyclopentanes-(**2a**)—(**2c**) react at room temperature with $[CPh_3][BF_4]$ to give the η^3-allylic complexes $[\text{Ru}(\eta^3\text{-CH}_2\text{CHCHMe})(\eta^6\text{-C}_6\text{Me}_6)\text{L}][\text{BF}_4]$ [L = PPh_3 (**3a**), $PMePh_2$ (**3b**), or PMe_2Ph (**3c**)].

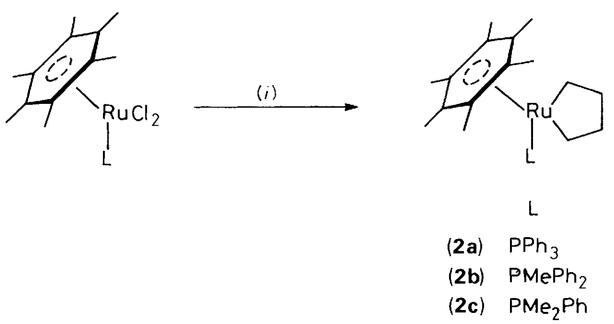
The preparation and study of metallacyclopentanes are of considerable current interest since it has been recognized that many important transition-metal-assisted reactions proceed *via* metallacyclic intermediates.[1] In this context we have studied several metallacyclopentane derivatives of Co^{III}, Rh^{III}, and Ir^{III}, d^6 systems, having η^5-cyclopentadienyl and triphenylphosphine ligands as protecting groups.[2–4] With the aim of studying other d^6 metallacyclopentanes having analgous ancillary ligands, we turned our attention to the $[\text{RuCl}_2(\eta^6\text{-C}_6\text{Me}_6)\text{L}]$ (L = tertiary phosphine) systems, which are known to give on alkylation stable dialkyl derivatives.[5]

Very few examples of ruthenacyclopentanes have been previously reported. Lindner *et al.*[6] have recently prepared $[\overline{\text{Ru}(\text{CH}_2\text{CH}_2\text{CH}_2\text{C}}\text{H}_2)(\text{CO})_4]$ which is stable at room temperature only under a carbon monoxide atmosphere. Bennett *et al.*[7] reported the formation of the stable substituted ruthenacyclopentane $[\underline{\text{Ru}(\text{CO})_2\{o\text{-Ph}_2\text{PC}_6\text{H}_4\text{C}}\text{HCH}_2\text{CH}_2\text{CHC}_6\text{H}_4\text{PPh}_2\text{-}o\}]$, *via* the dimerization of two ruthenium-bonded *o*-styryldiphenylphosphines.

We report here the preparation, the *X*-ray structures, and the reactivity towards the trityl cation of the ruthenacycles (**2a**)—(**2c**). A preliminary account of this research has been communicated.[8]

Results and Discussion

Preparation of the Ruthenacyclopentanes (**2a**)—(**2c**).—Treatment of the ruthenium dichlorides $[\text{RuCl}_2(\eta^6\text{-C}_6\text{Me}_6)\text{L}]$ [L = PPh_3 (**1a**), $PMePh_2$ (**1b**), or PMe_2Ph (**1c**)] with an excess of 1,4-dilithiobutane in diethyl ether followed by hydrolysis at 0 °C of the pentane-soluble material and then chromatographic purification yields the corresponding ruthenacyclopentanes (**2a**)—(**2c**) (Scheme 1). In the case of (**2c**) we observed the highest yield (37%) only when the hydrolysis step was omitted.



Scheme 1. (*i*) $Li(CH_2)_4Li$, Et_2O

Compounds (**2a**)—(**2c**) are yellow, crystalline, stable at room temperature under an inert atmosphere, and soluble in most organic solvents. Solutions in contact with air show signs of decomposition almost immediately, while the crystals decompose more slowly. In the ^{1}H n.m.r. spectra the C_6Me_6 and the phosphine ligands give well resolved signals, while the metallacyclic moiety gives complex multiplets that are of poor utility for structural identification. For this reason and since no structural information on ruthenacyclopentanes had been reported in the literature, we decided to carry out a diffractometric study on compounds (**2a**)—(**2c**).

Crystal Structure Analysis.—The final atomic co-ordinates are given in Table 1. The relevant bond distances and angles are compared in Table 2, where the averaged values are means weighted according to the reciprocal of the variances.

The results of thermal motion analysis (Table 3), as well as the

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix–xxii.

Table 1. Fractional co-ordinates (× 10^4) for compounds (**2a**)—(**2c**)

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Compound (**2a**)							
Ru	1 815.0(4)	2 291.9(3)	4 288.4(2)	C(15)	5 681(6)	4 025(4)	2 591(3)
P	1 960.9(13)	2 793.0(8)	3 180.1(7)	C(16)	4 236(5)	3 868(3)	2 733(3)
C(1)	3 755(6)	2 085(4)	5 020(3)	C(17)	−400(6)	2 027(4)	4 052(3)
C(2)	3 816(6)	2 925(4)	4 821(3)	C(18)	−650(8)	1 114(5)	4 044(5)
C(3)	2 576(7)	3 440(3)	4 894(3)	C(19)	513(9)	699(4)	3 671(5)
C(4)	1 296(6)	3 128(4)	5 199(3)	C(20)	1 988(6)	1 058(3)	3 872(3)
C(5)	1 269(6)	2 298(4)	5 444(3)	C(21)	1 406(5)	2 137(3)	2 430(3)
C(6)	2 460(7)	1 780(4)	5 363(3)	C(22)	2 317(6)	1 559(3)	2 128(3)
C(1M)	5 029(9)	1 524(6)	4 952(5)	C(23)	1 801(6)	1 004(4)	1 620(3)
C(2M)	5 230(7)	3 290(5)	4 581(4)	C(24)	379(7)	1 027(4)	1 410(3)
C(3M)	2 707(8)	4 341(4)	4 692(4)	C(25)	−522(6)	1 618(4)	1 682(3)
C(4M)	16(8)	3 684(4)	5 345(4)	C(26)	−14(6)	2 162(3)	2 185(3)
C(5M)	−63(8)	1 991(5)	5 830(3)	C(31)	906(5)	3 734(3)	2 952(3)
C(6M)	2 457(11)	902(4)	5 639(4)	C(32)	935(6)	4 091(3)	2 294(3)
C(11)	3 809(5)	3 070(3)	2 936(3)	C(33)	138(7)	4 792(4)	2 144(4)
C(12)	4 877(6)	2 467(3)	3 006(3)	C(34)	−747(7)	5 128(4)	2 651(4)
C(13)	6 295(5)	2 618(3)	2 841(3)	C(35)	−813(6)	4 776(4)	3 294(4)
C(14)	6 705(6)	3 403(4)	2 634(3)	C(36)	7(6)	4 083(4)	3 447(3)
Compound (**2b**)							
Ru	1 672.0(2)	1 648.7(4)	3 924.9(2)	C(13)	1 782(4)	4 041(8)	6 622(4)
P	2 072.1(7)	617.4(13)	5 166.3(6)	C(14)	2 549(4)	4 406(7)	7 095(3)
C(1)	1 336(3)	4 115(5)	3 623(3)	C(15)	3 192(4)	3 601(7)	7 014(3)
C(2)	2 119(3)	4 161(5)	4 181(3)	C(16)	3 070(3)	2 414(7)	6 472(3)
C(3)	2 749(3)	3 261(5)	4 052(3)	C(17)	1 564(3)	−660(5)	3 489(3)
C(4)	2 603(3)	2 374(5)	3 348(3)	C(18)	675(3)	−934(6)	3 004(3)
C(5)	1 815(3)	2 428(6)	2 754(3)	C(19)	183(3)	−487(6)	3 533(3)
C(6)	1 193(3)	3 294(6)	2 881(3)	C(20)	441(3)	1 131(6)	3 848(3)
C(1M)	654(4)	5 022(7)	3 775(4)	C(21)	1 398(3)	−673(6)	5 476(3)
C(2M)	2 308(4)	5 246(6)	4 884(3)	C(31)	3 002(3)	−589(5)	5 481(3)
C(3M)	3 595(3)	3 366(7)	4 656(3)	C(32)	3 256(3)	−1 341(6)	6 206(3)
C(4M)	3 280(3)	1 506(7)	3 181(3)	C(33)	3 935(3)	−2 266(7)	6 413(3)
C(5M)	1 687(4)	1 611(8)	1 974(3)	C(34)	4 376(3)	−2 427(7)	5 912(4)
C(6M)	372(3)	3 429(8)	2 230(4)	C(35)	4 143(3)	−1 674(7)	5 197(3)
C(11)	2 289(3)	2 046(5)	5 982(3)	C(36)	3 449(3)	−758(6)	4 978(3)
C(12)	1 651(3)	2 868(7)	6 079(3)				
Compound (**2c**)							
Ru	1 825.2(3)	1 686.8(2)	1 548.4(1)	C(6M)	−1 492(5)	499(5)	1 276(3)
P	3 676.6(10)	2 795.8(9)	1 950.0(5)	C(11)	3 753(4)	4 169(3)	1 527(2)
C(1)	−89(4)	2 060(4)	773(2)	C(12)	2 700(5)	4 937(4)	1 587(3)
C(2)	1 080(4)	2 414(3)	454(2)	C(13)	2 730(6)	5 996(4)	1 290(3)
C(3)	2 214(4)	1 650(3)	426(2)	C(14)	3 776(7)	6 282(5)	917(3)
C(4)	2 165(4)	532(3)	674(2)	C(15)	4 835(6)	5 541(5)	847(3)
C(5)	924(4)	166(3)	932(2)	C(16)	4 822(5)	4 486(4)	1 156(2)
C(6)	−186(4)	907(4)	987(2)	C(17)	2 671(4)	564(3)	2 366(2)
C(1M)	−1 295(6)	2 862(5)	826(3)	C(18)	1 601(6)	435(5)	2 864(3)
C(2M)	1 115(6)	3 563(4)	127(2)	C(19)	1 147(6)	1 603(5)	3 045(3)
C(3M)	3 462(5)	2 036(4)	72(3)	C(20)	758(4)	2 276(4)	2 382(2)
C(4M)	3 359(6)	−271(4)	620(3)	C(21)	3 966(5)	3 281(4)	2 850(2)
C(5M)	811(6)	−1 058(4)	1 133(3)	C(31)	5 413(4)	2 196(4)	1 888(3)

atomic ellipsoids of the ORTEP[9] drawings (Figure 1), show that internal motions are relevant. Of course it is not possible to discriminate between static and dynamic anisotropic displacements, nevertheless these results are useful for a critical evaluation of the geometries of these molecules. The thermal motion analysis was carried out in the rigid-body approximation of Schomaker and Trueblood[10] and the internal motions were taken into account according to the one-parameter model of Dunitz and White.[11,12] The data of Table 2 are not corrected for thermal motion.

Metal co-ordination sphere. The molecular structure of these compounds is of the usual 'three-legged piano stool' type, quite similar to those already described for the analogous rhodium(III) and iridium(III) metallacyclopentanes containing pentamethylcyclopentadienyl and triphenylphosphine co-ligands.[4] From Table 2 it appears that the Ru–C_6Me_6 distance shows a small but significant reduction with decreasing number of phenyl groups in the phosphine ligand. The same effect seems to be operating also for the P–Ru distance, while no effect on the Ru–C bonds and on the ruthenium involving angles has been detected.

Metallacyclic Moiety. The metallacyclopentane ring shows a twisted conformation which is intermediate between envelope (^{19}E) and half-chair (^{20}HC), with a pseudo-mirror along C(18) and the midpoint of the Ru–C(20) bond, and a pseudo-two-fold axis along C(20) and the midpoint of the C(17)–C(18) bond, as

Table 2. Selected bond lengths (Å), angles (°), and dihedral angles (°) for the complexes (**2a**)—(**2c**): Bz is the centroid of benzene in the hexamethylbenzene ligand

	(**2a**)	(**2b**)	(**2c**)
(*a*) Co-ordination sphere			
Ru–C(C_6Me_6) av.	2.288(11)	2.281(10)	2.274(11)
Ru–Bz	1.793(2)	1.784(2)	1.777(1)
Ru–P	2.271(3)	2.267(2)	2.261(1)
Ru–C(17)	2.136(5)	2.140(5)	2.150(4)
Ru–C(20)	2.153(6)	2.156(5)	2.153(5)
Bz–Ru–P	134.5(2)	135.1(2)	132.6(2)
Bz–Ru–C(17)	126.0(3)	125.9(2)	126.1(2)
Bz–Ru–C(20)	124.4(3)	124.6(2)	126.3(2)
P–Ru–C(17)	86.7(2)	86.7(2)	84.8(1)
P–Ru–C(20)	88.9(2)	87.8(2)	88.8(1)
C(17)–Ru–C(20)	79.1(2)	79.2(2)	79.2(2)
Ru–Bz $\wedge$ [C(1)–C(6)]	88.6(2)	88.4(2)	89.3(2)
(*b*) Metallacyclic moiety			
C(17)–C(18)	1.493(9)	1.526(6)	1.514(7)
C(18)–C(19)	1.460(12)	1.519(8)	1.513(8)
C(19)–C(20)	1.527(10)	1.528(7)	1.522(7)
Ru–C(17)–C(18)	110.4(4)	107.7(3)	108.6(3)
C(17)–C(18)–C(19)	110.1(6)	106.8(4)	107.3(4)
C(18)–C(19)–C(20)	111.3(7)	107.6(4)	109.2(4)
C(19)–C(20)–Ru	112.0(4)	112.6(4)	112.6(3)
(*c*) C_6Me_6 ligand			
C–C av.	1.422(9)	1.422(7)	1.420(6)
C–C(M) av.	1.512(4)	1.516(2)	1.515(3)
C(M)–[C(1)—C(6)] av.	0.10(3)	0.10(4)	0.07(4)
C–C–C (endo) av.	119.9(3)	119.9(3)	119.9(5)
C(M)–C $\wedge$ [C(1)—C(6)] av.	3.6(12)	3.4(10)	3.0(10)
Cone angle(*)	155.5	151.6	157.3
(*d*) Phosphine ligand			
P–C(11)	1.833(5)	1.851(5)	1.836(4)
P–C(21)	1.850(5)	1.838(6)	1.831(5)
P–C(31)	1.855(5)	1.860(5)	1.828(5)
Ru–P–C(11)	113.0(2)	114.4(2)	116.2(2)
Ru–P–C(21)	119.9(2)	120.6(2)	121.6(2)
Ru–P–C(31)	118.3(2)	118.4(2)	115.2(2)
C(11)–P–C(21)	101.2(2)	99.4(2)	98.0(2)
C(11)–P–C(31)	103.3(2)	102.1(2)	103.0(2)
C(21)–P–C(31)	98.5(2)	98.5(2)	99.7(2)
Cone angle (*)	136.2	138.0	120.8
(*e*) Phenyl rings			
C–C av.	1.385(4)	1.378(5)	1.381(5)
C–C(*ipso*)–C av.	117.6(2)	118.2(4)	117.8(4)
C–C(*ortho*)–C av.	121.2(4)	120.6(3)	121.1(4)
C–C(*meta*)–C av.	120.1(2)	120.4(3)	119.9(7)
C–C(*para*)–C av.	119.7(2)	119.6(4)	120.2(5)
Ru–P–C(11)–C(12)	54.6(5)	69.1(5)	64.3(4)
Ru–P–C(21)–C(22)	−83.7(5)	—	—
Ru–P–C(31)–C(36)	−3.1(5)	3.6(5)	—

(*) Calculated as twice the angle formed by the Ru–Bz or Ru–P 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.

Table 3. Analysis of thermal motion in compounds (**2a**)—(**2c**) where $\bar{\Delta}$ = mean difference of the mean-square vibrational amplitudes along the interatomic directions for all pairs of atoms, $\Delta U = U_{ij}(\text{obs.}) - U_{ij}(\text{calc.})$, $R_{wU} = [\Sigma w(\Delta U)^2/\Sigma w(U_o)^2]^{\frac{1}{2}}$, $\sigma(\Delta U) = [\Sigma(w\Delta U)^2/\Sigma w^2]^{\frac{1}{2}}$, $\bar{\sigma}(U_o)$ = mean estimated standard deviation (e.s.d) of U_o, r.b. = rigid body, and i.m. = internal motions

Compound	Treatment	$\bar{\Delta}$	R_{wU}	$\sigma(\Delta U)$	$\bar{\sigma}(U_o)$
(**2a**)	r.b.	0.0072(105)	0.109	0.0021	0.0029
	i.m.[a]		0.081	0.0018	
(**2b**)	r.b.	0.0073(106)	0.099	0.0020	0.0026
	i.m.[b]		0.079	0.0016	
(**2c**)	r.b.	0.0116(211)	0.145	0.0031	0.0037
	i.m.[c]		0.107	0.0023	

[a] Four groups: C(1)—C(6), C(1M)—C(6M) about Ru–Bz, C(12)—C(16) about P–C(11), C(22)—C(26) about P–C(21), and C(17)—C(20) about Ru–[C(18)–C(19)]. [b] Three groups: C(1)—C(6), C(1M)—C(6M) about Ru–Bz, C(12)—C(16) about P–C(11), and C(17)—C(20) about Ru–[C(18)—C(19)]. [c] Six groups: C(1)—C(6), about Ru–Bz, C(1M)—C(6M) about Ru–Bz, C(12)—C(16) about P–C(11), C(22)—C(26) about P–C(21), C(32)—C(36) about P–C(31), and C(17)—C(20) about Ru–[C(18)–C(19)].

Table 4. Puckering analysis of the metallacyclopentane rings. Puckering co-ordinates according to Cremer and Pople[13], asymmetry parameters according to Nardelli[14]

Compound	Q_T(Å)	φ_2(°)	Δ_s[C(18)]	Δ_2[C(20)]
(**2a**)	0.394(9)	242.0(10)	0.037(4)	0.043(3)
(**2b**)	0.499(4)	243.5(5)	0.038(3)	0.058(2)
(**2c**)	0.468(6)	243.0(5)	0.038(2)	0.053(2)

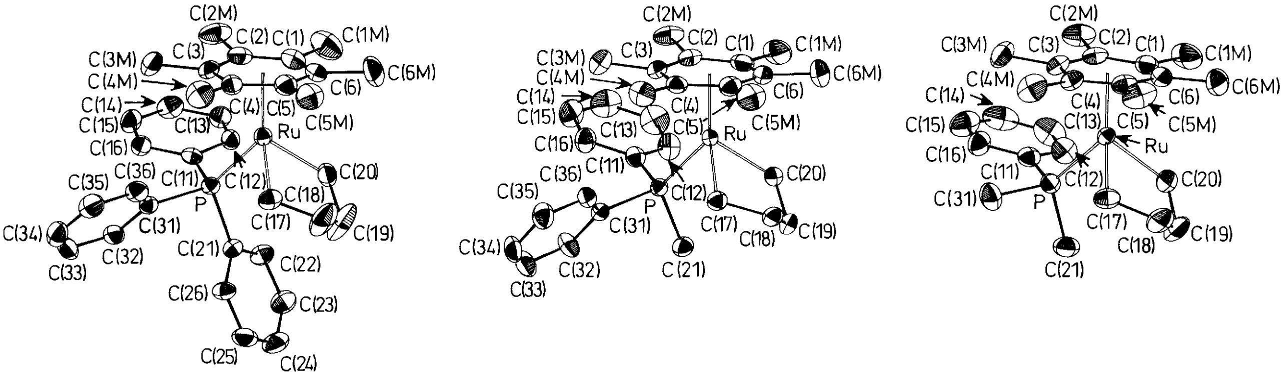
shown by the data in Table 4, where the relevant parameters of the ring puckering[13,14] are quoted. Compound (**2a**) shows a sensibly smaller total puckering amplitude, Q_T, but probably this flattening is not real and is due to the dynamic, or static, anisotropic displacements of C(18) and C(19) in (**2a**) (see Figure 1), which produce also apparent shortenings of the C(17)–C(18) and C(18)–C(19) distances, which are 1.493(9) and 1.460(12) Å, respectively.

Hexamethylbenzene ligand. As usually found in η^6-co-ordinated complexes of hexamethylbenzene, this ligand is not perfectly planar with the methyl groups showing the tendency to be out of the benzene plane in the opposite direction with respect to the metal. From the data in Table 5 it appears that the displacements are quite similar in the three compounds. In particular, for C(1M) and its *para*-corresponding C(4M) the displacements are smaller and in the opposite direction, while for the other pairs of *para*-corresponding methyls the displacements tend to be a little larger and in the same (positive) direction. In all cases the largest displacements are presented by C(2M) and C(3M) that are above the C(11) ⋯ C(16) of the phosphine phenyl group, and by C(5M) that is above the C(18) and C(19) atoms of the ruthenacyclopentane ring, indicating that the observed deformations are probably caused by intramolecular steric effects.

Molecular conformation. The orientation of the hexamethylbenzene and the phosphine ligands is shown by the Newman projections of Figure 2. These conformations correspond to points very near to minima of van der Waals potential energy as calculated for the free molecules upon rotation of hexamethylbenzene about the Ru ⋯ centroid of benzene ring (φ_1) direction and phosphine about the Ru–P (φ_2) direction, as shown by the curves in Figure 3 and the surfaces in Figure 4. In these plots the energy values are relative to the energy corresponding to the observed conformation in the crystal and counter-clockwise rotations are assumed as positive. These plots indicate that, while the rotation of the hexamethylbenzene ligand involves energy barriers not exceeding 60 kJ mol^{-1}, rotation of the phosphine ligand involves barriers about ten times larger. Considering the rotation of hexamethylbenzene, it appears that the crystalline conformation is not exactly

Table 5. Displacements, d (Å), of the methyl groups from the benzene plane in the hexamethylbenzene ligand: α is the angle (°) formed by the C–C(M) bond and the benzene plane. A positive value means that the displacement is in the opposite direction with respect to the metal atom, a negative one that it is towards the metal atom

Compound	(2a)		(2b)		(2c)		Average	
	d	α	d	α	d	α	d	α
C(1M)	−0.009(9)	−1.0(4)	−0.073(7)	−1.3(3)	−0.043(6)	0.0(3)	−0.05(2)	−0.7(4)
C(2M)	0.222(8)	7.4(4)	0.222(6)	7.4(3)	0.190(5)	6.0(2)	0.21(1)	6.6(5)
C(3M)	0.106(7)	4.0(4)	0.112(6)	4.1(3)	0.101(5)	3.7(2)	0.11(1)	3.8(2)
C(4M)	0.085(7)	3.9(4)	0.050(6)	2.7(3)	−0.021(5)	0.3(2)	0.03(3)	1.5(10)
C(5M)	0.119(7)	3.9(3)	0.123(7)	4.2(3)	0.128(5)	3.9(2)	0.12(1)	4.0(1)
C(6M)	0.083(8)	2.7(3)	0.142(7)	4.6(3)	0.046(6)	1.3(2)	0.09(3)	2.4(9)



(2a) (2b) (2c)

Figure 1. ORTEP drawings of compounds (**2a**)—(**2c**) showing thermal ellipsoids at 40% probability. The H-atoms are omitted for clarity

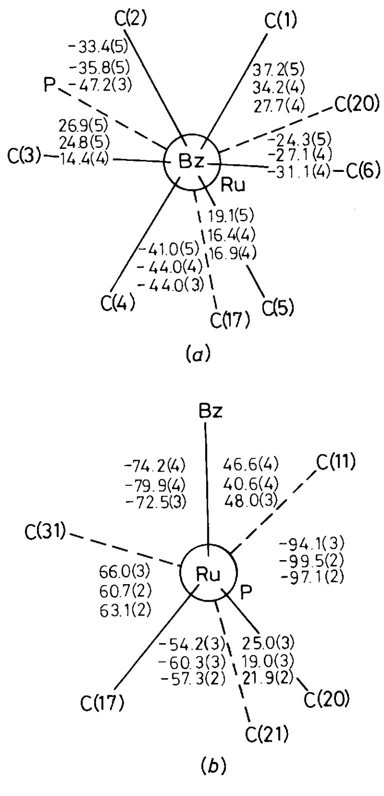


Figure 2. Newman projections along (*a*) the Bz ··· Ru and (*b*) Ru–P directions. The values of the torsion angles refer to compounds (**2a**), (**2b**), and (**2c**) respectively from the top to the bottom of each group of data

coincident with the potential-energy minimum, being shifted by a few degrees [6.5, $\Delta E = -4.4$; 8.5, $\Delta E = -6.0$; 4.0°, $\Delta E = -1.0$ kJ mol^{-1} for compounds (**2a**), (**2b**), and (**2c**) respectively; see Figure 3]. It is possible that this situation is a consequence of packing effects.

The surfaces in Figure 4, which shows the effects of concomitant rotations about φ_1 and φ_2 on the potential energy, indicate that quite severe steric interactions occur upon rotation of the phosphine, and that, as expected, these interactions increase with increasing of number of phosphine phenyl groups. This analysis shows that the conformation of the ancillary ligands is essentially governed by steric effects and the structure of the whole molecule permits open access to the reacting species to reach the metallacyclopentane moiety.

The molecules are packed in the unit cell by van der Waals forces.

Reaction of the Ruthenacyclopentanes (**2a**)—(**2c**) *with the Trityl Cation.*—The ruthenacyclopentanes (**2a**)—(**2c**) react easily with $[CPh_3][BF_4]$ at room temperature to give the cationic η^3-1-methylallyl complexes (**3a**)—(**3c**) in good yields (Scheme 2).

The structural assignment of (**3a**)—(**3c**) is based mainly on analytical and spectroscopic data (see Experimental section). The interpretation of the ^1H n.m.r. spectra was not easy and the assignments have been made by analogy with other cationic η^3-allylic complexes.[3,4] In the fast atom bombardment (f.a.b.) mass spectra the positive ions show molecular peaks at m/z 581, 519, and 457 respectively. Intense peaks are observed in all the spectra corresponding to the fragments $[M-(CH_2CHCHMe)]^+$ and $[M-(\text{phosphine})]^+$. In addition all the spectra show a quite intense signal due to the loss of the allylic group and of a hydrogen atom from the molecular ion with the probable formation of a relatively stable ion bearing an

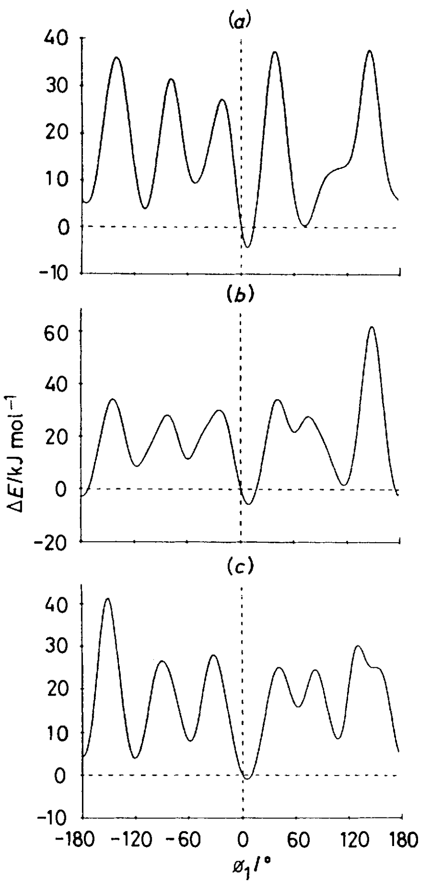


Figure 3. Calculated difference potential-energy profiles for the rotation of hexamethylbenzene about the Ru ··· Bz direction in the free molecules (*a*) (**2a**), (*b*) (**2b**), and (*c*) (**2c**). The zero of the energy is assumed for the conformation in the crystal

orthometallated phosphine, analogously to what has been already observed in the case of rhodium and iridium allylic cationic complexes.[4] Final confirmation of the structures has been achieved by preparing (**3a**)—(**3c**) by reaction of the dichloro compounds (**1a**)—(**1c**) with the 3-butenyl Grignard reagent, followed by reaction with $AgBF_4$ (Scheme 2).

Although we have no direct experimental support, we believe that the reaction of compounds (**2a**)—(**2c**) with $[CPh_3][BF_4]$ involves most probably a hydrogen abstraction from one of the β positions of the metallacyclic moiety, as we have demonstrated in the reaction of pallada-, rhoda-, and iridacyclopentanes with the trityl cation.[3]

Experimental

The reactions and manipulations of the organometallics were carried out under dinitrogen or argon, using standard techniques. The solvents were dried and distilled prior to use. The compounds $[\{RuCl_2(\eta^6\text{-}C_6Me_6)\}_2]$,[15] $[RuCl_2(\eta^6\text{-}C_6Me_6)L]$ [L = PPh_3 (**1a**) or $PMePh_2$ (**1b**)],[5,15] $Li(CH_2)_4Li$,[16] and $MgBr(CH_2CH_2CHCH_2)$[17] were prepared as described. Proton n.m.r. spectra were recorded on Varian T60, Varian Gemini 200, and VXR-300 instruments. 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, Università di Pisa.

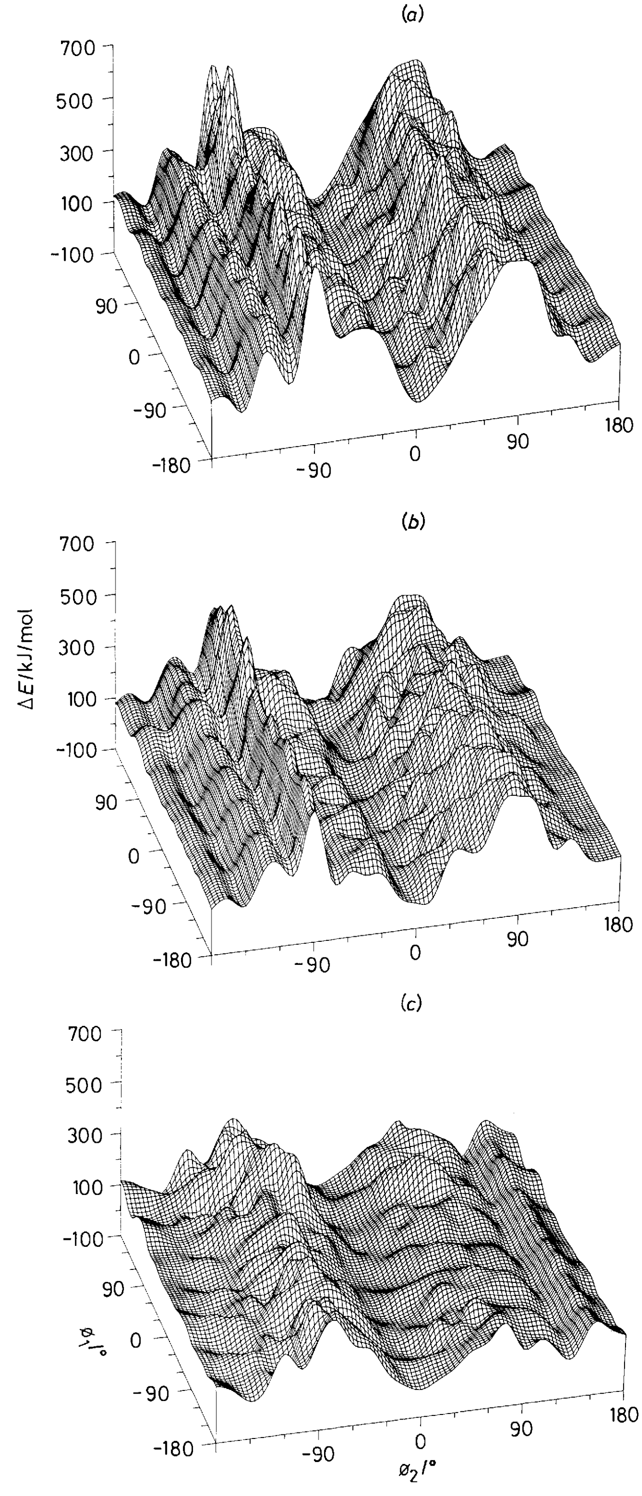
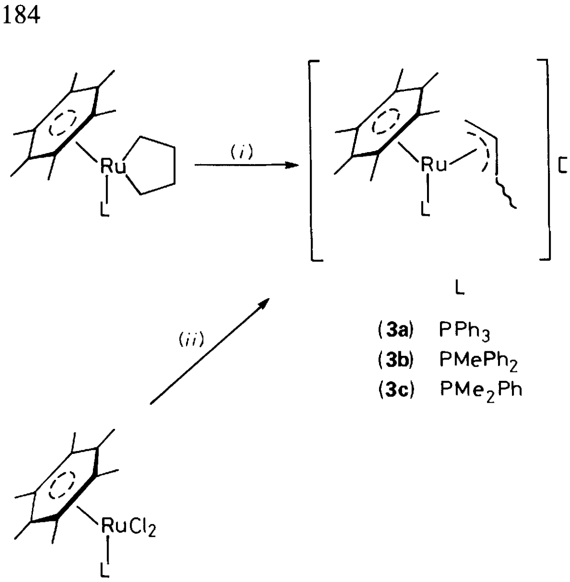


Figure 4. Calculated difference potential-energy surfaces for the rotation of hexamethylbenzene about the Ru ··· Bz direction (φ_1) and phosphine about the Ru–P direction (φ_2) in the free molecules (*a*) (**2a**), (*b*) (**2b**), and (*c*) (**2c**). The zero of the energy is assumed for the conformation in the crystal

Dichloro(dimethylphenylphosphine) (η^6-*hexamethylbenzene*)-*ruthenium*(II) (**1c**).—To a suspension of $[\{RuCl_2(\eta^6\text{-}C_6Me_6)\}_2]$ (1.07 g, 1.60 mmol) in $CHCl_3$ (50 cm^3) was added dimethylphenylphosphine (0.89 g, 6.41 mmol). The reaction mixture was heated under reflux for 6 h, then was allowed to cool to room temperature and filtered. The red filtered solution was evaporated under reduced pressure to approximately half volume and then hexane (60 cm^3) was added.



Scheme 2. (i) $[CPh_3][BF_4]$, CH_2Cl_2; (ii) (a) $MgBr(CH_2CH_2CHCH_2)$–Et_2O, (b) $AgBF_4$

The red-brown microcrystalline product was collected and washed with hexane (3 × 10 cm^3). After drying *in vacuo*, 1.26 g (83% yield) of compound (**1c**) were obtained (Found: C, 51.10; H, 6.30; Cl, 14.90. Calc. for $C_{20}H_{29}Cl_2$ PRu: C, 50.85; H, 6.20; Cl, 15.01%). ^1H N.m.r. ($CDCl_3$, reference $SiMe_4$, 60 MHz); δ 1.78 (d, 6 H, PMe_2, J_{HP} 11), 1.87 (d, 18 H, C_6Me_6, J_{HP} 0.7 Hz), and 7.2—8.0 (m, 5 H, Ph).

*(Butane-*1,4-*diyl)*(η^6-*hexamethylbenzene)(triphenylphosphine) ruthenium*(II) (**2a**).—The compound $[RuCl_2(\eta^6\text{-}C_6Me_6)(PPh_3)]$ (**1a**) (0.30g, 0.50 mmol) suspended in diethyl ether (15 cm^3) was treated at 0 °C with 1,4-dilithiobutane (4.0 cm^3 of a 0.63 mol dm^{-3} diethyl ether solution, 2.52 mmol). The reaction mixture was then stirred at room temperature for 2 h. The yellow solution was evaporated, and the residue extracted with pentane (80 cm^3). The pentane extract was hydrolyzed at 0 °C with water (6 cm^3) and the organic layer dried over anhydrous sodium sulphate. The pentane solution was concentrated to *ca.* 9 cm^3 and chromatographed through a column of neutral alumina. Elution with pentane gave a yellow-green band. Removal of the solvent left a yellow solid (**2a**) (0.082 g, 28%), which was crystallized from pentane at −20 °C (0.063 g) (Found: C, 71.15; H, 7.30. Calc. for $C_{34}H_{41}PRu$: C, 70.20; H, 7.10%). ^1H N.m.r. (C_6D_6), reference $SiMe_4$, 300 MHz): δ 1.13—1.45 (m, 4 H, CCH_2CH_2C), 1.70 (s, 18 H, C_6Me_6), 1.75—2.00 (m, 4 H, CH_2CCCH_2), 7.10—7.23 (m, 9 H, H_{meta} and H_{para}), and 7.65—7.80 (m, 6 H, H_{ortho}).

*(Butane-*1,4-*diyl)*(η^6-*hexamethylbenzene)(methyldiphenylphosphine)ruthenium*(II) (**2b**).—Following the procedure reported for (**2a**), $[RuCl_2(\eta^6\text{-}C_6Me_6)(PMePh_2)]$ (**1b**) (0.283 g, 0.53 mmol) suspended in diethyl ether (15 cm^3) was treated with 1,4-dilithiobutane (5.1 cm^3 of a 0.52 mol dm^{-3} diethyl ether solution, 2.7 mmol) to give 0.094 g (34% yield) of yellow crystals of (**2b**) (Found: C, 67.65; H, 7.60. Calc. for $C_{29}H_{39}PRu$: C, 67.00; H, 7.55%). ^1H N.m.r. (C_6D_6, reference $SiMe_4$, 300 MHz): δ 1.55—1.92 (m, 8 H, $CH_2CH_2CH_2CH_2$), 1.72 (s, 18 H, C_6Me_6), 1.80 (d, 3 H, PMe, J_{HP} 7.6 Hz), 7.10—7.25 (m, 6 H, H_{meta} and H_{para}), and 7.45— 7.55 (m, 4 H, H_{ortho}).

*(Butane-*1,4-*diyl)(dimethylphenylphosphine)*(η^6-*hexamethylbenzene)ruthenium*(II) (**2c**).—The compound $[RuCl_2(\eta^6\text{-}C_6Me_6)(PMe_2Ph)]$ (**1c**) (0.348 g, 0.74 mmol) suspended in diethyl ether (15 cm^3) was treated with 1,4-dilithiobutane (5.9 cm^3 of a 0.63 mol dm^{-3} diethyl ether solution, 3.7 mmol) at 0 °C. The reaction mixture was then stirred at room temperature for 2 h. The orange-yellow solution was evaporated, and the residue extracted with pentane (60 cm^3). The pentane solution was concentrated to *ca.* 8 cm^3 and chromatographed through a column of neutral alumina. Elution with a mixed solvent, pentane–diethyl ether (3:1), gave a yellow-green band. Evaporation of the solvent gave a yellow solid, (**2c**) (0.124 g, 37%). The product was crystallized from pentane at −20 °C to give yellow crystals (0.097 g) (Found: C, 63.30; H, 8.20. Calc. for $C_{24}H_{37}PRu$: C, 63.00; H, 8.15%). ^1H N.m.r. (C_6D_6, reference $SiMe_4$, 300 MHz): δ 1.38 (d, 6 H, PMe_2, J_{HP} 7.8 Hz), 1.73 (s, 18 H, C_6Me_6), 1.91—2.18 (m, 8 H, $CH_2CH_2CH_2CH_2$), 7.10—7.25 (m, 3 H, H_{meta} and H_{para}), and 7.40—7.50 (m, 2 H, H_{ortho}).

Reaction of Compound (**2a**) *with* $[CPh_3][BF_4]$: *Formation of* (η^6-*hexamethylbenzene)*(η^3-1-*methylallyl)(triphenylphosphine)ruthenium*(II) *Tetrafluoroborate* (**3a**).—A solution of $[CPh_3][BF_4]$ (0.077 g, 0.23 mmol) in CH_2Cl_2 (3 cm^3) was added dropwise to a solution of compound (**2a**) (0.136 g, 0.234 mmol) in CH_2Cl_2 (2 cm^3), while stirring at 0 °C. The temperature was maintained at 0 °C for 5 min and at 20 °C for 15 min, then the resulting red-orange solution was concentrated (1 cm^3) and added to diethyl ether (80 cm^3). The white microcrystalline solid was collected, washed repeatedly with diethyl ether, and dried, yield 0.138 g (88%) (Found: C, 61.20; H, 6.10; P, 4.70. Calc. for $C_{34}H_{40}BF_4PRu$: C, 61.15; H, 6.05; P, 4.65%, M^+ 581). F.a.b. mass spectrum (positive ion, argon): M^+ 581. ^1H N.m.r. ($CDCl_3$, reference $SiMe_4$, 200 MHz): δ 1.44 (d, 3 H, CH*Me*, J_{HH} 6.02), 1.7—1.8 (m, 1 H, H_{anti}), 1.83 (br s, 18 H, C_6Me_6), 1.90—2.05 (m, 1 H, C*H*Me), 2.5 (br dd, 1 H, H_{syn}, J_{HH} 7.2 Hz), 3.18 (m, 1 H, $H_{central}$), and 7.5 (m, 15 H, Ph).

Reaction of Compound (**2b**) *with* $[CPh_3][BF_4]$: *Formation of* (η^6-*hexamethylbenzene)*(η^3-1-*methylallyl)(methyldiphenylphosphine)ruthenium*(II) *Tetrafluoroborate* (**3b**).—A similar reaction between compound (**2b**) (0.050 g, 0.096 mmol) and $[CPh_3][BF_4]$ (0.031 g, 0.093 mmol) in CH_2Cl_2 (4 cm^3) gave white-cream microcrystals of (**3b**), yield 0.047 g (80%) (Found: C, 57.60; H, 6.40; P, 5.20. Calc. for $C_{29}H_{38}BF_4PRu$: C, 57.50; H, 6.30; P, 5.10%; M^+ 519). F.a.b. mass spectrum (positive ion, argon): M^+ 519. ^1H N.m.r. ($CDCl_3$, reference $SiMe_4$, 200 MHz): δ 1.29 (d, 3 H, PMe, J_{HP} 8.5), 1.43 (d, 3 H, CH*Me*, J_{HH} 6.2), 1.6—1.8 (m, 1 H, H_{anti}), 1.94 (s, 18 H, C_6Me_6), 2.0—2.2 (m, 1 H, C*H*Me), 2.47 (dd, 1 H, H_{syn}, J_{HH} 2.0, 6.9 Hz), 3.21 (m, 1 H, $H_{central}$, and 7.5 (m, 10 H, Ph).

Reaction of Compound (**2c**) *with* $[CPh_3][BF_4]$: *Formation of* *(Dimethylphenylphosphine)*(η^6-*hexamethylbenzene)*(η^3-1-*methylallyl)ruthenium*(II) *Tetrafluoroborate* (**3c**).—A similar reaction between compound (**2c**) (0.050 g, 0.109 mmol) and $[CPh_3][BF_4]$ (0.036 g, 0.109 mmol) in CH_2Cl_2 (4 cm^3) gave white-cream microcrystals of (**3c**), yield 0.049 g (83%) (Found: C, 53.10; H, 6.70; P, 5.75. Calc. for $C_{24}H_{36}BF_4PRu$: C, 53.05; H, 6.65; P, 5.70%; M^+ 457). F.a.b. mass spectrum (positive ion, argon): M^+ 457. ^1H N.m.r. ($CDCl_3$, reference $SiMe_4$, 200 MHz): δ 1.35 (d, 3 H, PMe, J_{HP} 8.4), 1.36 (d, 3 H, PMe, J_{HP} 8.5), 1.49 (d, 3 H, CH*Me*, J_{HH} 6.3), 1.56 (dd, 1 H, H_{anti}, J_{HH} 15.8, 10.7), 1.90 (d, 18 H, C_6Me_6, J_{HP} 0.7 Hz), 2.05—2.25 (m, 1 H, C*H*Me), 2.44 (dd, 1 H, H_{syn}, J_{HH} 7.1, 2.4 Hz), 3.26 (m, 1 H, $H_{central}$), and 7.5 (m, 5 H, Ph).

Reaction of Compound (**1a**) *with* $MgBr(CH_2CH_2CHCH_2)$, *then with* $AgBF_4$: *Formation of* (**3a**).—To a stirred suspension of compound (**1a**) (0.300 g, 0.50 mmol) in diethyl ether (20 cm^3), $MgBr(CH_2CH_2CHCH_2)$ (0.70 mmol, 1.1 cm^3 of a 0.624 mol dm^{-3} diethyl ether solution) and four drops of 1,4-dioxane were added at room temperature. The mixture was stirred for 24 h at room temperature, then CH_2Cl_2 (20 cm^3) was added; finally the

Table 6. Experimental data for the crystallographic analyses[a]

Compound	**(2a)**	**(2b)**	**(2c)**
Formula	$C_{34}H_{41}PRu$	$C_{29}H_{39}PRu$	$C_{24}H_{37}PRu$
M	581.7	519.7	457.6
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$
a/Å	9.249(3)	17.463(13)	9.575(6)
b/Å	16.160(7)	8.708(6)	11.899(8)
c/Å	19.094(21)	17.749(13)	19.494(12)
β/°	90.70(1)	109.15(4)	97.96(2)
U/Å^3	2854(4)	2 550(3)	2 200(2)
D_c/Mg m^{-3}	1.354	1.354	1.382
No. of reflections for lattice parameters	28	32	32
(θ range/°)	(19.2—23.8)	(20.8—24.8)	(20.8—24.7)
F(000)	1 216	1 088	960
Crystal size/mm	0.21 × 0.37 × 0.56	0.13 × 0.40 × 0.64	0.42 × 0.26 × 0.40
μ/mm^{-1}	0.613	0.678	0.776
Absorption correction (min., max.)	0.956, 1.063	1.002, 1.059	—
Extinction correction (min., max.)	0.953, 1.039	—	—
Scan width/°	1.6	1.4	1.4
θ range/°	3—24	3—25	3—25
h range	−10 to 10	−19 to 19	−11 to 11
k range	0—18	0—10	0—14
l range	0—21	0—20	0—23
Standard reflection	1 0 9	$\bar{6}$ 0 4	2 3 7
Scan mode	ω	ω	θ—2θ
No. of measured reflections	4 840	4 977	4 217
No. of reflections used in refinement [$I \geqslant 2\sigma(I)$]	3 203	3 412	3 080
R(int)	0.016	0.024	0.022
Max. least-squares shift-to-error ratio	0.12	0.40	0.41
Min. max. height in final Δρ/e Å^{-3}	−0.11, 0.13	−0.36, 0.54	−0.12; 0.25
No. of parameters refined	453	436	383
$R = \Sigma\lvert\Delta F\rvert/\Sigma\lvert F_o\rvert$	0.0425	0.0395	0.0330
$R' = [\Sigma w(\Delta F)^2/\Sigma wF_o^2]^{\frac{1}{2}}$	0.0490	0.0475	0.0429
$S = [\Sigma w(\Delta F)^2/(N-P)]^{\frac{1}{2}}$[b]	1.204	1.063	0.893
k, g in $w = k/[\sigma^2(F_o) + gF_o^2]$	1.375, 0.0005	1.173, 0.0006	0.981, 0.0008

[a] Details in common: $Z = 4$; Philips PW1100 diffractometer; Mo-K_α radiation (λ = 0.71 069 Å). Scan speed 0·1° min^{-1}; no intensity variation of standard reflection. [b] P = Number of parameters, N = number of observations.

mixture was treated with water (3 × 10 cm^3). The organic layer was dried over anhydrous Na_2SO_4, concentrated to 3 cm^3, and added to diethyl ether (80 cm^3). The light pink microcrystalline solid was collected, washed repeatedly with diethyl ether, and dried. The solid was dissolved in acetone (10 cm^3) and treated with $AgBF_4$ (0.064 g, 0.33 mmol) in acetone (4 cm^3). A rapid reaction took place and a precipitate formed. After stirring for 30 min, the suspension was filtered and the solution evaporated to dryness. The residue was dissolved in CH_2Cl_2 (3 cm^3) and the solution was poured into diethyl ether (80 cm^3) to give compound (**3a**) (0.172 g, 52%).

Reaction of Compound (**1b**) *with* $MgBr(CH_2CH_2CHCH_2)$, *then with* $AgBF_4$: *Formation of* (**3b**).—A similar reaction between compound (**1b**) (0.300 g, 0.56 mmol) and $MgBr(CH_2CH_2CHCH_2)$ (0.75 mmol, 1.2 cm^3 of a 0.624 mol dm^{-3} diethyl ether solution) followed by treatment with $AgBF_4$ (0.049 g, 0.25 mmol) gave compound (**3b**) (0.125 g, 37%).

Reaction of Compound (**1c**) *with* $MgBr(CH_2CH_2CHCH_2)$, *then with* $AgBF_4$: *Formation of* (**3c**).—A similar reaction between compound (**1c**) (0.300 g, 0.63 mmol) and $MgBr(CH_2CH_2CHCH_2)$ (0.96 mmol; 1.6 cm^3 of a 0.624 mol dm^{-3} diethyl ether solution) followed by treatment with $AgBF_4$ (0.045 g, 0.023 mmol) gave (**3c**) (0.103 g, 30%).

Crystal-Structure Analysis of Compounds (**2a**)—(**2c**).—Table 6 gives the experimental data concerning the crystal-structure analyses. The lattice parameters were determined by measuring accurately centred reflections at high θ by using Mo-$K_{\alpha 1}$ (λ = 0.709300 Å) radiation, at room temperature (294 K). The intensity data were corrected for Lorentz and polarization effects, and when absorption and extinction effects were corrected for the empirical method of Walker and Stuart[18] was used.

The structures were solved by the Patterson methods of the SHELX 86 program.[19] The hydrogen atoms were located by Fourier difference calculations and refined isotropically. The refinements were carried out by anisotropic least squares of F using the SHELX 76 program.[20]

The atom–atom non-bonded potential-energy calculations were carried out using a function of the 'exp-6-1' type: $E_{jk} = B_{jk}\exp(-C_{jk}r_{jk}) - A_{jk}r_{jk}^{-6}$, disregarding the coulombic energy and assuming the H atoms to be in calculated positions (C–H = 1.07 Å).

The atomic scattering factors were taken from ref. 21. The calculations were performed on the GOULD-SEL 32/77 computer of the Centro di Studio CNR per la Strutturistica Diffrattometrica (Parma). The programs LQPARM,[22] PARST,[23] ABSORB,[24] THMV,[25] ROTENER[26] were also used.

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

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