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Axially asymmetric metal alkyls

VIII *. The ruthenium metallacycle $[\text{Ru}\{(2\text{-CH}_2\text{C}_6\text{H}_4)_2\}(\text{PPhMe}_2)_3]$ and *o*-metallated $[\overline{\text{Ru}\{\text{PC}}_6\text{H}_4(\text{Me})_2\}\text{X}(\text{PPhMe}_2)_3]$ ($\text{X} = \text{Cl, Br}$) **

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Abstract

Reaction of *cis*-$[\text{RuCl}_2(\text{PPhMe}_2)_4]$ with $\{(\text{TMEDA})\text{Li}\}_2\{(2\text{-CH}_2\text{C}_6\text{H}_4)_2\}$ yields the thermally unstable metallacycloheptadiene, $[\text{Ru}\{(2\text{-CH}_2\text{C}_6\text{H}_4)_2\}(\text{PPhMe}_2)_3]$ (1), which in the solid has a distorted square pyramidal structure with the two ligating carbon atoms in the basal plane (mean Ru–C 2.14 Å), although there is an agostic-H interaction to an *o*-hydrogen of a phenyl group (2.80 Å) *trans* to the apical P-centre, and a secondary interaction to one of the *β*-carbon atoms of the metallacycle (2.63(4) Å) effectively saturating the metal centre. Treatment of *trans*-$[\text{RuCl}_2(\text{PPhMe}_2)_4]$ with $2\text{-}[(\text{THF})_n\text{ClMgCH}_2]\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{Me-}2'$ in refluxing THF yields the *o*-metallated product, $[\overline{\text{Ru}\{\text{PC}}_6\text{H}_4(\text{Me})_2\}\text{Cl}(\text{PPhMe}_2)_3]$ (2) which has been characterized by NMR spectroscopy, and by an X-ray structure determination for the corresponding bromide, $[\text{Ru}\{\text{PC}_6\text{H}_5(\text{Me})_2\}\text{Br}(\text{PPhMe}_2)_3]$ (2′).

1. Introduction

In Parts 1–5 [1–5] of the present series, we developed some organometallic chemistry based on $(2\text{-CH}_2\text{C}_6\text{H}_4)_2^{2-}$ ($= \text{R}_2^{2-}$), initially an organodilithium complex, $\{\text{Li(TMEDA)}\}_2(\text{R}_2)$ (TMEDA = *N,N′*-tetramethylethylenediamine) [1,3,5] and a di-Grignard reagent, $\{(\text{THF})_n\text{ClMg}\}_2(\text{R}_2)$ (THF = tetrahydrofuran) [2,3,5]. These transfer reagents yielded novel axially asymmetric, 9-membered metallacycle rings (metallacycloheptatdienes) for Si [1], Sn [2], Ti, Zr, Hf [5], Nb, Ta [3], W [4] and a bimetallic species for V [3]. In addition, some metallacycle chemistry has been developed for the related trimethylsilyl-substituted dianion $\{2\text{-CH(SiMe}_3)\text{C}_6\text{H}_4\}_2^{2-}$, involving use of a lithium complex as the transfer reagent [5,6], and lithium reagents based on the related binaphthyl dianion $(2\text{-CH}_2\text{C}_{10}\text{H}_6)_2^{2-}$ and substituted biphenyl dianion $(2\text{-CH}_2\text{-6-MeC}_6\text{H}_3)_2^{2-}$ have been prepared [7]. These also have potential in forming metallacycloheptadienes.

We have now further developed the transition metal chemistry of R_2^{2-} and focus on ruthenium because of its potential in C–H activation and in catalysis. Readily available ruthenium(II) phosphinechloro complexes were chosen as suitable species for metathetical exchange with the above dilithium and di-Grignard reagents of R_2^{2-}. In addition, we have examined the possibility of using an appropriate transfer reagent of $(2\text{-CH}_2\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{Me-}2')$ with the same ruthenium complexes with a view to forming bis-monoalkylruthenium(II) species. These can in principle undergo *ζ*-elimination, *via* formation of metallacycles based on R_2^{2-} with extrusion of di-tolyl. Such an elimination has a precedent in the formation of *o*-xylylene [8], 2,3-naphthoquinodimethane [9] and related derivatives of ruthenium [10] *via* *δ*-elimination, although these

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* For Part VII, see ref. 6.

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species are more like π-complexes than metallacyles. The ligand R_2^{2-} may also participate in polyhapto bonding, for example as η^3-allyl for one or both arms of the hydrocarbyl group, in a similar fashion to that established for the parent benzyl ligand [11]. Ruthenium(II) metacyclobutanes have also been generated by use of an elimination method associated with dialkylation of ruthenium(II) chlorophosphine arene species [12].

As in the present system, *o*-xylylene metallacycles/π-complexes are accessible *via* metathetical exchange involving the corresponding di-Grignard reagent [13], which like the above di-Grignard reagent [2], was originally prepared by the classical method of Grignard reagent formation from the bulk metal. However, both di-Grignard reagents are now more conveniently prepared in high yield by using magnesium(anthracene)$(THF)_3$ as the source of metal which is delivered by electron transfer processes [14].

2. Experimental section

General procedures are described in Parts 1–3 of this series [1–3]. Compounds *cis*-$[RuCl_2(PPhMe_2)_4]$ [15], *trans*-$[RuCl_2(PPhMe_2)_4]$ [8]. $\{Li(TMEDA)\}_2(R_2)$ [1], $\{(THF)_nClMg\}_2(R_2)$ [2,14], and 2-$(THF)_nClMgCH_2]C_6H_4C_6H_4Me$-2′ [2] were prepared by published procedures. Coupling constants for the ^{31}P NMR spectrum of **2** were calculated using the PANIC program.

2.1. *Synthesis of* $Ru\{(2\text{-}CH_2C_6H_4)_2\}(PPhMe_2)_3]$ *(1)*

To a suspension of *cis*-$[RuCl_2(PPhMe_2)_4]$ [6] (0.56 g, 0.77 mmol) in THF (30 ml) at −78°C was added slowly a solution of $\{Li(TMEDA)\}_2(R_2)$ [1] (0.33 g, 0.77 mmol) in THF (10 ml), and the mixture was slowly warmed to room temperature during 2 h, resulting in a colour change from pale yellow to deep red/brown. The solvent was removed *in vacuo* and the residue extracted with toluene. Filtration of the extract, concentration *in vacuo*, addition of some diethyl ether and storage at −30°C for several days yielded dark red crystals of the title compound (0.26 g, 49% yield); m.p. 151–154°C. Mass spectrum (EI): *m/e* 557 $(M^+(Ru^{101}) - PPhMe_2)$; 419 $(M^+ - 2PPhMe_2)$.

2.2. *Synthesis of* $[\overline{Ru\{PC}_6H_4(Me)_2\}Cl(PPhMe_2)_3]$ *(2)*

To a suspension of *trans*-$[RuCl_2(PPhMe_2)_4]$ [8] (0.6 g, 0.83 mmol) in THF (30 ml) was added 2.50 ml of a 0.676 M solution of 2-$[(THF)_nClMgCH_2]C_6H_4C_6H_4$-Me-2′ [2]. The mixture was heated under reflux for 16 h, the solvent was removed *in vacuo* and the residue extracted with toluene and the extract filtered and concentrated *in vacuo*. An equal volume of hexane was added and the solution kept at −30°C for several days to yield orange crystals of the title compound (0.26 g, 46% yield); m.p. 193–195°C. ^1H NMR (300 MHz, C_6D_6, 25°C): δ 0.26 (d, 6H, $J(HP)^* = 9.0$ Hz, P(1)Me); 1.60 (d, 6H, $J(HP)^* = 5.5$ Hz, P(3)Me); 1.78 (t, 6H, $J(HP)^* = 2.6$ Hz, P(2,3)Me); 1.98 (t, 6H, $J(HP)^* = 3.7$ Hz, P(2,3)Me); 6.4–7.3 (phenyl resonances) (* apparent coupling constants). ^{13}C NMR (75.43 MHz, C_6D_6, 25°C): δ 15.0, 17.6, 18.5, 21.4 (Me); 120–143 (m, C_6H_4 + Ph). ^{31}P NMR (121.44 MHz, C_6D_6, 25°C): δ −40.73 (q, $J_{1,3} = 21.9$ Hz, $J_{1,3} = 21.9$ Hz, $J_{1,2/1,4} = 26.0$ Hz, P(1)); −1.92 (t, $J_{2,3/3,4} = 23.4$ Hz, $J_{2,4}$ 0 = Hz, P(2,4)); −0.77 (q, $J_{2,3/3,4} = 23.4$ Hz, $J_{1,3} = 21.9$ Hz, P(3)).

2.3. *Structure determinations*

Suitable prismatic crystals of **1** were grown from toluene at −30°C; when the same procedure was used for **2**, the crystals proved to be the isolobal bromide, **2′**, rather than the chloride, which is a consequence of the presence of traces of bromide in the ruthenium(III) chloride starting material for the synthesis of *trans*-$[RuCl_2(PPhMe_2)_4]$. The refinement behaviour was consistent with full occupancy by the bromine, as were the associated geometrical parameters. Unique diffractometer data sets were measured using an Enraf-Nonius CAD4 diffractometer with crystals mounted in capillaries; specimens of **1** were small and weakly diffracting, and the data presented are the best from a number of attempts. The structures were solved by direct methods and refined by full matrix least squares refinement using the XTAL system [16]. Final coordinates are given in Tables 1 and 2, with relevant crystal data summarized in Table 3, and non-hydrogen atom numberings are shown in Figures 1 and 2. For compound **2′** anisotropic thermal parameters were refined for the non-hydrogen atoms; for compound **1**, there were insufficient data to support this and only the ruthenium and phosphorus atoms were refined anisotropically. All x, y, x and $U_{iso}(H)$ were included in both cases as constrained estimates. Residuals on $|F|$ at convergence R, R_w are quoted. Lists of U_{ij} values, hydrogen atom parameters, bond distances and angles have been deposited at the Cambridge Crystallographic Centre.

3. Results and discussion

3.1. *Synthesis and NMR studies*

Scheme 1 summarizes details of the syntheses of the new compounds **1** and **2**. Compound **1** was prepared from *cis*-$[RuCl_2(PMe_2Ph)_4]$ and $\{Li(TMEDA)\}_2(R_2)$ under mild conditions. The alkylation is associated with elimination of one phosphine ligand. This type of elimination has been noted for other alkylation reactions involving $[RuCl_2(PMe_2Ph)_4]$ [10]. The di-Grig-

TABLE 1. Non-hydrogen atom parameters for $[Ru\{(2\text{-}CH_2C_6H_4)_2\}(PPhMe_2)_3]$ (**1**)

Atom	x	y	z	$U \times 10^3$ (Å^2)
Ru	0.2720(2)	0.1394(3)	0.1251(2)	–[a]
Ligand				
C(A1)	0.178(2)	0.011(4)	0.085(2)	55(12)
C(A2)	0.203(2)	−0.072(3)	0.140(1)	11(8)
C(A3)	0.167(2)	−0.050(3)	0.198(2)	50(12)
C(A4)	0.193(2)	−0.129(3)	0.254(2)	36(9)
C(A5)	0.245(2)	−0.225(4)	0.253(2)	56(12)
C(A6)	0.282(2)	−0.239(4)	0.192(2)	52(11)
C(A7)	0.261(2)	−0.164(3)	0.134(2)	38(10)
C(B1)	0.367(2)	0.019(3)	0.100(2)	38(10)
C(B2)	0.347(2)	−0.088(3)	0.054(1)	15(9)
C(B3)	0.380(2)	−0.106(3)	−0.006(2)	33(10)
C(B4)	0.354(2)	−0.210(3)	−0.047(2)	29(9)
C(B5)	0.301(2)	−0.300(3)	−0.027(2)	40(11)
C(B6)	0.269(2)	−0.282(4)	0.033(2)	47(11)
C(B7)	0.295(2)	−0.179(2)	0.073(1)	13(9)
Dimethylphenylphosphine ligands				
P(1)	0.1752(7)	0.2554(9)	0.1723(5)	–[a]
C(101)	0.196(2)	0.275(3)	0.265(2)	41(11)
C(102)	0.162(2)	0.416(3)	0.155(2)	52(12)
C(11)	0.059(2)	0.220(3)	0.154(2)	45(11)
C(12)	0.018(2)	0.174(3)	0.203(2)	52(12)
C(13)	−0.069(2)	0.137(5)	0.189(2)	69(12)
C(14)	−0.107(2)	0.156(4)	0.121(2)	70(13)
C(15)	−0.069(3)	0.191(4)	0.070(2)	64(14)
C(16)	0.014(2)	0.233(4)	0.088(2)	48(11)
P(2)	0.2673(6)	0.2448(11)	0.0295(5)	–[a]
C(201)	0.317(3)	0.395(4)	0.034(2)	75(15)
C(202)	0.318(3)	0.179(4)	−0.035(2)	64(14)
C(21)	0.165(2)	0.272(3)	−0.026(2)	26(9)
C(22)	0.110(2)	0.181(3)	−0.057(2)	40(11)
C(23)	0.035(2)	0.204(4)	−0.094(2)	53(12)
C(24)	0.000(3)	0.313(4)	−0.103(2)	71(14)
C(25)	0.048(3)	0.405(4)	−0.079(2)	71(14)
C(26)	0.129(2)	0.395(3)	−0.035(2)	43(11)
P(3)	0.3900(6)	0.2366(9)	0.1937(5)	–[a]
C(301)	0.397(2)	0.400(3)	0.216(2)	48(12)
C(302)	0.492(2)	0.225(3)	0.168(2)	29(9)
C(31)	0.418(2)	0.167(3)	0.277(1)	30(10)
C(32)	0.375(2)	0.063(3)	0.290(1)	21(9)
C(33)	0.392(2)	0.000(3)	0.353(2)	45(11)
C(34)	0.454(2)	0.041(3)	0.405(2)	37(10)
C(35)	0.495(2)	0.141(4)	0.394(2)	55(11)
C(36)	0.482(2)	0.202(4)	0.331(2)	59(13)

[a] Anisotropic thermal parameters (form: $\exp(-2\pi^2(U_{11}h^2a^{*2} + \cdots + 2U_{23}klb^*c^*))$. $10^3 \times U_{11,22,33,12,13,23}$ Å^2: Ru, 25(2), 28(2), 24(2), 3(2), −2(1), 8(2); P(1), 61(7), 23(6), 32(6), −12(6), 3(5), −17(6); P(2), 36(7), 66(9), 30(6), 6(7), 9(5), −13(7); P(3), 32(6), 30(7), 43(7), −17(6), −2(5), −2(6).

nard reagent $\{(THF)_nClMg\}_2(R_2)$ failed to react with *cis*-$[RuCl_2(PMe_2Ph)_4]$ under the same conditions.

There was no evidence for reaction of *trans*-$[RuCl_2(PMe_2Ph)_4]$ with 2 equiv. of 2-$[(THF)_nClMgCH_2]C_6H_4C_6H_4Me$-2′ at room temperature. Under more forcing conditions, the *o*-metallated product, **2**, was obtained, and presumably arises from an intermediate (alkyl halide) complex which rapidly undergoes elimination of di-tolyl in the refluxing THF. No alkylated product could be isolated from the reaction mixtures. Even the *trans*-ruthenium(II) phosphinechloro complex, which is more likely to yield a stable dialkyl, gave the *o*-metallated product and there was seemingly no transfer of the second alkyl group. This may be due to the steric hindrance of this group, and for the second alkylation a more nucleophilic lithium reagent may be necessary; such reagents have been widely used in related reactions by Cole-Hamilton *et al.* for eliminations yielding ruthenium *o*-xylylene and related complexes [12]. In this context the aforementioned need to use a di-lithium reagent to generate **1** is noteworthy, although here the linked alkyl groups would be less sterically demanding than two unidentate alkyls. More-

TABLE 2. Non-hydrogen atom coordinates for $[Ru\{PC_6H_4(Me)_2\}Br(PPhMe_2)_3]$ (**2′**)

Atom	x	y	z
Br	0.38271(5)	0.26136(5)	0.69142(9)
Ru	0.44094(3)	0.26487(3)	0.42753(6)
P(1)	0.5096(1)	0.2795(1)	0.2207(2)
C(11)	0.5746(4)	0.3278(4)	0.3332(8)
C(12)	0.5407(4)	0.3227(4)	0.4672(8)
C(13)	0.5763(5)	0.3572(4)	0.5867(9)
C(14)	0.6439(5)	0.3921(4)	0.5633(11)
C(15)	0.6763(5)	0.3936(5)	0.4276(11)
C(16)	0.6417(5)	0.3607(5)	0.3097(10)
C(101)	0.5636(5)	0.2176(4)	0.1234(9)
C(102)	0.4794(5)	0.3260(4)	0.0569(9)
P(2)	0.3742(1)	0.3657(1)	0.4193(2)
C(21)	0.3830(5)	0.4269(4)	0.2732(9)
C(22)	0.4475(5)	0.4750(4)	0.2707(10)
C(23)	0.4553(6)	0.5122(4)	0.1642(11)
C(24)	0.4000(6)	0.5206(5)	0.0577(11)
C(25)	0.3355(6)	0.4831(5)	0.0567(11)
C(26)	0.3271(5)	0.4356(4)	0.1635(10)
C(201)	0.2713(5)	0.3627(5)	0.4347(11)
C(202)	0.3977(5)	0.4180(4)	0.5764(10)
P(3)	0.3410(1)	0.2030(1)	0.3193(2)
C(31)	0.3619(4)	0.1224(4)	0.2413(9)
C(32)	0.3994(5)	0.1180(5)	0.1105(10)
C(33)	0.4168(7)	0.0592(5)	0.0490(11)
C(34)	0.3965(6)	0.0027(5)	0.1163(13)
C(35)	0.3605(6)	0.0048(5)	0.2425(12)
C(36)	0.3419(5)	0.0644(4)	0.3066(10)
C(301)	0.2951(5)	0.2384(5)	0.1541(10)
C(302)	0.2587(5)	0.1835(5)	0.4282(12)
P(4)	0.5123(1)	0.1783(1)	0.5333(2)
C(41)	0.5861(4)	0.1351(4)	0.4369(8)
C(42)	0.6575(5)	0.1635(4)	0.4263(9)
C(43)	0.7138(5)	0.1315(5)	0.3479(11)
C(44)	0.6982(6)	0.0739(5)	0.2828(11)
C(45)	0.6286(6)	0.0455(5)	0.2906(11)
C(46)	0.5732(5)	0.0761(4)	0.3674(10)
C(401)	0.5670(5)	0.2009(5)	0.7012(9)
C(402)	0.4598(5)	0.1099(4)	0.6068(9)

TABLE 3. Summary of X-ray diffraction data for $[Ru\{(2\text{-}CH_2C_6H_4)_2\}(PPhMe_2)_3]$ (**1**) and $[Ru\{PC_6H_4(Me)_2\}Br(PPhMe_2)_3]$ (**2'**)

	1	2'
Formula	$C_{38}H_{45}PP_4Ru$	$C_{32}H_{43}BrP_4Ru$
Mol wt	696.4	733.2
Space group	$P2_1/c$(non-standard no. 14)	$P2_1/n$(no. 14)
a (Å)	16.04(1)	17.669(5)
b (Å)	11.06(3)	20.531(7)
c (Å)	19.82(1)	9.078(2)
β (°)	101.03(7)	92.42(2)
V (Å^3)	3450.0	3290.0
Z	4	4
D_{calcd} (g cm^{-3})	1.34	1.48
$F(000)$	1448	1496
Crystal dimensions (mm)	0.25 × 0.3 × 0.3	0.2 × 0.2 × 0.25
Temperature (°C)	25	25
Radiation	Mo Kα (λ = 0.71073 Å, graphite monochromator)	
μ (cm^{-1}) (uncorrected)	6.1	19.7
2θ limit (°)	40	50
No. collected reflections	3267	5742
No. obsd reflections [$I > 3.0\sigma(I)$]	920	3938
R	0.068	0.048
R_w	0.084	0.054

over, stronger nucleophiles may be essential for alkylation at low temperatures to circumvent *o*-metallation, which becomes prevalent at higher temperatures, and to facilitate elimination of one of the phosphines, as during the formation of **1**. *o*-Metallation of arylphosphines is well documented in ruthenium(II) chemistry [10,17,18].

Compound **1** rapidly decomposes in solution, including in benzene and toluene, and this precluded acquisition of NMR data, and thus the assignment of structure and the postulation of an agostic H-atom [19,20] close to an unsaturated metal centre, and some metal π-hydrocarbyl interaction, are based on a single crystal structure determination (see below). Mass spectral data gave $M^+ - PPhMe_2$ and $M^+ - 2PPhMe_2$ as the highest peaks, which at least confirmed the presence of the hydrocarbyl group in the bulk sample. The instability of this compound may be due to facile *o*-metallation involving the agostic H-atom and an adjacent methylene group. Indeed, this complex can be regarded as a model intermediate for the *o*-metallation reaction [17].

Structural assignment for compound **2** was possible from NMR spectroscopic data and from the results of the diffraction study of the corresponding bromide. The ^1H NMR spectra are second order and for the mutually *trans*-phosphines, two 1:2:1 triplets were observed [21] for the methyl resonance owing to virtual coupling to both P-centres, and non-equivalence of methyl groups attached to the same phosphine. For *cis*-phosphines, a 1:1 doublet was observed in each case. Assignment of the ^1H NMR resonances were confirmed by selectively decoupling individual P-centres. Thus upon decoupling at −4960 Hz (relative to H_3PO_4), the apparent doublet at δ 0.26 collapsed to a singlet. Similarly decoupling at −242 Hz resulted in

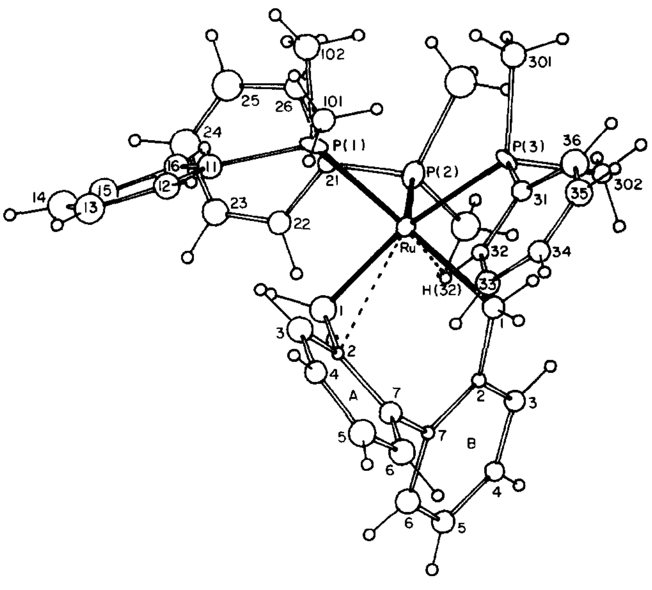


Fig. 1. Molecular projection of $[Ru\{(2\text{-}CH_2C_6H_4)_2\}(PPhMe_2)_3]$ (**1**) showing labelling scheme; thermal ellipsoids are drawn at the 20% probability level and hydrogens have arbitrary radii. Selected bond distances (Å) and angles (°) are as follows: Ru–P(1) 2.34(1); Ru–P(2) 2.21(1); Ru–P(3) 2.37(1); Ru–C(A1) 2.11(4); Ru–C(B1) 2.16(4); Ru ··· H(32) 2.8; P(1)–Ru–P(2) 97.9(4); P(1)–Ru–P(3) 92.3(4); P(1)–Ru–C(A1) 92.2(11); P(1)–Ru–C(B1) 169.7(9); P(2)–Ru–P(3) 98.4(4); P(2)–Ru–C(A1) 97.4(11); P(2)–Ru–C(B1) 92.1(10); P(3)–Ru–C(A1) 162.9(10); P(3)–Ru–C(B1) 83.5(9); C(A1)–Ru–C(B1) 89.1(14); Ru–P(1,2,3)–C(11,12,13) 121(1), 119(1), 111(1).

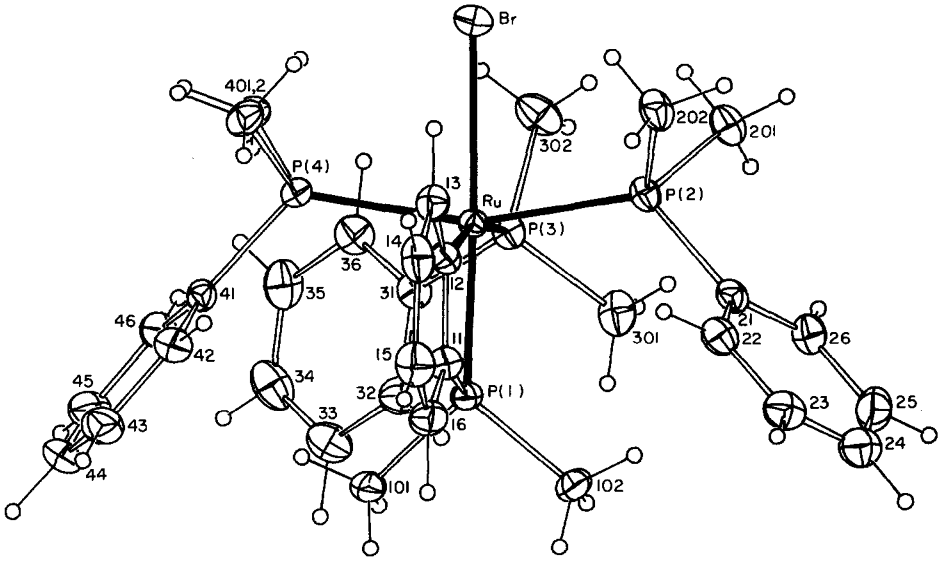
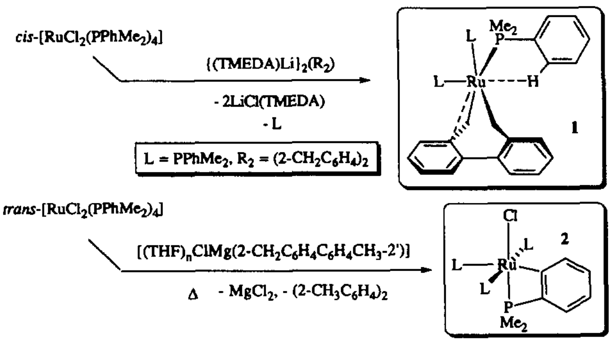


Fig. 2. Molecular projection of $[\overline{\mathrm{Ru\{PC_6}}\mathrm{H_4(Me)_2\}Br(PPhMe_2)_3}]$ (**2′**) showing labelling scheme; thermal ellipsoids are drawn at the 20% probability level and hydrogens have arbitrary radii. Selected bond distances (Å) and angles (°) are as follows: Ru–Br 2.648(1); Ru–P(1) 2.298(2); Ru–P(2) 2.381(2); Ru–P(3) 2.355(2); Ru–P(4) 2.359(2); Ru–C(12) 2.144(7); Br–Ru–P(1) 168.98(6); Br–Ru–P(2) 80.86(6); Br–Ru–P(3) 92.85(6); Br–Ru–P(4) 80.36(6); Br–Ru–C(12) 102.2(2); P(1)–Ru–P(2) 97.97(8); P(1)–Ru–P(3) 98.17(8); P(1)–Ru–P(4) 98.01(7); P(1)–Ru–C(12) 66.8(2); P(2)–Ru–P(3) 95.40(8); P(2)–Ru–P(4) 157.30(7); P(2)–Ru–C(12) 85.8(2); P(3)–Ru–P(4) 98.16(8); P(3)–Ru–C(12) 164.9(2); P(4)–Ru–C(12) 85.8(2); Ru–P(1,2,3,4)–C(11,21,31,41) 87.4(3), 124.1(3), 119.1(3), 123.3(2); P(1,2,3,4)–C(11,21,31,41)–C(12,22,32,42) 99.7(5), 119.5(6), 119.9(6), 119.7(6).

collapse of the two apparent triplets at δ 1.78 and 1.98 to singlets, and decoupling at −103 Hz resulted in a singlet at δ 1.60.

3.2. *Solid state structures*

Compounds **1** and **2′** consist of discrete molecules with the asymmetric unit in space group $P2_1/c$ or a variant of it, and thus in **1**, the crystals are a racemic mixture of the axially asymmetric metallacycle. Molecules of both **1** and **2′** are devoid of symmetry, with the potential *m*-symmetry in the latter lost in the solid by a torsion along the Ru–P(3) linkage (Fig. 2). In **1** the metal centres are five coordinate square pyramidal, with the ligating C-centres in the basal plane, but there is an agostic H-atom interaction in a position almost *trans* to the apical-P centre, and a close β-C–Ru contact (see below). Molecules of **2′** have distorted octahedral geometry, with the halogen *trans* to the P-atom associated with the *o*-metalled ligand. Key bond distances and angles defining the metal coordination spheres in each case are given in Figs. 1 and 2.



Scheme 1.

While the precision of the structure determination of **1** is low, there are some geometrical features worthy of comment. The hydrocarbyl group has a relatively large torsion along the biphenyl axis, 67(2)°, beyond that expected from geometrical considerations for a large heteroatom in the metallacycle ring [1–5]. This almost certainly arises from a secondary Ru–π interaction to one of the β-C atoms which causes a departure from the usual 2 symmetry found in other metal centres attached to R_2^{2-} [2–5]; the Ru ··· β-C(A2) contact is at 2.63(4) Å whereas for C(2B) the corresponding distance is 3.23(4) Å. The tungsten metallacycle $W(R_2)_2O^-$ [4] has only marginally longer metal–C distances than in the present case, 2.162(5)–2.191(4) Å (*cf.* 2.11(4) and 2.16(4) in **1**), yet the torsion is considerably less, 52.9 and 63.1°. This is the opposite trend to that expected in the absence of electronic effects.

The Ru-*ipso*-C-β-C angles are also diagnostic for the presence of a π-interaction; in the tungsten species, they are opened to 117.0 and 121.2°, whereas the corresponding values for **1** are 94(2) and 123.(2)°, respectively, for Ru-C(A, B1)-β-C(A, B2), with the low value indicative of the π-interaction. This type of interaction is common for benzylic type ligands attached to low valent transition metal species [11] since **1** is a 16 electron species (ignoring the π-interaction and the presence of an agostic H-atom involving H(32)). The estimated Ru-H(32) distance is 2.80 Å (Ru-C(32) 3.47(4) Å), similar to that found in $[RuHCl(PPh_3)_3]$, 2.85 Å [22], and $[Ru(SC_6F_5)_2\{PPh_3)_2]$, 2.80 and 2.86 Å [19], but significantly longer than in $[RuCl_2(PPh_3)_3]$, 5.29 Å [23]. An agostic interaction is also reflected in the Ru-P(3)-C(31) angle, 111(1)°, *ca.* 10° less than the corresponding angle for P(1) and P(2). This weak interaction, along with the π-interaction, effectively brings about coordination saturation at the formally Ru^{II} centre.

Distortion from an octahedral coordination environment about the metal centre in **2′** arises from the strained five membered chelate ring for the *o*-metallated phosphine; the C(12)-Ru-P(1) angle is 66.8(2)°, with Ru-P(1)-C(11) at 87.4(3)° and P(1)-C(11)-C(12) at 96.3(4)°, respectively, *ca.* 35° and 20° less than corresponding values for the other phosphines in the same molecule. Overall the ring strain is similar to that for related Ru^{II} species [12,17,24], and for the metal centre the *trans*-phosphines are pushed towards the bromine, whereas the coordinated carbon and P(3) are directed away (Fig. 2). The Ru-P distances for both the *o*-metallated phosphine, and the neutral phosphines are within the limits established for related Ru^{II} species [17,24], and the Ru-C distance, 2.144(7) Å, agrees well with that in **1** (mean 2.14 Å), and in $[Ru(\eta\text{-}C_5H_5)(C_6H_4PPh_2)(PPh_3)]$ (2.149(5) Å) [17], although for related complexes of the type $[Ru(C_6H_4PRR')X(\eta\text{-}C_6Me_6)]$, R and R′ = alkyl or aryl, X = halide or alkyl, there is a scatter of Ru-C(*o*-metallated) internuclear separations, 2.039(9)-2.224(5) Å [12,17]. Earlier work on $[Ru(\eta\text{-}C_5H_5)(C_6H_4PPh_2)(PPh_3)]$ revealed that the ring strain in *o*-metallated Ru^{II} species is usually accommodated by angular distortions with little effect on internuclear separations [17].

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