

Cyclopentadienyl-ruthenium and -osmium chemistry

XXIX *. The effect of chelation on Ru–C(*sp*²) bond lengths: X-ray structures of $\text{Ru}(\overline{\text{C}_6\text{H}_4\text{PPh}_2})(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)\cdot 0.5\text{CH}_2\text{Cl}_2$ and $\text{Ru}\{\overline{\text{C}(\text{=CMePh})\text{CH}(\text{PPh}_2)\text{CH}_2\text{PPh}_2}\}(\eta\text{-C}_5\text{H}_5)$

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Abstract

The molecular structures $\text{Ru}(\overline{\text{C}_6\text{H}_4\text{PPh}_2})(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)$ (**1**) and $\text{Ru}\{\overline{\text{C}(\text{=CMePh})\text{CH}(\text{PPh}_2)\text{CH}_2\text{PPh}_2}\}(\eta\text{-C}_5\text{H}_5)$ (**2**) have been determined. In **1**, strain about the RuPCC chelate ring is accommodated largely by contraction of the intra-ring angles about the relevant atoms. In **2** there are similar contractions, together with marked lengthening of the Ru–C(*sp*²) bond (to 2.149(5) Å) and of the C–C bond (1.534(7) Å) from the vinyl α -carbon to the CHPPH₂ group of the chelating tertiary phosphine; the latter bond is 0.11 Å shorter than that in the iron analogue. Crystal data: **1** (as 0.5CH₂Cl₂ solvate): triclinic, space group $P\bar{1}$, *a* 8.409(2), *b* 19.055(5), *c* 21.921(9) Å, α 94.10(3), β 97.02(2), γ 99.92(2)°, *U* 3418.6 Å³, *Z* = 4; 2007 data (*I* ≥ 2.5σ(*I*)) were refined to *R* = 0.047, *R*_w = 0.051; **2**: triclinic, space group $P\bar{1}$, *a* 12.141(1), *b* 14.004(1), *c* 11.333(1) Å, α 112.19(1), β 101.15(1), γ 69.01(1)°, *U* 1662.0 Å³, *Z* = 2, 3788 data (*I* ≥ 2.5σ(*I*)) were refined to *R* = 0.047, *R*_w = 0.050.

Introduction

The chemistry of complexes containing Ru–C bonds is currently attracting some attention, and systems containing $\eta\text{-C}_5\text{H}_5$ and tertiary phosphine ligands have provided much new chemistry of interest [1]. In the course of recent studies, we have

* For Part XXVIII see ref. 6.

determined the X-ray structures of two complexes containing chelate C-bonded ligands, namely $\text{Ru}(\text{C}_6\text{H}_4\text{PPh}_2)(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)$ (**1**) and $\text{Ru}\{\text{C}(\text{=CMePh})\text{-CH}(\text{PPh}_2)\text{CH}_2(\text{PPh}_2)\}(\eta\text{-C}_5\text{H}_5)$ (**2**), and report below on the unusual lengthening of the Ru–C(*sp*²) bonds in these complexes.

Results

Molecular structure of $\text{Ru}(\text{C}_6\text{H}_4\text{PPh}_2)(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)$ (**1**)

Cyclometallation of the PPh₃ ligand in RuX(PPh₃)₂(η-C₅H₅) complexes is readily achieved by heating the methyl derivative (X = Me) [2]; an improved synthesis is described in the Experimental section. The crystal structure of $\text{Ru}(\text{C}_6\text{H}_4\text{PPh}_2)(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)$ (**1**) has been determined and shows that the asymmetric unit comprises two molecules of **1** together with one molecule of occluded CH₂Cl₂. However there are no significant differences between the two molecules of **1** and the following discussion is confined to the parameters determined for molecule A. A plot of molecule A is shown in Fig. 1, together with the atom numbering scheme which is common to both molecules.

As found for other RuXL₂(η-C₅H₅) complexes, the coordination about the ruthenium is distorted octahedral, comprising the η-C₅H₅ ligand (Ru–C(cp) 2.203(19)–2.294(18), av. 2.244 Å), two phosphorus atoms and the aromatic carbon. The two Ru–P distances (Ru–P(1) 2.277(5), Ru–P(2) 2.295(5) Å) are not significantly different, although geometries about the P atoms are (see below). The Ru–P distances compare with the separations found in Ru(C₂Ph)(dppe)(η-C₅H₅) (2.245 (av.) Å) [3], but are shorter than those found in Ru{C[=C(CN)₂]CPh=CXY}(dppe)-

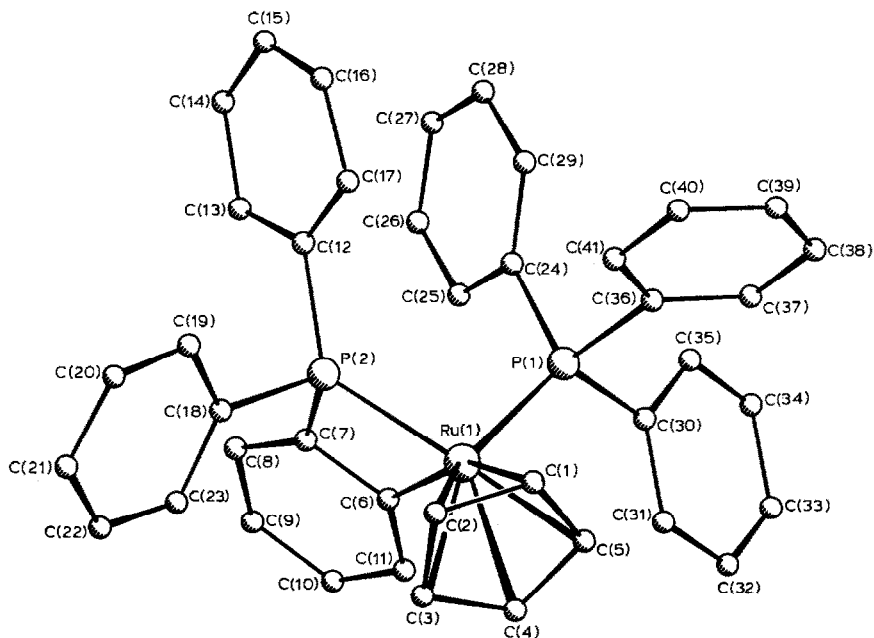
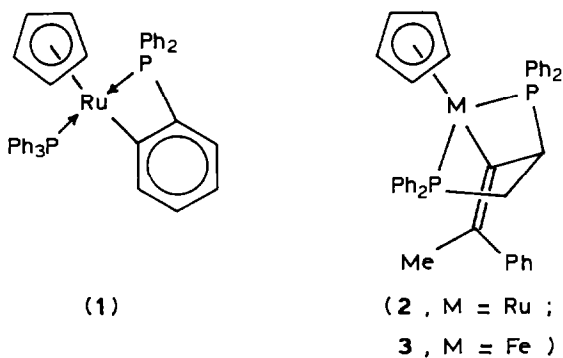


Fig. 1. A plot of a molecule of $\text{Ru}(\text{C}_6\text{H}_4\text{PPh}_2)(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)$ (**1**), showing atom-numbering scheme.



($\eta\text{-C}_5\text{H}_5$) (X = H, Y = $\text{C}_6\text{H}_4\text{NO}_2\text{-4}$, 2.283(3), 2.319(3) [4]; X = Y = CN, 2.280(1), 2.340(1) Å [5]). The Ru–C(6) distance (2.07(2) Å) is ca. 0.04 Å shorter than calculated for the sum of covalent radii; it can be compared with the value of 2.07(1) Å found for the Ru–C(sp^2) bond in Ru{*trans*-C(CO₂Me)=CH(CO₂Me)}-(dppe)($\eta\text{-C}_5\text{H}_5$) [6].

It is not surprising to find that the formation of the four-membered RuPCC ring considerably distorts the geometry at ruthenium; the intraring angle ($67.2(5)^\circ$) is much less than the normal octahedral angle, but somewhat surprisingly, the C(6)–Ru–P(1) ($90.2(5)^\circ$) and P(1)–Ru–P(2) angles ($97.8(2)^\circ$) are not significantly enlarged as a result, see Fig. 2. The P–C(ring) distances in the PPh_3 ligand range from 1.86(2) Å, but in the metallated tertiary phosphine ligand range from 1.80(2) to 1.87(1) Å. Similarly, while Ru–P(1)–C(ring) ($111.9(4)$ – $119.7(4)^\circ$) and C(ring)–P–C(ring) angles ($99.6(5)$ – $103.3(5)^\circ$) are fairly constant, those involving the metallated phosphine (Ru–P(2)–C(7) $87.0(6)$, Ru–P(2)–C(12) $131.7(5)$, Ru–P(2)–C(18) $116.1(4)^\circ$) vary much more, with the anticipated contraction found for the intraring angle. This is reflected in the C(7)–P(2)–C(12) angle of $113.5(7)^\circ$, but not in the other C–P–C angles. Angles about C(7) are C(6)–C(7)–C(8) $123(2)$,

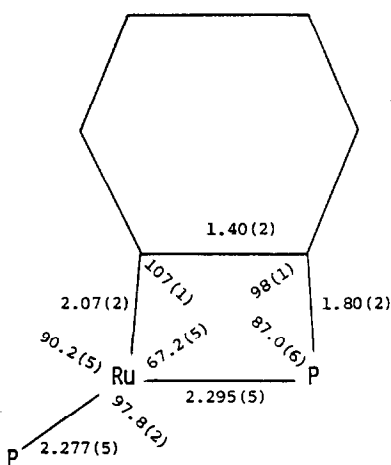


Fig. 2. Diagram of the chelate ring in 1, showing bond distances and intra-ring angles.

C(6)–C(7)–P(2) 98(1) and C(8)–C(7)–P(2) 139(1)°. The RuPCC ring is essentially planar (dihedral Ru–P(2)–C(7)/Ru–C(6)–C(7) 0.2° (molecule A), 4.1° (molecule B)).

In summary, therefore, the presence of the four-membered chelate ring formed by intramolecular metallation of one of the PPh₃ ligands results in only a small shortening of the atom separations compared with comparable non-cyclic complexes, but with considerable distortion of the geometry about Ru, C(6), C(7) and P(2), with no angle within the four-membered ring exceeding 108° (Fig. 2). Angles about C(6) are also strained, with C(7)–C(6)–Ru 107(1) and C(11)–C(6)–Ru 133(1)°, although C(7)–C(6)–C(11) is normal (120(2)°).

Molecular structure of $\overline{\text{Ru}\{\text{C}(\text{=CMePh})\text{CH}(\text{PPh}_2)\text{CH}_2\text{PPh}_2\}}(\eta\text{-C}_5\text{H}_5)$ (2)

Attempts to add nucleophiles (H⁻, OR⁻, Me⁻) to the α-carbon of the vinylidene ligand in [Ru(C=CMePh)(L₂)(η-C₅H₅)]⁺ (L₂ = (PPh₃)₂, dpmm or dppe) have proved unsuccessful. Only in the case of LiMe was a neutral product obtained with the dpmm or dppe complexes. As found previously with the analogous iron complex [7], however, deprotonation of the coordinated bis-tertiary phosphine and subsequent

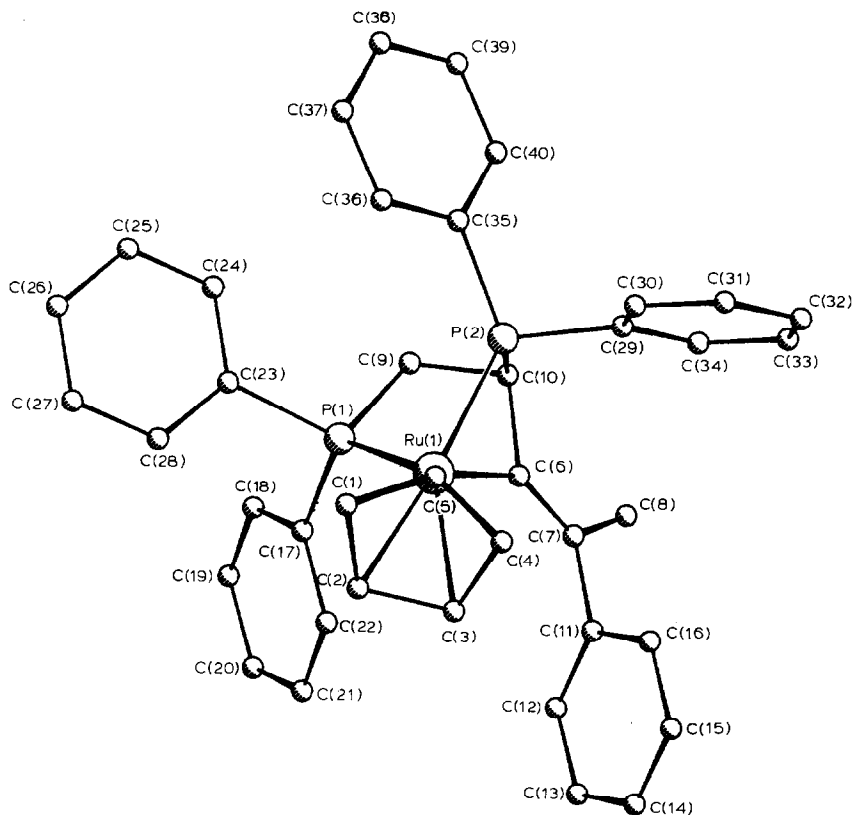


Fig. 3. A plot of a molecule of $\overline{\text{Ru}\{\text{C}(\text{=CMePh})\text{CH}(\text{PPh}_2)\text{CH}_2\text{PPh}_2\}}(\eta\text{-C}_5\text{H}_5)$ (2), showing atom-numbering scheme.

intramolecular attack had occurred, to give the chelate complexes **2** and **3**. The molecular structure of **2** is shown in Fig. 3.

The bicyclic ligand occupies three coordination positions, with the $\eta\text{-C}_5\text{H}_5$ ligand completing the distorted octahedral environment of the metal. The Ru–C(cp) distances (range 2.204(6)–2.235(6), av. 2.222 Å) are within the overall range of similar distances reported on many other occasions. The two Ru–P distances (2.239(1), 2.241(2) Å) are somewhat shorter than those in **1**, and ca. 0.06 Å shorter than in several dppe complexes (see above). The Ru–C(6) separation (2.149(5) Å) is the longest Ru–C(sp^2) bond reported in this series, exceeding those in Ru{C(OPrⁱ)=CHPh}(CO)(PPh₃)($\eta\text{-C}_5\text{H}_5$) [8] and Ru{C(CO₂Me)=CH(CO₂Me)}-(dppe)($\eta\text{-C}_5\text{H}_5$) [6] by ca. 0.05 and 0.08 Å, respectively. In {Ru(CO)₂($\eta\text{-C}_5\text{H}_5$)₂($\mu\text{-CH}_2$)}, the Ru–C(sp^3) bond length is 2.18 Å [9]. Within the vinyl ligand, the C(6)–C(10) single bond is 1.534(7) Å, while the C(6)=C(7) double bond is 1.329(8) Å.

Angles subtended at the metal atom by the three ligand atoms are all < 90° (P(1)–Ru–P(2) 85.1(1), P(1)–Ru–C(6) 74.3(2), P(2)–Ru–C(6) 64.8(1)°), while those about C(6) show the influence of the small ring size: the intraring angle Ru–C(6)–C(10) is 100.6(3)°, while Ru–C(6)–C(7) has opened to 136.9(4), and C(10)–C(6)–C(7) is nearly normal at 122.5(5)°. The four-membered ring is folded

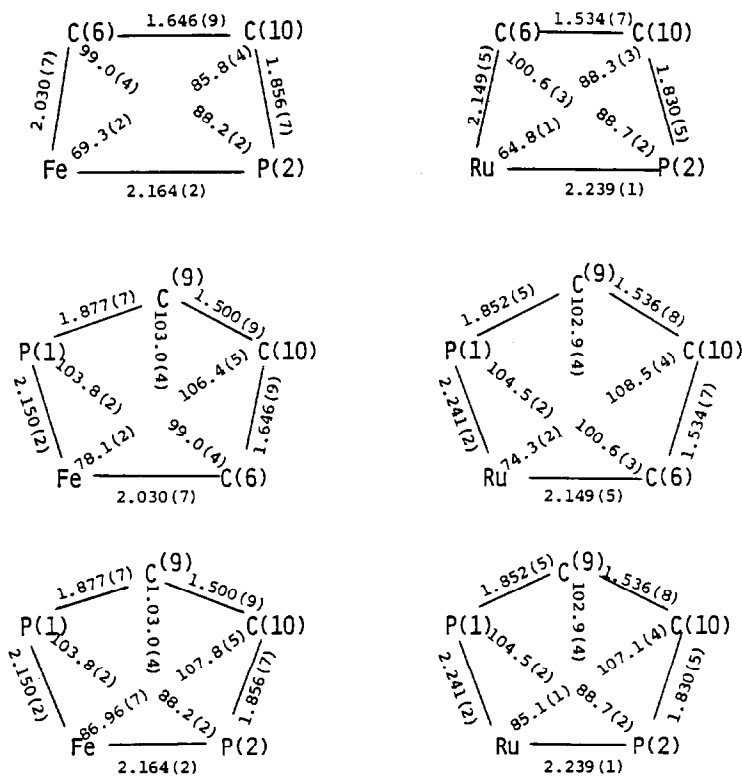
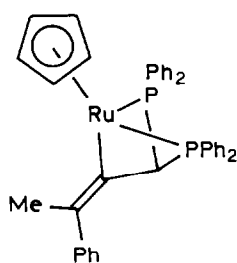


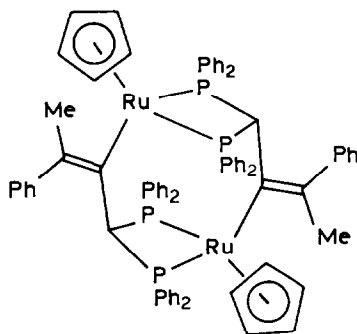
Fig. 4. Diagrams of the chelate rings in **2** and the iron analogue **3** [7]. Atoms in the latter have been renumbered to correspond with those of **2**.

about the Ru–C(10) vector (dihedral Ru–C(6)–C(10)/Ru–P(2)–C(10) 47.5°; cf. 47.4° in **3**).

The above data confirm the strained nature of the bicyclic chelate system (Fig. 4), which appears to be relieved by unusual lengthening of the Ru–C σ -bond, and by unusually large deformations about C(6). Comparison with the iron analogue **3**, which is not isomorphous with **2** (data are also included in Fig. 4), shows that the Fe–C(cp) (2.108 Å, av.) and Fe–C(6) (2.030(7) Å) distances are about 0.12 Å shorter, and the Fe–P (2.150(2), 2.164(2) Å) are about 0.08 Å shorter, than those found in **2**. The angles within the four- and five-membered rings are generally similar, except for those about the metal atoms, which contract (by ca. 2° for P–M–P or ca. 4° for P–M–C angles) or about C(10), which increase by 0.7–2.5°, in the ruthenium complex. The most significant difference between the two complexes is found in the C(6)–C(10) separation, which is 0.11 Å longer in the iron derivative. It is evident that the presence of the larger ruthenium atom allows ring strain to be reduced as a result of increased atom separations; nevertheless, the unusual lengthening of the C(6)–C(10) single bond presages enhanced reactivity at C(6).



(4a)



(4b)

We have not yet been able to obtain X-ray quality crystals of the dppm-derived chelate complex **4**, which contains a smaller 4/4/4 cyclic system; mass spectrometric evidence shows that this complex is mononuclear, so that the alternative ligand-bridged structure (**4b**) is unlikely. The unusual reactivity of these strained systems is shown in their reactions with HCl, CO, olefins and alkynes, and will be reported elsewhere.

Conclusions

These structural studies have confirmed the usual tendency for strain in small chelate rings to be relieved by angular distortions rather than by increasing atomic separations. However, in the case of **2**, both mechanisms operate, the Ru–C(6) and C(6)–C(10) bonds being unusually long, and hence would be expected to display increased reactivity.

Experimental

General conditions. All reactions were carried out under nitrogen; no special precautions were taken to exclude air during work-up, since these complexes proved to be stable in air as solids, and for short times in solution.

Instruments. Perkin–Elmer 683 double-beam spectrometer, NaCl optics (IR); Bruker WP80 spectrometer (^1H NMR at 80 MHz, ^{13}C NMR at 20.1 MHz); GEC-Kratos MS3074 mass spectrometer (mass spectra at 70 eV ionising energy, 4 kV accelerating potential).

FAB mass spectra were obtained on a VG ZAB 2HF instrument equipped with a FAB source. Argon was used as the exciting gas, with source pressures typically 10^{-6} mbar; the FAB gun voltage was 7.5 kV, current 1 mA. The ion accelerating potential was 8 kV. The matrix was 3-nitrobenzyl alcohol. The complexes were made up as ca. 0.5 M solutions in acetone or dichloromethane; a drop was added to drop of matrix and the mixture was applied to the FAB probe tip.

Starting materials. $\text{RuCl}(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)$ and $\text{Ru}(\text{C}_2\text{Ph})(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)$ were made by the literature methods [10].

Preparation of $\overline{\text{Ru}(\text{C}_6\text{H}_4\text{PPh}_2)(\eta\text{-C}_5\text{H}_5)}$ (1)

A mixture of $\text{RuCl}(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)$ (1.0 g, 1.35 mmol) and methyllithium (12 ml of a 1.4 M solution in ether) in benzene (60 ml) was stirred for 16 h then treated with water (3 ml). The organic layer was separated, dried over NaSO_4 , filtered, and evaporated to dryness. The yellow solid was heated in a Carius tube at 160–163°C under vacuum for 90 min and the residue then extracted with dichloromethane. The extract was chromatographed and elution with benzene afforded a yellow band, the material from which was crystallized from dichloromethane/light petroleum to give yellow crystals of $\overline{\text{Ru}(\text{C}_6\text{H}_4\text{PPh}_2)(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)}$ (1) (509 mg, 55%) m.p. 219°C (lit. [2] 223–225°C). ^1H NMR: δ (CDCl_3) 4.34 (s, 5H, C_5H_5), 6.76–7.41 (m 29H, $\text{C}_6\text{H}_4 + \text{Ph}$). ^{13}C NMR: δ (CDCl_3) 80.69 (s, C_5H_5), 120–140 (m, $\text{C}_6\text{H}_4 + \text{Ph}$).

Preparation of $\overline{\text{Ru}\{\text{C}(\text{=CMePh})\text{CH}(\text{PPh}_2)\text{CH}_2\text{PPh}_2\}(\eta\text{-C}_5\text{H}_5)}$ (2)

A suspension of $[\text{Ru}(\text{C}=\text{CMePh})(\text{dppe})(\eta\text{-C}_5\text{H}_5)][\text{PF}_6]$ [11] (65 mg, 0.079 mmol) in tetrahydrofuran (10 ml) was treated with LiMe (0.1 ml of a 1.4 M solution in ether, 0.14 mmol) at -63°C ; the pink suspension immediately dissolved to give a yellow solution. The mixture was allowed to warm to room temperature, solvent was then removed in vacuo, and a benzene extract of the residue was eluted through silica (60–120 mesh) with dichloromethane. Addition of methanol and concentration afforded yellow crystals of $\overline{\text{Ru}\{\text{C}(\text{=CMePh})\text{CH}(\text{PPh}_2)\text{CH}_2\text{PPh}_2\}(\eta\text{-C}_5\text{H}_5)}$ (2) (31 mg, 58%), m.p. 168–170°C (dec) (Found: C, 70.0; H, 5.5; M (mass spectrometry), 680. $\text{C}_{40}\text{H}_{36}\text{P}_2\text{Ru}$ calcd: C, 70.7; H, 6.3%; M , 680). IR (Nujol): 1598m, 1482m, 1438s, 1280m, 1120m, 1101s, 1080m, 1027m, 1000m, 845m, 840m, 790m, 744m, 695s cm^{-1} . ^1H NMR: δ (CDCl_3) 1.61 (s, 3H, CH_3); 1.93 (m, 1H, CH); 2.28 (m, 2H, CH_2); 4.26 (s, 5H, C_5H_5); 7.84 (m, 25H, Ph).

Preparation of $\overline{\text{Ru}\{\text{C}(\text{=CMePh})\text{CH}(\text{PPh}_2)_2\}(\eta\text{-C}_5\text{H}_5)}$ (4)

A pale orange suspension of $[\text{Ru}(\text{C}=\text{CMePh})(\text{dppm})(\eta\text{-C}_5\text{H}_5)]\text{I}$ [11] (102 mg, 0.13 mmol) in THF (10 ml) was treated with LiMe (0.85 ml of a 1.4 M solution in Et_2O , 1.19 mmol) to give a yellow solution. The solvent was removed in vacuo. The residue was dissolved in benzene and the solution washed through silica to remove any excess LiMe. Removal of solvent (rotary evaporation) and crystallisation ($\text{CH}_2\text{Cl}_2/\text{EtOH}$) afforded yellow $\overline{\text{Ru}\{\text{C}(\text{=CMePh})\text{CH}(\text{PPh}_2)_2\}(\eta\text{-C}_5\text{H}_5)}$ (4) (39 mg, 45%), m.p. 125–130°C. Found: C, 69.2; H, 5.2; M (mass spectrometry), 666; $\text{C}_{39}\text{H}_{34}\text{P}_2\text{Ru}$ calcd: C, 70.4; H, 5.2%; M , 666. IR (Nujol): 1595m(br), 1490m(sh),

1485m, 1470m(br), 1440s, 1380m, 1070m, 1030m, 1000m, 910m(br), 790m, 770m, 750m, 740m(sh), 725m, 705s, 695s cm^{-1} . ^1H NMR: δ (CDCl_3) 1.64 (s, 1H, CH), 1.73 (s, 3H, Me), 4.54 (s, 5H, C_5H_5), 7.42 (m, 25H, Ph).

Crystallography

Intensity data for 4173 (5933 for **2**) reflections were measured at room temperature on an Enraf–Nonius CAD4F diffractometer fitted and Mo-K_α (graphite monochromatized) radiation, λ 0.71073 Å, with the use of the $\omega : 2\theta$ scan technique. No significant decomposition of either crystal occurred during the data collections. Routine corrections were made for Lorentz and polarization effects [12] and for absorption employing an analytical procedure [12]. Relevant crystal data are summarized in Table 1.

For **1**, the structure was solved by direct methods, while for **2**, normal heavy-atom methods were used; both structures were refined by a full-matrix least-squares procedure based on F [12]. Owing to the weakly diffracting nature of the crystal of **1**, only data up to a maximum Bragg angle of 17° were included, so that the limited data precluded the inclusion of hydrogen atoms in the model. For **2**, hydrogen atoms were included at calculated positions (C–H 0.97 Å). For both models, phenyl carbons were refined as hexagonal rigid groups with individual isotropic thermal

Table 1

Crystal data and refinement details for complexes **1** and **2**

	1	2
Formula	$\text{C}_{41}\text{H}_{34}\text{P}_2\text{Ru} \cdot 0.5\text{CH}_2\text{Cl}_2$	$\text{C}_{40}\text{H}_{36}\text{P}_2\text{Ru}$
<i>MW</i>	732.2	679.8
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$ (C_i^1 , No. 2)	$P\bar{1}$ (C_i^1 , No. 2)
<i>a</i> (Å)	8.409(2)	12.141(1)
<i>b</i> (Å)	19.055(5)	14.004(1)
<i>c</i> (Å)	21.921(9)	11.333(1)
α ($^\circ$)	94.10(3)	112.19(1)
β ($^\circ$)	97.02(2)	101.15(1)
γ ($^\circ$)	99.92(2)	69.01(1)
Vol. (Å ³)	3418.6	1662.0
<i>Z</i>	4	2
<i>D</i> _c (g cm ⁻³)	1.423	1.358
<i>F</i> (000)	1500	700
μ (cm ⁻¹)	6.10	5.50
Transmission factors	0.9363; 0.8761	0.9500; 0.9246
θ limits ($^\circ$)	1–17	1–25
No. of data collected	4173	5933
No. of unique data	3968	4961
No. of unique data used with $I \geq 2.5\sigma(I)$	2007	3788
<i>R</i>	0.047	0.047
<i>k</i>	0.87	3.48
<i>g</i>	0.0026	0.0001
<i>R</i> _w	0.051	0.050
ρ_{max} (e Å ⁻³)	0.39	0.96

Table 2

Fractional atomic coordinates ($\times 10^5$ for Ru, $\times 10^4$ for remaining atoms) for $\overline{\text{Ru}(\text{C}_6\text{H}_4\text{PPh}_2)(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)\cdot 0.5\text{CH}_2\text{Cl}_2}$; note that primed atoms refer to the second molecule comprising the asymmetric unit

Atom	x	y	z
Ru(1)	2685(19)	37941(8)	23365(7)
Ru(1')	-30842(18)	14390(8)	-22364(7)
P(1)	-1080(6)	4607(3)	1892(2)
P(2)	311(6)	4211(3)	3348(2)
P(1')	-5061(6)	673(3)	-2861(2)
P(2')	-3490(6)	954(3)	-1333(2)
C(1)	2639(22)	3855(10)	1908(9)
C(2)	2676(24)	3475(10)	2436(9)
C(3)	1443(22)	2827(10)	2345(9)
C(4)	560(22)	2832(10)	1751(9)
C(5)	1217(23)	3451(10)	1463(9)
C(6)	-1824(21)	3356(9)	2703(8)
C(7)	-1653(20)	3647(9)	3316(8)
C(8)	-2816(23)	3442(10)	3715(9)
C(9)	-4125(24)	2914(10)	3470(10)
C(10)	-4341(24)	2595(10)	2857(10)
C(11)	-3214(23)	2828(10)	2456(8)
C(12)	419(14)	5117(7)	3718(6)
C(13)	-604(14)	5252(7)	4151(6)
C(14)	-416(14)	5935(7)	4457(6)
C(15)	794(14)	6483(7)	4330(6)
C(16)	1817(14)	6348(7)	3897(6)
C(17)	1630(14)	5665(7)	3591(6)
C(18)	1694(16)	3848(5)	3931(6)
C(19)	3099(16)	4286(5)	4245(6)
C(20)	4149(16)	4004(5)	4664(6)
C(21)	3793(16)	3283(5)	4768(6)
C(22)	2389(16)	2845(5)	4453(6)
C(23)	1339(16)	3128(5)	4035(6)
C(24)	-2046(15)	5211(5)	2383(6)
C(25)	-3395(15)	4882(5)	2636(6)
C(26)	-4208(15)	5292(5)	3001(6)
C(27)	-3672(15)	6030(5)	3113(6)
C(28)	-2323(15)	6358(5)	2859(6)
C(29)	-1510(15)	5949(5)	2494(6)
C(30)	-2823(14)	4272(6)	1273(6)
C(31)	-2995(14)	3586(6)	975(6)
C(32)	-4284(14)	3337(6)	503(6)
C(33)	-5400(14)	3774(6)	330(6)
C(34)	-5228(14)	4460(6)	628(6)
C(35)	-3939(14)	4709(6)	1100(6)
C(36)	273(13)	5242(7)	1484(6)
C(37)	-144(13)	5407(7)	882(6)
C(38)	974(13)	5862(7)	603(6)
C(39)	2508(13)	6153(7)	926(6)
C(40)	2925(13)	5988(7)	1528(6)
C(41)	1808(13)	5533(7)	1807(6)
C(1')	-1825(24)	1889(10)	-3009(9)
C(2')	-847(22)	1405(10)	-2723(9)
C(3')	-351(22)	1718(10)	-2103(9)
C(4')	-1021(22)	2349(10)	-1988(9)
C(5')	-1914(21)	2455(9)	-2570(8)
C(6')	-4818(20)	1847(9)	-1797(8)

continued

Table 2 (continued)

Atom	x	y	z
C(7')	-5055(21)	1497(9)	-1261(8)
C(8')	-6025(23)	1663(10)	-814(9)
C(9')	-6854(22)	2235(10)	-940(9)
C(10')	-6695(22)	2579(9)	-1455(9)
C(11')	-5694(21)	2400(9)	-1874(8)
C(12')	-1879(15)	1277(7)	-685(6)
C(13')	-1667(15)	1988(7)	-439(6)
C(14')	-431(15)	2253(7)	48(6)
C(15')	594(15)	1808(7)	289(6)
C(16')	382(15)	1097(7)	43(6)
C(17')	-855(15)	832(7)	-445(6)
C(18')	-4108(16)	24(7)	-1203(6)
C(19')	-5391(16)	-180(7)	-867(6)
C(20')	-5880(16)	-899(7)	-780(6)
C(21')	-5086(16)	-1415(7)	-1029(6)
C(22')	-3804(16)	-1211(7)	-1364(6)
C(23')	-3314(16)	-492(7)	-1452(6)
C(24')	-4126(16)	109(7)	-3389(4)
C(25')	-3231(16)	-383(7)	-3145(4)
C(26')	-2402(16)	-765(7)	-3526(4)
C(27')	-2468(16)	-656(7)	-4151(4)
C(28')	-3364(16)	-164(7)	-4394(4)
C(29')	-4193(16)	218(7)	-4013(4)
C(30')	-6430(16)	1060(5)	-3408(6)
C(31')	-7828(16)	633(5)	-3739(6)
C(32')	-8867(16)	934(5)	-4146(6)
C(33')	-8508(16)	1662(5)	-4223(6)
C(34')	-7110(16)	2089(5)	-3893(6)
C(35')	-6071(16)	1788(5)	-3485(6)
C(36')	-6645(15)	57(5)	-2553(6)
C(37')	-7700(15)	374(5)	-2225(6)
C(38')	-8944(15)	-53(5)	-1982(6)
C(39')	-9132(15)	-797(5)	-2066(6)
C(40')	-8077(15)	-1114(5)	-2394(6)
C(41')	-6833(15)	-686(5)	-2638(6)
C(42)	6733(33)	1559(16)	4356(13)
Cl(1)	6351(11)	1801(4)	5084(4)
Cl(2)	8588(10)	1346(5)	4333(5)

parameters and the Ru and P atoms in **1** were refined anisotropically as were the non-phenyl atoms in **2**. A weighting scheme, $w = k/[\sigma^2(F) + gF^2]$, was included in each model and the refinements continued until convergence. No special features were noted from the analysis of variance, which indicated that an appropriate weighting scheme had been applied in both cases. Refinement details are listed in Table 1.

Scattering factors for neutral Ru (corrected for f' and f'') were from ref. 13 and values for the remaining atoms were those incorporated in SHELX [12]. Data solution and refinement were performed with the SHELX program system on the University of Adelaide's VAX11/780 computer system.

Table 3

Fractional atomic coordinates ($\times 10^5$ for Ru, $\times 10^4$ for remaining atoms for $\text{Ru}\{\text{C}[\text{C}=\text{CMePh}]\text{CH}(\text{PPh}_2)\text{-CH}_2\text{PPh}_2\}(\eta\text{-C}_5\text{H}_5)$)

Atom	x	y	z
Ru	21278(4)	16164(3)	19943(5)
P(1)	1257(1)	2231(1)	3827(2)
P(2)	2981(1)	2919(1)	2974(2)
C(1)	2984(7)	-176(5)	1491(7)
C(2)	1794(6)	21(4)	994(7)
C(3)	1639(3)	549(5)	91(7)
C(4)	2716(9)	680(6)	46(8)
C(5)	3551(7)	226(5)	900(9)
C(6)	993(5)	3239(4)	2177(6)
C(7)	100(5)	3714(4)	1493(6)
C(8)	-553(6)	4931(5)	1899(7)
C(9)	1201(5)	3674(4)	4536(6)
C(10)	1523(4)	3887(4)	3433(6)
C(12)	-1454(3)	2959(3)	50(4)
C(13)	-1891(3)	2433(3)	-1163(4)
C(14)	-1228(3)	2059(3)	-2216(4)
C(15)	-127(3)	2211(3)	-2058(4)
C(16)	311(3)	2737(3)	-845(4)
C(11)	-353(3)	3111(3)	208(4)
C(18)	-882(3)	2837(3)	4914(3)
C(19)	-2080(3)	2966(3)	4883(3)
C(20)	-2696(3)	2589(3)	3723(3)
C(21)	-2114(3)	2081(3)	2593(3)
C(22)	-915(3)	1951(3)	2625(3)
C(17)	-300(3)	2329(3)	3785(3)
C(24)	2580(4)	1971(3)	6129(5)
C(25)	3084(4)	1379(3)	6957(5)
C(26)	2883(4)	398(3)	6707(5)
C(27)	2179(4)	10(3)	5629(5)
C(28)	1675(4)	602(3)	4802(5)
C(23)	1876(4)	1583(3)	5051(5)
C(30)	4594(3)	2682(3)	1396(4)
C(31)	5016(3)	2927(3)	519(4)
C(32)	4371(3)	3848(3)	189(4)
C(33)	3304(3)	4524(3)	734(4)
C(34)	2882(3)	4280(3)	1611(4)
C(29)	3527(3)	3359(3)	1942(4)
C(36)	4673(3)	2186(2)	4771(4)
C(37)	5383(3)	2334(2)	5909(4)
C(38)	5441(3)	3370(2)	6656(4)
C(39)	4788(3)	4257(2)	6264(4)
C(40)	4078(3)	4110(2)	5126(4)
C(35)	4020(3)	3074(2)	4380(4)

Fractional atomic coordinates are listed in Tables 2 and 3 and the numbering schemes used are shown in Figs. 1 and 3, while selected interatomic bond distances and angles are given in Figs. 2 and 4, respectively. Listings of thermal parameters, hydrogen atom parameters, interatomic bond distances and angles, and of the observed and calculated structure factors are available from the authors.

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