Substituted Cyclopentadienyl Complexes. Part 4.† The Catalysed Synthesis and Proton Nuclear Magnetic Resonance Spectra of [Ru(η^5-C_5H_4Me)(CO)(L)I] and [Ru(η^5-C_9H_7)(CO)(L)I] (L = phosphine or isocyanide) and the Crystal Structure Determination of [Ru(η^5-C_9H_7)(CO){P($CH_2Ph)_3$}I]‡

Mohamed S. Loonat, Laurence Carlton, Jan C. A. Boeyens, and Neil J. Coville*
Department of Chemistry, University of the Witwatersrand, PO Wits 2050, Johannesburg, Republic of South Africa

---

The reaction between [Ru(η^5-C_5H_4Me)$(CO)_2$I] and L [L = $P(OMe)_3$, $P(OEt)_3$, $P(OPr^i)_3$, PPh_3, PMe_2Ph, Bu^tNC, or 2,6-$Me_2C_6H_3NC$] or [Ru(η^5-C_9H_7)$(CO)_2$I] and L [L = $P(OMe)_3$, $P(OEt)_3$, $P(OPr^i)_3$, $P(OC_6H_4Me$-*o*$)_3$, PPh_3, or $P(CH_2Ph)_3$] in the presence of [{Fe(η^5-C_5H_5)$(CO)_2$}$_2$] as catalyst yields the new substituted products [Ru(η^5-C_5H_4Me)(CO)(L)I], (**1**) and [Ru(η^5-C_9H_7)-(CO)(L)I], (**2**). The new products have been characterized by a combination of i.r. and n.m.r. spectroscopy and mass spectrometry. Ring proton resonances of complexes (**1**) have been assigned by nuclear Overhauser enhancement (n.O.e.) spectra [L = $P(OMe)_3$, PMe_2Ph, $PMePh_2$, or 2,6-$Me_2C_6H_3NC$]. The n.O.e. spectra also reveal preferential conformations of the cyclopentadienyl ring when L is large. Such spectra were also recorded for complexes (**2**) [L = $P(OC_6H_4Me$-*o*$)_3$ or $P(CH_2Ph)_3$] and together with coupling constant data are consistent with a ligand orientation in which L = $P(CH_2Ph)_3$ is found preferentially under the central carbon atom of the cyclopentadienyl indenyl ring. This was further confirmed by a crystal structure determination of [Ru(η^5-C_9H_7)(CO)-{$P(CH_2Ph)_3$}I]·0.5C_6H_6: space group $P\bar{1}$, $Z = 2$, $a = 9.923(2)$, $b = 11.055(4)$, $c = 14.543(3)$ Å, $\alpha = 84.52(2)$, $\beta = 77.72(2)$, $\gamma = 82.74(2)^\circ$, and $R = 0.0560$.

In recent publications we reported the synthesis as well as an n.m.r. study of the complexes [Fe(η^5-C_5H_4Me)(CO)(L)I] and [Fe(η^5-C_9H_7)(CO)(L)I] (L = phosphine, phosphite, or isocyanide).[1,2] In the n.m.r. study we established that the size of the ligand, L, influenced the chemical shifts of the ring proton[1] and carbon atoms[2] and that conformational aspects of the ring with respect to the ligand set (CO, L, I) could be determined. There are other factors that could influence the chemical shifts of the ring proton (or carbon) atoms and these include the ring substituents, the metal atom, the number of ligands in the ligand set, *etc*. In this publication we report on the syntheses and a proton n.m.r. study of the complexes [Ru(η^5-C_5H_4Me)-(CO)(L)I], (1), and [Ru(η^5-C_9H_7)(CO)(L)I], (2) (L = Group 15 donor ligand or RNC) which allows an assessment of the effect of varying the central metal atom (Ru for Fe) on the ring proton chemical shifts. The crystal structure of [Ru(η^5-C_9H_7)(CO){$P(CH_2Ph)_3$}I] was determined to assist with the n.m.r. characterization.

Very few complexes of the type [Ru(ring)A(B)X] (ring = monosubstituted cyclopentadienyl) have been synthesized.[3] The two general approaches used to obtain these complexes, which contain a chiral Ru atom, start from [Ru(ring)-$(PPh_3)_2$X][4—7] or [Ru(ring)$(CO)_2$X],[8] the latter complex containing relatively substitution-inert CO groups. The reaction between fulvenes and [$Ru_3(CO)_{12}$] has also led to a range of ruthenium complexes containing a monosubstituted cyclopentadiene ring.[9,10] Recently the synthesis of a series of [Ru(ring)A_2X] complexes has been reported starting from [Ru(ring)(cod)H] (cod = cyclo-octa-1,5-diene).[11] A range of ruthenium complexes containing a *disubstituted* cyclopentadienyl ring has also been reported,[12] typically where the ring is the indenyl ligand, C_9H_7.[13—16]

A report on some aspects of this work has been published.[17]

Experimental

The complexes [$Ru_3(CO)_{12}$] and [{Fe(η^5-C_5H_5)$(CO)_2$}$_2$] were purchased from Strem Chemicals as were most of the Group 15 donor ligands. The isocyanides were obtained from Fluka AG. The complex [Ru(η^5-C_9H_7)$(CO)_2$I] was synthesized by the literature method.[16e] All reactions were routinely performed under an inert atmosphere in dry, degassed solvents. M.p.s were determined on a Kofler hot-stage apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 580B spectrophotometer, ^{1}H n.m.r. spectra on a Bruker AC 200 spectrometer, and mass spectra on a Varian MAT CH5 spectrometer operating at 70 eV (1.12×10^{-17} J). Column chromatography was performed on silica gel (Merck 'Kieselgel 60,' 60—200 μm). Microanalyses were performed by the Microanalytical Laboratories, Council for Scientific and Industrial Research, Pretoria.

Nuclear Overhauser enhancement (n.O.e.) spectra[18] were recorded on *ca.* 20 mmol dm^{-3} solutions in deoxygenated C_6D_6 as described previously.[1,19,20]

Preparation of [Ru(η^5-C_5H_4Me)$(CO)_2$I].—The complex [$Ru_3(CO)_{12}$] (635 mg, 1 mmol) and distilled heptane (100 cm^3) was placed in a round bottomed flask. To this mixture was added freshly cracked methylcyclopentadiene (1 cm^3). The solution was brought to reflux and the reaction monitored by t.l.c. (silica gel, eluant CH_2Cl_2). When all the starting material had been consumed, excess of MeI (1 cm^3) was added to the warm solution ($\pm$45 °C) and the mixture was allowed to stir for 6 h. The orange-brown precipitate which formed was filtered off and washed with pentane to give a rust-orange solid. This solid was dissolved in benzene and eluted through a hexane-washed column with benzene. The required complex as well as a small amount of [{Ru(η^5-C_5H_4Me)$(CO)_2$}$_2$] were separated by this procedure. The iodo-complex was recrystallized from CH_2Cl_2–

---

† For Part 3 see ref. 17.

‡ Carbonyl(η^5-indenyl)iodo(tribenzylphosphine)ruthenium(II).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

hexane (78% yield) and characterized by i.r. and n.m.r. spectroscopy.

Table 1. Experimental and analytical data for the new ruthenium complexes

L	Reaction time[a]/h	Yield/ %	M.p./°C	Analysis[b]/% C	H
$[Ru(\eta^5\text{-}C_5H_4Me)(CO)(L)I]$					
$P(OMe)_3$	2	80	Oil		
$P(OEt)_3$	2.5	80			
$P(OPr^i)_3$	3	90	123—125	36.1	5.30
				(35.4)	(5.20)
PMe_2Ph	0.8	80	74—76	38.4	3.90
				(38.1)	(3.85)
$PMePh_2$	1.3	73			
PPh_3	5	66	181—182		
Bu^tNC[c]	1	77	90—91	35.2	4.15
				(34.5)	(3.85)
$2,6\text{-}Me_2C_6H_3NC$[d]	0.7	74	143—144	41.2	3.40
				(41.1)	(3.45)
$[Ru(\eta^5\text{-}C_9H_7)(CO)(L)I]$					
$P(OMe)_3$	2[e]	50	Oil		
$P(OEt)_3$	11[f]	60	74—76		
$P(OPr^i)_3$[g]	9	76	124—125	39.8	4.80
				(39.4)	(4.85)
$P(OC_6H_4Me\text{-}o)_3$[h]			144—145	51.5	3.60
				(51.5)	(3.90)
PPh_3	6	63		56.3	3.80
				(55.6)[i]	(3.70)[i]
$P(CH_2Ph)_3$	96	30	153—155	55.3	4.20
				(55.2)	(4.20)

[a] Time required for disappearance of starting material or until spectrum remains constant with time; as monitored by i.r. spectroscopy. [b] Calculated values in parentheses. [c] N 3.50 (3.35%). [d] N 3.15 (3.00%). [e] Reaction time in the absence of catalyst 11 h. [f] Reaction performed in the absence of catalyst. [g] Mass spectrum: 580 (88) M^+, 552 (37) $[M - CO]^+$, 344 (81) $[M - CO - L]^+$, and 217 (100%) $[M - CO - L - I]^+$. [h] Reaction of $[Ru(\eta^5\text{-}C_9H_7)(CO)_2I]$ with $P(OC_6H_4Me\text{-}o)_3$ yielded $[Ru(\eta^5\text{-}C_9H_7)(CO)_2L]^+$ (45 min, 50% yield). This complex was converted into the required complex with NMe_3O in CH_2Cl_2 (90% yield). [i] Calc. for $[Ru(\eta^5\text{-}C_9H_7)(CO)(PPh_3)I]\cdot 0.5C_6H_6$.

Preparation of $[Ru(\eta^5\text{-}C_5H_4Me)(CO)(L)I]$ [L = $P(OMe)_3$, $P(OPr^i)_3$, $P(OEt)_3$, PPh_3, PMe_2Ph, Bu^tNC, *or* $2,6\text{-}Me_2C_6H_3NC$].—The complex $[Ru(\eta^5\text{-}C_5H_4Me)(CO)_2I]$ (100 mg, 0.25 mmol) and ligand (0.28 mmol) were added to benzene (10 cm^3) and the solution brought to reflux; $[\{Fe(\eta^5\text{-}C_5H_5)(CO)_2\}_2]$ (10 mg) was added to the refluxing solution. The reaction was monitored by i.r. spectroscopy and considered complete when the ν(CO) vibration at 2 020 cm^{-1} disappeared or remained constant with time (Table 4). After solvent removal, the crude red-orange product was dissolved in benzene and passed through a silica-gel column (wetted with hexane, eluted with benzene). A small amount of $[Ru(\eta^5\text{-}C_5H_4Me)(CO)_2I]$ was initially eluted, followed by the required product (orange-red complex), and finally trace amounts of a green complex. The required complex, after recrystallization from hexane–CH_2Cl_2, was characterized by analytical and spectroscopic techniques (Tables 1—3).

Preparation of $[Ru(\eta^5\text{-}C_9H_7)(CO)(L)I]$ [L = $P(OMe)_3$, $P(OEt)_3$, $P(OPr^i)_3$, PPh_3, *or* $P(CH_2Ph)_3$].—The complex $[Ru(\eta^5\text{-}C_9H_7)(CO)_2I]$ (100 mg, 0.24 mmol) and L (0.30 mmol) were added to benzene (5 cm^3) and the solution brought to reflux; $[\{Fe(\eta^5\text{-}C_5H_5)(CO)_2\}_2]$ (5 mg) was added and the reaction monitored by i.r. spectroscopy. When the ν(CO) vibration at 2 020 cm^{-1} had disappeared, or remained constant with time, the reaction was taken as complete. The yellow-brown solution was pumped to dryness and the crude material eluted with benzene under nitrogen through a 15-cm silica column washed with hexane. Small amounts of starting material were initially eluted as a yellow band. The next (orange) band contained the required product. On occasion traces of a third green band were also noticed but no attempt was made to isolate the material contained. Recrystallization from pentane–CH_2Cl_2 gave the required products. I.r., n.m.r, and analytical data for the new complexes are reported in Tables 1 and 4.

Reaction of $[Ru(\eta^5\text{-}C_9H_7)(CO)_2I]$ *with* $PMePh_2$.—The complex $[Ru(\eta^5\text{-}C_9H_7)(CO)_2I]$ (100 mg, 0.24 mmol) and $PMePh_2$ (100 mg, 0.48 mmol) together with $[\{Fe(\eta^5\text{-}C_5H_5)(CO)_2\}_2]$ (5 mg) were heated at reflux in benzene (5 cm^3). The reaction was monitored by i.r. spectroscopy. A yellow precipitate formed slowly and the reaction was terminated after 96 h. The cooled solution was filtered through a cellulose column and the precipitate washed with benzene. The benzene washings contained unreacted $[Ru(\eta^5\text{-}C_9H_7)(CO)_2I]$. The yellow precipitate was then washed through the cellulose column with CH_2Cl_2 and the salt was reprecipitated on addition of hexane. Counter-ion exchange with NH_4PF_6 yielded a complex believed to be $[Ru(\eta^5\text{-}C_9H_7)(CO)(PMePh_2)_2]PF_6$ [ν(CO) (CH_2Cl_2) 1 977 cm^{-1}; n.m.r. ($CDCl_3$) 1.67 (P*Me*Ph$_2$), 5.67 (H^1, H^3), and 5.27 (H^2)].

Crystal and Molecular Structure of $[Ru(\eta^5\text{-}C_9H_7)(CO)\{P(CH_2Ph)_3\}I]$.—*Data collection.* The compound $[Ru(\eta^5\text{-}C_9H_7)(CO)\{P(CH_2Ph)_3\}I]$ was synthesized *via* the $[\{Fe(\eta^5\text{-}C_5H_5)(CO)_2\}_2]$-catalysed thermal reaction between $[Ru(\eta^5\text{-}C_9H_7)(CO)_2I]$ and tribenzylphosphine. Recrystallization from benzene–hexane under nitrogen at −20 °C yielded orange cube-shaped crystals. A crystal measuring 0.20 × 0.20 × 0.10 mm was selected for crystallographic analysis. Preliminary investigation by standard Weissenberg photography established the space group as $P\bar{1}$. Refined cell constants were obtained during data collection on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.7107 Å) at room temperature (20 °C).

Crystal data. $C_{31}H_{28}IOPRu\cdot 0.5C_6H_6$, $M = 753.68$, a = 9.923(2), b = 11.055(4), c = 14.543(3) Å, α = 84.52(2)°, β = 77.72(2)°, γ = 82.74(2)°, U = 1 542.56 Å^3, $F(000)$ = 710, Z = 2, D_c = 1.63 g cm^{-3}, μ = 14.50 cm^{-1}.

Lorentz and polarization corrections were applied and the data were empirically corrected for absorption effects using the method of North *et al.*[21] Data were collected in ω—2θ scan mode in the region $2 < \theta < 25°$ with *hkl* limits of $-11 \leqslant h \leqslant 11$, $-13 \leqslant k \leqslant 13$, and $0 \leqslant l \leqslant 17$.

A total of 5 644 reflections was measured at a speed of 0.9—5.5° min^{-1} with a scan width 0.6 + 0.35 tanθ. After omission of all unobserved reflections with $F < 3\sigma(F)$ a unique data set of 4 642 observations was retained.

Structure solution and refinement. Structure analysis and refinement were carried out using the program SHELX 76.[22] Initial co-ordinates for the iodine, ruthenium, and phosphorus atoms were derived from a Patterson synthesis, and the positions of the other non-hydrogen atoms in the molecule were found by Fourier difference syntheses. Residual electron density after initial refinement was found to correspond to a disordered benzene of crystallization. A pair of rotationally disordered, half-weight rigid benzene molecules refined in the plane of the residual density adequately resolved the problem. Positional parameters for all atoms and anisotropic thermal parameters for the non-hydrogen atoms were refined by full-matrix least squares (Table 5). Refinement was considered complete when all

Table 2. Spectral data for the $[Ru(\eta^5\text{-}C_5H_4Me)(CO)(L)I]$ complexes

L	I.r.[a] $\nu(CO)/cm^{-1}$	N.m.r.[b,c] Me	H^2	H^3	H^4	H^5	$\frac{H^2 + H^5}{2}$	$\frac{H^3 + H^4}{2}$
$P(OMe)_3$[f]	1 969	1.95 (2.0)	4.54	4.53	4.41	4.47	4.51	4.47
$P(OEt)_3$[g]	1 966	1.97 (1.4)	4.62	4.50	4.50	4.59	4.61	4.50
$O(OPr^i)_3$[h]	1 967	1.98 (1.7)	4.68	4.50	4.50	4.67	4.68	4.50
PMe_2Ph[i]	1 947	1.80	4.30	4.12	4.03	4.23	4.27	4.08
$PMePh_2$[j]	1 952	1.86	4.36	4.14	4.14	4.30	4.33	4.14
PPh_3[k]	1 953	1.97 (1.3)	4.37	4.17	4.17	4.33	4.35	4.17
Bu^tNC[l]	1 979[m]	1.86	4.49	4.45	4.45	4.49	4.49	4.45
$2,6\text{-}Me_2C_6H_3NC$[n]	1 986[o]	1.89	4.50	4.51	4.51	4.50	4.50	4.51
CO	1 994, 1 953	1.65	4.17	4.17	4.17	4.17	4.17	4.17

L	$\left(\frac{H^2 + H^5}{2} - \frac{H^3 + H^4}{2}\right)$	Δ $(H^2 - H^5)$	Δ $(H^3 - H^4)$	$\frac{H^1 + H^2 + H^3 + H^4}{4}$	C_5H_5[d]	$(C_5H_5 - C_5H_4Me)$[e]
$P(OMe)_3$[f]	0.04	0.07	0.12	4.49	4.66	0.17
$P(OEt)_3$[g]	0.11	0.03	0	4.55	4.72	0.17
$P(OPr^i)_3$[h]	0.18	0.01	0	4.59	4.75	0.16
PMe_2Ph[i]	0.19	0.07	0.09	4.17	4.40	0.23
$PMePh_2$[j]	0.19	0.06	0	4.23	4.45	0.22
PPh_3[k]	0.18	0.04	0	4.26	4.49	0.23
Bu^tNC[l]	0.04	0	0	4.47	4.65	0.18
$2,6\text{-}Me_2C_6H_3NC$[n]	−0.01	0	0	4.50	4.71	0.21
CO	0.00	0.00	0	4.17		

[a] Recorded in $CHCl_3$. [b] Recorded in C_6D_6. [c] δ relative to $SiMe_4$. [d] C_5H_5 for $[Ru(\eta^5\text{-}C_5H_5)(CO)(L)I]$; data taken from refs. 24 and 26. [e] Difference in ring proton resonances between $[Ru(\eta^5\text{-}C_5H_5)(CO)(L)I]$ and the average value of the ring resonances for $[Ru(\eta^5\text{-}C_5H_4Me)(CO)(L)I]$. [f] OMe, 3.41 (d) [$J$(P–H) = 12.1 Hz]. [g] CH_2, 3.99 and 3.98 (qnt.)[J(H–H) = 7.1, J(P–H) = 7.1]; CH_3, 1.08 (t) [J(H–H) = 7.1 Hz]. [h] CH_3, 1.15 and 1.25 (d) [J(H–H) = 6.1 Hz]; CH, 4.91 and 4.86 (d of spt) [J(H–H) = 6.1, J(P–H) = 9.5 Hz]. [i] P*Me*$_2$Ph, 1.76 (d) [J(P–H) = 9.8], 1.62 (d) [J(P–H) = 9.8 Hz]; aromatic, 7.3 and 7.0 (ratio 2:3). [j] P*Me*Ph$_2$, 2.16 (d) [J(P–H) = 9.3 Hz]; aromatic, 7.50, 7.35, and 7.02 (ratio 2:2:6). [k] Aromatic: *ortho*, 7.6m *meta* and *para*, 7.0 (m). [l] CH_3 0.94. [m] $\nu(NC)$ 2 137 cm^{-1}. [n] CH_3, 2.18; aromatic, 6.7—6.8. [o] $\nu(NC)$ 2 153 cm^{-1}.

Table 3. Mass spectral data for the $[Ru(\eta^5\text{-}C_5H_4Me)(CO)(L)I]$ complexes

L	Fragment Ions[a] M^+	$[M - CO]^+$	$[M - CO - L]^+$	$[C_6H_4MeRu]^+$	Other
$P(OMe)_3$	460 (75)	432 (100)	308 (31)	181 (68)	$[M - CO - OMe - H]^+$, 400 (34)
$P(OEt)_3$	502 (74)	474 (60)	308 (36)	181 (100)	$[M - CO - OEt]^+$, 429 (23) $[M - CO - OEt_2]^+$, 400 (29)
$P(OPr^i)_3$[b]	544 (23)	516 (9)	308 (49)	181 (100)	$[M - CO - I + H]^+$ or $[M - CO - (Pr^i)_3 + 3H]^+$ 390 (18)
PMe_2Ph	474 (100)	446 (87)	308 (13)	181 (50)	$[M - CO - I - Me - H]^+$, 303 (43) $[M - CO - I]^+$, 319 (83)
PPh_2Mc	536 (100)	508 (64)	308 (31)	181 (73)	$[M - CO - I]^+$, 381 (95) $[M - CO - I - Me]^+$, 366 (47)
PPh_3	598 (41)	570 (45)	308 (13)	181 (42)	$[M - CO - I - Ph]^+$, 372 (25) $[M - CO - I]^+$, 443 (100)
$2,6\text{-}Me_2C_6H_3NC$	467 (30)	439 (50)	308 (23)	181 (100)	$[M - CO - I]^+$, 312 (93)

[a] Percentage abundance given in parentheses. Only the most intense ions with $m/z > 100$ are listed; ^{102}Ru isotope. [b] Numerous fragments are formed by breakdown of the $P(OPr^i)_3$ ligand, *e.g.* m/z 448 (6), 432 (7), 414 (9), and 374 (10%).

parameter shifts were less than 2.5σ at the stage where R was 0.0560. Unit weights were used. Residual density nowhere exceeded 1.4 e Å^{-3} An ORTEP[23] diagram indicating the numbering system used is given in Figure 1 and a packing diagram is shown in Figure 2.

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

Results and Discussion

The reaction between $[Ru_3(CO)_{12}]$ and cyclopentadiene in heptane followed by addition of MeI readily gave $[Ru(\eta^5\text{-}C_5H_5)(CO)_2I]$ in good yield.[16e] The replacement of cyclopentadiene by freshly cracked methylcyclopentadiene also readily yielded $[Ru(\eta^5\text{-}C_5H_4Me)(CO)_2I]$ by a similar route. This ruthenium complex was characterized by i.r. and n.m.r. spectroscopy (Table 2).

Extension of the reaction to the indenyl ligand however gave poor yields of $[Ru(\eta^5\text{-}C_9H_7)(CO)_2I]$ as well as substantial amounts of $[Ru_4(CO)_7(\mu\text{-}CO)_2(\eta^2,\eta^5,\eta^2\text{-}C_9H_7)(\eta^5\text{-}C_9H_9)]$.[16e] A change of the reaction solvent to methyl ethyl ketone as suggested by Efraty and co-workers[16e] did give the required product in *ca.* 30% yield with i.r. and n.m.r. data identical to the reported literature values (Table 4).

The reaction between $[Ru(\eta^5\text{-}C_5H_4Me)(CO)_2I]$ and

Table 4. I.r. and n.m.r. data for the indenylruthenium complexes

L	I.r.[a] ν(CO)/ cm^{-1}	N.m.r.[b]										
					$H^1 + H^3/2$		$\Delta(H^1 - H^3)$					
		H^1	H^2	H^3	Ru	Fe[d]	Ru	Fe[d]	J $(H^1 - H^2)$	J $(P-H^2)$	θ[c]/°	Other
CO	2 042, 1 991	477 (d)	4.44 (t)	4.77	4.77	4.43	0	0	2.7			
$P(OMe)_3$	1 950	5.03	4.93	4.97	5.00	4.61	0.06	0.81	2.8	*e*	107	CH_3 3.27 (d) [*J*(P–H) = 12.2]; indenyl 6.8, 7.2 (m)
$P(OEt)_3$	1 954	5.02	5.06	5.02	5.02	4.65	0.04	0.86	*e*	*e*	109	CH_3 1.03 (t) [*J*(H–H) = 7.0, CH_2 (m)]; indenyl 6.8, 7.2 (m)
$P(OPr^i)_3$	1 964	5.32	5.15 (dt)	4.89	5.11	4.71	0.43	1.87	2.8	1.0	130	CH_3 1.20 (d) [*J*(H–H) = 6.1], 1.13 (d) [*J*(H–H) = 6.1], CH 4.76 (dq) [*J*(P–H) = 9.7, *J*(H–H) = 6.1], indenyl 6.9, 72
$P(OC_6H_4Me\text{-}o)_3$	1 986	5.07	4.83 (dt)	4.32	4.70	4.34	0.75	2.26	2.8	1.1	141	CH_3 2.16, indenyl, 6.9 (m, H^4) 7.2 (H^7)
PPh_3	1 954	5.49	4.89	3.94	4.82	4.28	1.55	0.33	2.6	0.5	145	indenyl, 6.25 (m, H^4), 6.66 (H^5), 7.1 (H^6), 7.09 (H^7), 7.5 (*ortho* proton)
$P(CH_2Ph)_3$	1 950	4.17 (d)	4.71 (dt)	4.17	4.17	4.02	0.00	3.12	2.1	0.8	165	CH_2, 3.41 (AB q) [*J*(P–H) = 9.4, *J*(H–H) = 14.2], 3.26 [*J*(P–H) = 10.0, *J*(H–H) = 14.2], 6.8—7.3 indenyl (m)

[a] Recorded in CH_2Cl_2. [b] Recorded in C_6D_6 relative to $SiMe_4$; δ, *J* in Hz. [c] Tolman cone angle. [d] From ref. 1. [e] Not determined.

Table 5. Fractional atomic co-ordinates (× 10^4) for non-hydrogen atoms of [Ru(η^5-C_9H_7)(CO){$P(CH_2Ph)_3$}I]

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
I	606(1)	4 575(1)	2 395(1)	C(21)	1 090(12)	2 063(12)	639(9)
Ru	1 974(1)	2 392(1)	2 792(1)	C(22)	1 410(12)	1 788(12)	−373(9)
P	2 573(3)	2 101(3)	1 230(2)	C(23)	1 468(14)	2 690(13)	−1 074(10)
O	−573(9)	1 294(15)	3 029(7)	C(24)	1 755(14)	2 406(17)	−2 022(10)
C(10)	258(22)	1 619(14)	2 903(10)	C(25)	1 933(15)	1 207(16)	−2 239(11)
C(1)	3 349(16)	1 092(14)	3 506(10)	C(26)	1 863(13)	306(14)	−1 537(10)
C(2)	4 125(15)	2 073(16)	3 040(10)	C(27)	1 601(13)	568(13)	−621(10)
C(3)	3 490(16)	3 160(16)	3 459(11)	C(31)	3 745(11)	705(10)	910(8)
C(4)	2 372(15)	2 856(13)	4 209(9)	C(32)	3 477(11)	−463(11)	1 488(8)
C(5)	1 393(17)	3 553(14)	4 875(11)	C(33)	4 551(13)	−1 162(12)	1 813(10)
C(6)	506(18)	2 972(16)	5 549(11)	C(34)	4 376(16)	−2 250(13)	2 324(11)
C(7)	492(18)	1 696(17)	5 580(11)	C(35)	3 108(18)	−2 695(14)	2 502(12)
C(8)	1 360(17)	1 027(15)	4 952(10)	C(36)	2 017(14)	−2 034(13)	2 178(10)
C(9)	2 309(15)	1 579(13)	4 246(10)	C(37)	2 187(12)	−925(11)	1 685(9)
C(11)	3 506(12)	3 256(11)	443(9)	Ca	3 784(33)	5 416(90)	5 618(47)
C(12)	4 854(12)	3 487(11)	670(8)	Cb	4 331(86)	4 185(69)	5 698(39)
C(13)	4 873(14)	4 335(11)	1 307(9)	Cc	4 417(87)	6 219(23)	4 886(66)
C(14)	6 101(16)	4 510(13)	1 562(11)	Cd	4 022(67)	5 978(68)	5 306(53)
C(15)	7 314(16)	3 874(15)	1 167(13)	Ce	3 852(51)	4 790(96)	5 719(26)
C(16)	7 319(14)	3 066(13)	490(12)	Cf	5 224(104)	6 202(31)	4 630(51)
C(17)	6 090(14)	2 872(12)	265(10)	Cen *	3 129	2 152	3 692

* Cen = Ring centroid.

Table 6. The effect of catalysts on the reaction [Ru(η^5-C_5H_4Me)$(CO)_2I$] + $P(OMe)_3$ $\longrightarrow$ [Ru(η^5-C_5H_4Me)(CO){$P(OMe)_3$}I]

Catalyst	Reaction time (h)*	Catalyst	Reaction time (h)*
none	80	Ru–Al_2O_3 (5%)	24
[{Fe(η^5-C_5H_5)$(CO)_2$}$_2$]	1	Pd–Al_2O_3 (5%)	48
[{Mo(η^5-C_5H_5)$(CO)_3$}$_2$]	Erratic	Pt–Al_2O_3 (5%)	55
PdO	8		

* As determined by i.r. spectroscopy.

$P(OMe)_3$ in refluxing benzene was found to be very slow (Table 6). This reaction was then used as a model reaction to establish whether reactivity could be increased by the addition of transition-metal complexes acting as catalysts. The results of this study are shown in Table 6 and, as can be seen, [{Fe(η^5-C_5H_5)$(CO)_2$}$_2$] proved to be the best catalyst for this reaction. This complex was also found to catalyse the reaction between either [Ru(η^5-C_9H_7)$(CO)_2I$] or [Ru(η^5-C_5H_4Me)$(CO)_2I$] and a range of phosphines, phosphites, and isocyanides L (Table 1). With few exceptions (see below) the reaction yielded [Ru(η^5-C_5H_4Me)(CO)(L)I], (**1**), or [Ru(η^5-C_9H_7)(CO)(L)I], (**2**).

The reaction between [Ru(η^5-C_5H_4Me)$(CO)_2I$] and 1.5 equivalents of RNC (R = 2,6-$Me_2C_6H_3$) was observed to yield both [Ru(η^5-C_5H_4Me)(CO)(CNR)I] (see Tables 1 and 2) and [Ru(η^5-C_5H_4Me)$(CNR)_2I$]. The latter complex was characterized by i.r. [C_6D_6: ν(NC) 2 125, 2 080, and 2 055 (sh) cm^{-1}] and ^1H n.m.r. spectroscopy [C_6D_6; δ 4.76 (C_5H_4Me) and 4.80 (multiplets)]. These spectroscopic values correlate well with

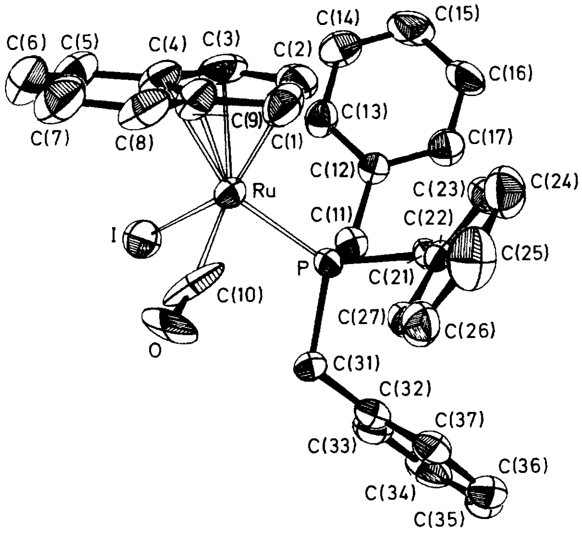


Figure 1. ORTEP[23] diagram of $[Ru(\eta^5\text{-}C_9H_7)(CO)\{P(CH_2Ph)_3\}I]$

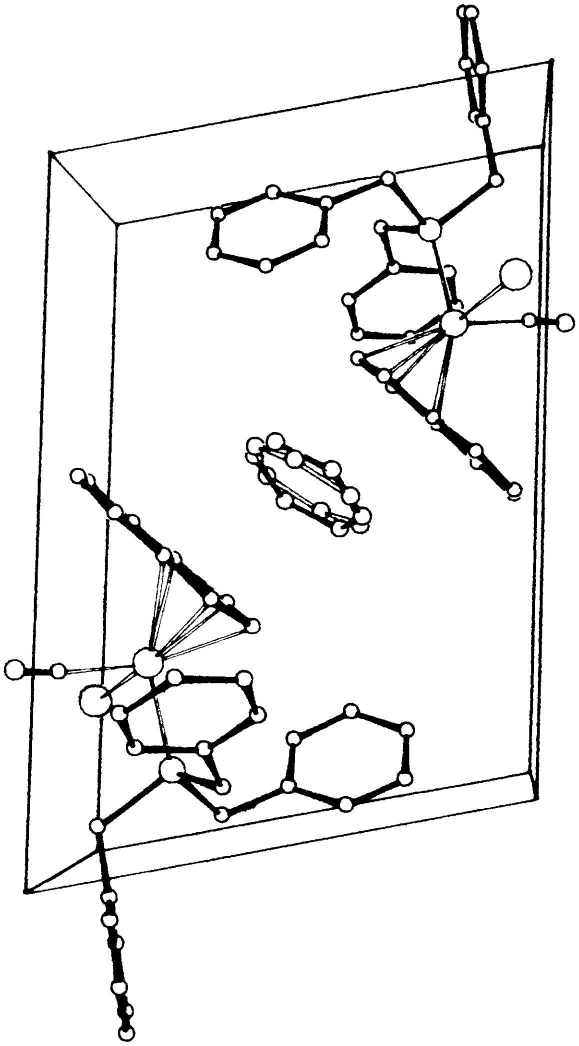


Figure 2. Packing diagram of $[Ru(\eta^5\text{-}C_9H_7)(CO)\{P(CH_2Ph)_3\}I]\cdot 0.5C_6H_6$ viewed down the *a* axis

similar data obtained for the $[Ru(\eta^5\text{-}C_5H_5)(CO)_n(CNR)_{2-n}I]$ (n = 1 or 2) complexes.[24]

The n.m.r. spectrum of the crude product mixture from the reaction between $[Ru(\eta^5\text{-}C_5H_4Me)(CO)_2I]$ and $P(OMe)_3$ in the presence of $[\{Fe(\eta^5\text{-}C_5H_5)(CO)_2\}_2]$ also revealed small amounts of $[Fe(\eta^5\text{-}C_5H_5)(CO)\{P(OMe)_3\}I]$ {$<3\%$; ^1H n.m.r. (C_6D_6) 4.29 (C_5H_5) [J(P–H) = 1.0] and 3.43 [$P(OMe)_3$] [J(P–H) = 12.2 Hz]}[25] and $[Ru(\eta^5\text{-}C_5H_5)(CO)\{P(OMe)_3\}I]$ {2%; ^1H n.m.r. (C_6D_6) 4.60 (C_5H_5) [J(P–H) 1.1] and 3.40 [$P(OMe)_3$] [J(P–H) = 11.2 Hz]}.[26] Similar products were detected for some of the other reactions between $[Ru(\eta^5\text{-}C_5H_4Me)(CO)_2I]$ and L reported in this study. The formation of these products is consistent with the mechanism previously proposed for similarly catalysed reactions.[27]

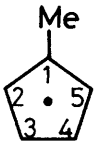
The new complexes have been fully characterized and analytical and spectroscopic data are reported in Tables 1—4. The single CO absorption in the i.r. spectrum between 1 990 and 1 940 cm^{-1} readily identified the complexes as monocarbonyl ruthenium(II) complexes. The parent ion and fragment ions resulting from loss of CO, L, and I were identified in the mass spectra of the new C_5H_4Me complexes. The characteristic isotopic pattern for Ru assisted in the fragment-ion characterization[28a] but only the ^{102}Ru isotopic data are reported in Table 3. The n.m.r. spectra gave the correct intensity ratio of cyclopentadienyl to ligand resonances and the resonances were observed in the correct region of the spectrum. The average value for the four cyclopentadienyl proton resonances is downfield from the cyclopentadienyl proton resonances of the corresponding $[Ru(\eta^5\text{-}C_5H_5)(CO)(L)I]$ complexes. This downfield shift is due to the electron-donating effect of the ring methyl group.[1] Further details of the n.m.r. spectra are discussed below.

Whereas the reaction between $[Ru(\eta^5\text{-}C_5H_4Me)(CO)_2I]$ and L readily gave complexes (**1**) in high yield, the products from the reaction of $[Ru(\eta^5\text{-}C_9H_7)(CO)_2I]$ and L usually gave (**2**), but for L = $PMePh_2$ and $P(OC_6H_4Me\text{-}o)_3$ salts were formed (see below). Also, no reaction was observed between $[Ru(\eta^5\text{-}C_9H_7)(CO)_2I]$ and L = $P(C_6H_{11})_3$ (refluxing benzene, 48 h), as detected by i.r. spectroscopy. The reaction between $[Ru(\eta^5\text{-}C_9H_7)(CO)_2I]$ and L also resulted in the growth of an i.r. absorption at 1 850 cm^{-1} when L = $P(CH_2Ph)_3$, PPh_3, or $PMePh_2$,[28b] but no attempt was made to maximize or characterize the complex giving rise to this absorption band.

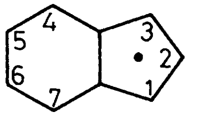
Reaction between $[Ru(\eta^5\text{-}C_9H_7)(CO)_2I]$ and $PMePh_2$ did not yield the required product, (**2**). Although ν(CO) absorptions of the starting material were observed to disappear with time, no corresponding growth of an absorption at 1 950 cm^{-1} was observed. After a long reaction time a complex deposited from solution, and after metathesis with PF_6 a complex believed to be $[Ru(\eta^5\text{-}C_9H_7)(CO)(PMePh_2)_2]PF_6$ (see Experimental section) was isolated.

N.M.R. Spectra.—$[Ru(\eta^5\text{-}C_5H_4Me)(CO)(L)I]$. A major objective in our study was to ascertain the effect of the larger Ru atom (relative to Fe) on the relative positions of the four cyclopentadienyl ring resonances and consequently to determine whether conformational information relating the cyclopentadiene to the ligand set could be established. In our previous study we observed a correlation between protons H^2 and H^5, *i.e.* $\Delta(H^2 - H^5)$, and the Tolman cone angle.[29] [The numbering system used for the methylcyclopentadienyl (*a*) and indenyl rings (*b*) is shown below.]

N.O.e difference spectra recorded on [(**1**); L = $P(OMe)_3$, PMePh, $PMePh_2$, or $2,6\text{-}Me_2C_6H_3NC$] were used to assign the resonances for H^2 to H^5. It was assumed that those results were transferable to other related complexes and all assignments are recorded in Table 2. Since the four cyclopentadienyl resonances are closely clustered in (**1**) no attempt was made to evaluate coupling constants for these complexes.



(*a*)



(*b*)

Our results clearly indicate that *smaller* separation of the ring proton resonances H^2 and H^5 is observed relative to the iron data. This is not unexpected and relates to the larger atomic radius of Ru relative to Fe.[30] The data also indicate no correlation between $\Delta(H^2 - H^5)$ and θ, but this result may be due to the small range of $\Delta(H^2 - H^5)$ values under consideration.

The n.O.e. data also provide limited information on the ligand set conformations. Thus irradiation of the methyl ligand resonances [P(O*Me*)$_3$, P*Me*$_2$Ph, and P*Me*Ph$_2$] or the *ortho*-phenyl resonances (PMe$_2$*Ph* and PMe*Ph*$_2$) results in different growth patterns for the resonances H^2 to H^5. For the P(OMe)$_3$ complex near equal growth of *all four* resonances H^2 to H^5 occurs (implying unrestricted ligand rotations) while, for instance, irradiation of the two different *ortho* protons in the PMePh$_2$ complex results in different growth patterns for H^2 to H^5. Corresponding growth patterns for the *ortho* protons on irradiation of the ring protons H^2 to H^5 were also observed. These latter findings are consistent with the PMePh$_2$ ligand spending more of its time in the region around protons H^3 and H^4. Thus even though the $\Delta(H^2 - H^5)$ values are smaller for the ruthenium than the iron complexes, room-temperature ligand conformations can still be detected from the n.O.e. data.

The phenomenon of restricted rotation of a substituted cyclopentadienyl ring relative to a ligand set appears to be quite general and has been reported for a range of substituted cyclopentadienyl transition-metal complexes.[31]

[Ru(η^5-C$_9$H$_7$)(CO)(L)I]. The n.m.r. spectra of a range of transition metal–indenyl complexes have been extensively studied and analysed.[32] From these studies it has become apparent that electronic factors associated with the metal–ligand set below the metal–indenyl ring influence the distortion of the ring from planarity (allyl–ene ring bonding mode) and the positioning of the metal relative to the centre of the cyclopentadienyl ring (ring-slip distortion). These features have been quantified and correlated with a range of physical parameters, including n.m.r. spectra data.[32] Steric factors have generally not been considered important in these studies. However, our earlier study on [Fe(η^5-C$_9$H$_7$)(CO)(L)I] complexes suggested that steric factors may play a role in influencing the indenyl proton n.m.r. data. Further, to investigate this possibility we have carried out a detailed n.m.r. study of a series of [Ru(η^5-C$_9$H$_7$)(CO)(L)I] complexes and a comparison with our earlier iron data has been made. As with the Ru(C$_5$H$_4$Me) complexes our particular interest has been an attempt to correlate ligand conformations with n.m.r. data.

A comparison of the n.m.r. data for the iron[1] and ruthenium indenyl complexes reveals that $\Delta(H^1 - H^3)$ increases with the Tolman cone angle,[29] θ, for the phosphite ligands but anomalous behaviour is detected for L = PPh$_3$ and P(CH$_2$Ph)$_3$. Consideration of the phosphite ligand data only reveals that (*i*) a larger difference $\Delta(H^1 - H^3)$ is observed for the iron than the corresponding ruthenium complexes and (*ii*) δ [$(H^1 + H^3)/2$] and δ (H^2) lie upfield for the Ru complexes relative to the Fe complexes. We chose to investigate a representative member of this group, [Ru(η^5-C$_9$H$_7$)(CO){P(OC$_6$H$_4$Me-*o*)$_3$}I] in greater

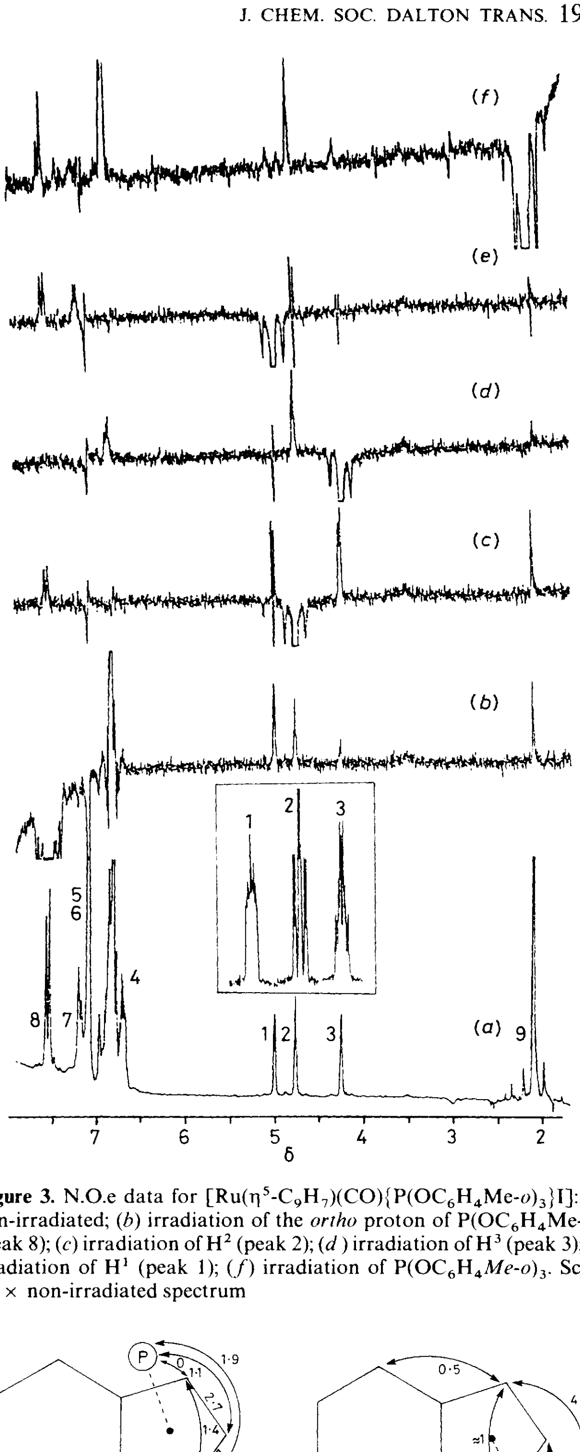


Figure 3. N.O.e data for [Ru(η^5-C$_9$H$_7$)(CO){P(OC$_6$H$_4$Me-*o*)$_3$}I]: (*a*) non-irradiated; (*b*) irradiation of the *ortho* proton of P(OC$_6$H$_4$Me-*o*)$_3$ (peak 8); (*c*) irradiation of H^2 (peak 2); (*d*) irradiation of H^3 (peak 3); (*e*) irradiation of H^1 (peak 1); (*f*) irradiation of P(OC$_6$H$_4$*Me*-*o*)$_3$. Scale: 32 × non-irradiated spectrum

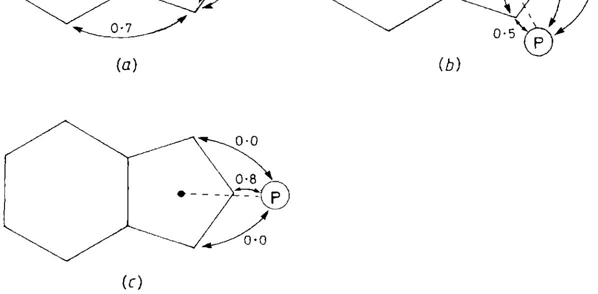


Figure 4. Coupling constant data (Hz) for [Ru(η^5-C$_9$H$_7$)(CO)(L)I] where L = P(OC$_6$H$_4$Me-*o*)$_3$ (*a*), PPh$_3$ (*b*), or P(CH$_2$Ph)$_3$ (*c*)

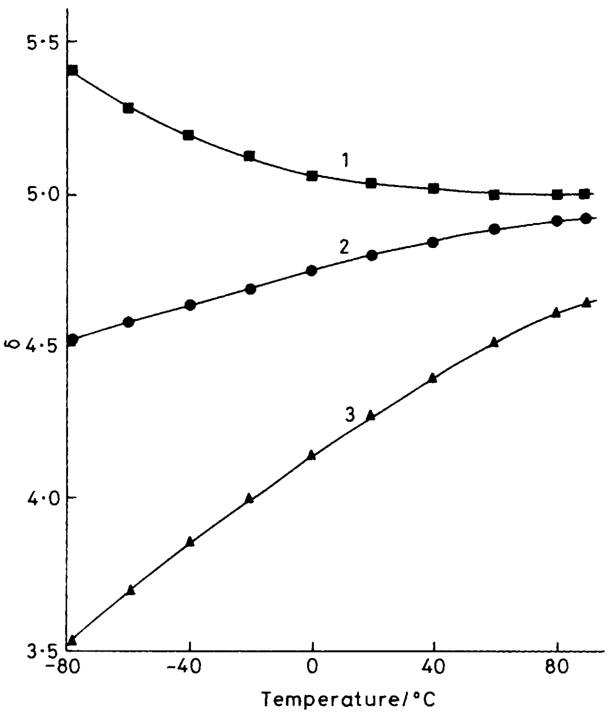


Figure 5. Effect of temperature on the proton resonances H^1 (■), H^2 (●), and H^3 (▲) of [Ru(η^5-C_9H_7)(CO){P(OC_6H_4Me-*o*)$_3$}I]

detail and the n.m.r. spectrum of this complex is shown in Figure 3(*a*). Resonances 1—3 are shown greatly expanded in the inset. A large separation of the resonances H^1, H^2, and H^3 is apparent and the protons can be viewed as part of an AMX coupled system. With this assumption, coupling constants were determined (from decoupling experiments) and are given in Figure 4 as are the coupling data for L = PPh_3 and P(OC_6H_4Me-*o*)$_3$. Significantly different values of *J*(P–H) for the three different ring protons are observed and imply that the three different protons are on average in different environments relative to the Group 15 donor ligand.

N.O.e. spectra were recorded on the complex and permitted assignment of the various proton resonances [see Figure 3(*c*)—(*e*)]. Further, irradiation of the ligand *ortho* methyl [Figure 3(*f*), 9] and *ortho* ring proton [Figure 3(*b*), 8] resulted in different growth patterns for H^1, H^2, and H^3 and suggests that on average that the ligand is closer to H^1 and H^2 than to H^3. This result implies that the stronger *J*(P–H) coupling to H^3 is due to a *trans* coupling effect. This contrasts with our findings for related monosubstituted cyclopentadienyl complexes.[33]

Further, to confirm our findings on the conformational behaviour, variable temperature (v.t.) n.m.r. spectra were recorded on [Ru(η^5-C_9H_7)(CO){P(OC_6H_4Me-*o*)$_3$}I]. The effect of temperature (−80 to +80 °C) on protons H^1, H^2, and H^3 is shown in Figure 5. It is clear that even at +80 °C total unrestricted rotation has not yet taken place. Over the temperature range studied there is no crossover of the H^2 or δ [(H^1 + H^3)/2] resonances, *i.e.* normal behaviour is observed.[31a] It is worth noting that v.t. n.m.r. data recorded for the [Ru(η^5-C_9H_7)(CO)(PPh_3)I] complex give similar results to those discussed above.[17] It is thus proposed that for the [Ru(η^5-C_9H_7)(CO)(L)I] (L = phosphite) complexes that the phosphite ligands orientate themselves in an average solution with a preferred conformation in which they are *close to the indenyl arene ring*. Similar ligand orientations relative to the indenyl ring have been rationalized by Faller *et al.*[32a] as due to *trans* directing factors.

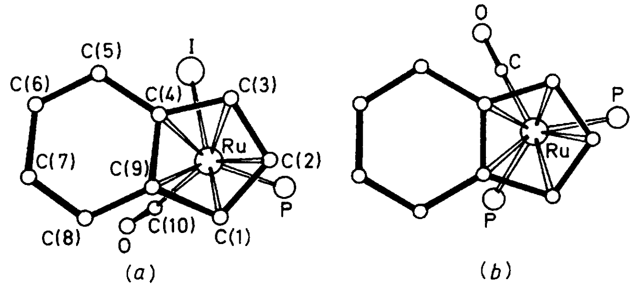


Figure 6. Projection of (*a*) [Ru(η^5-C_9H_7)(CO){P(CH_2Ph)$_3$}I] and (*b*) [Ru(η^5-C_9H_7)(CO)(PPh_3)$_2$]$^+$ down the ruthenium-ring centroid axis. The latter diagram was plotted from data given in ref. 15

Table 7. Selected bond lengths (Å) and angles (°) for [Ru(η^5-C_9H_7)(CO){P(CH_2Ph)$_3$}I]

Ru–I	2.691(1)	Ru–P	2.266(3)
Ru–C(10)	1.97(2)	Ru–C(1)	2.20(2)
Ru–C(2)	2.22(2)	Ru–C(3)	2.24(2)
Ru–C(4)	2.29(2)	Ru–C(5)	2.29(1)
P–C(11)	1.835(12)	P–C(21)	1.862(14)
P–C(31)	1.846(11)	O–C(10)	0.92(2)
C(1)–C(2)	1.44(2)	C(1)–C(9)	1.42(2)
C(2)–C(3)	1.41(2)	C(3)–C(4)	1.43(2)
C(4)–C(5)	1.42(2)	C(4)–C(9)	1.42(2)
C(5)–C(6)	1.34(2)	C(6)–C(7)	1.41(3)
C(7)–C(8)	1.33(2)	C(8)–C(9)	1.39(2)
I–Ru–P	89.6(1)	I–Ru–C(10)	89.7(5)
P–Ru–C(10)	91.0(4)	Ru–P–C(11)	118.2(4)
Ru–P–C(21)	115.1(4)	Ru–P–C(31)	115.6(4)
C(11)–P–C(21)	99.9(6)	C(11)–P–C(31)	100.5(5)
C(21)–P–C(31)	105.3(6)	C(2)–C(3)–C(4)	108.3(14)
C(1)–C(9)–C(4)	108.2(12)	C(1)–C(2)–C(3)	107.5(12)
C(3)–C(4)–C(9)	108.0(12)	C(9)–C(1)–C(2)	107.9(13)

The n.m.r. data for the phosphine complexes (*e.g.* L = PPh_3) suggest that different ligand orientations are observed for Ru and Fe. For the Ru(PPh_3) complex the large Δ(H^1 − H^3) separation suggests a similar ligand orientation as found for the phosphites, *i.e.* the PPh_3 orientated on average preferentially towards H^1 (or H^3) protons. However, on changing the PPh_3 ligand to the P(CH_2Ph)$_3$ the value of Δ(H^1 − H^3) changes from 1.55 to 0.00 (H^1 and H^3 are coincident). This remarkable effect arises from a change in the orientation of the ligand set such that the P(CH_2Ph)$_3$ ligand now finds itself orientated *away* from the indenyl arene ring. This presumably is a *steric* effect and arises from the large ligand cone angle (165°).[29] An *X*-ray structure determination performed on this complex confirmed this ligand orientation (see below). The *J*(P–H) coupling constant data [Figure 4(*b*)] are also quite different from the coupling constant data for the PPh_3 and P(OC_6H_4Me-*o*)$_3$ complexes. Finally n.O.e. spectra recorded for the benzylphosphine complex indicated growth of the resonances of the CH_2 protons on irradiation of H^1 and H^3, consistent with the solid-state structure and further supporting the suggested conformational preference of the ligand set.

Crystal Structure Determination of [Ru(η^5-C_9H_7)(CO){P(CH_2Ph)$_3$}I].—Bond length and bond angle data for the indenyl complex are given in Table 7 and a projection diagram of the molecule viewed down the ruthenium–ring centroid axis is shown in Figure 6. Points to note are: (1) The Ru–I bond distance is slightly shorter than observed in similar cyclopentadienyl structures, *e.g.* [Ru(η^5-C_5H_5)($CNBu^t$)$_2$I] (2.717 Å)[24] and [Ru(η^5-C_5H_4R)(CO)(PPh_3)I] (R = neomenthyl = *c*-2-isopropyl-*t*-5-methylcyclohexan-*r*-yl) (2.708 Å);[8b] (2) as has been observed in many other structures,

Table 8. Slip parameters for ruthenium indenyl complexes

Complex	Δ^a/Å	Fold angle^b/°	Hinge angle^c/°
$[Ru(\eta^5-C_9H_7)(CO)\{P(CH_2Ph)_3\}I]$	0.10	5.59	3.32
$[Ru(\eta^5-C_9H_7)(CO)(PPh_3)_2]ClO_4$^{d}	0.10	5.19	3.77

^{a} $\Delta = d\{[Ru-C(4),C(9)] - [Ru-C(1),C(3)]\}$. ^{b} Fold angle = angle between normals to least-squares planes defined by C(1)—C(3) and C(4)—C(9). ^{c} Hinge angle = angle between normals to least-squares planes defined by C(1),C(2),C(3) and C(1),C(3),C(4),C(9). ^{d} Values calculated from data in ref. 15.

the Ru can be viewed as residing at the centre of an octahedron and not a tetrahedron[34] (*i.e.* OC–Ru–I, OC–Ru–P, and I–Ru–P angles are close to 90°); (3) the benzene portion of the indenyl ring shows localized bonding, as has been observed in other indenyl-containing structures;[32] (4) in contrast to the many studies carried out on $[Fe(\eta^5-C_5H_5)(CO)(PPh_3)X]$ complexes which indicate that one of the phenyl rings of the PPh_3 ligands is orientated underneath the X group,[34] the benzyl ligand has an arrangement such that all of the phenyl rings are orientated *away* from the X (X = I) ligand in our structure.

Methods for analysing the distortion of the cyclopentadienyl ring have been described in the literature.[32] We have analysed our data as well as those for a closely related structure $[Ru(\eta^5-C_9H_7)(CO)(PPh_3)_2]^+$ [15] by the method of Marder *et al.*[32b] and the results of this analysis are shown in Table 8. As can be seen the two structures show similar features and only small distortions of the cyclopentadiene ring are observed when compared with the data collected by Marder *et al.*[32b] The two structures both have PR_3 ligands *trans* to the indenyl ring even though on electronic grounds the CO groups would have been predicted to orientate themselves *trans* to the benzene indenyl ring. Steric effects dominated by the bulky PR_3 groups must be responsible for the final ligand arrangements.

Acknowledgements

We thank the Foundation for Research and Development and the University for financial assistance, and Dr. S. Dobson for collecting the crystallographic data and assistance with the structure determination.

References

1 P. Johnston, M. S. Loonat, W. L. Ingham, L. Carlton, and N. J. Coville, *Organometallics*, 1987, **6**, 2121.
2 L. Carlton, P. Johnston, and N. J. Coville, *J. Organomet. Chem.*, 1988, **339**, 339.
3 E. A. Seddon and K. R. Seddon, 'The Chemistry of Ruthenium,' Elsevier, Amsterdam, 1984; M. O. Albers, D. J. Robinson, and E. Singleton, *Coord. Chem. Rev.*, 1987, **79**, 1; G. Consiglio and F. Morandini, *Chem. Rev.*, 1987, **87**, 761; M. A. Bennett, M. I. Bruce, and T. W. Matheson, in 'Comprehensive Organometallic Chemistry,' eds. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon, Oxford, 1982, vol. 4.
4 R. J. Haines and A. L. du Preez, *J. Organomet. Chem.*, 1975, **84**, 357.
5 L. B. Reventos and A. G. Alonso, *J. Organomet. Chem.*, 1986, **309**, 179.
6 M. I. Bruce, R. C. F. Gardner, B. L. Goodall, F. G. A. Stone, R. J. Doedens, and J. A. Moreland, *J. Chem. Soc., Chem. Commun.*, 1974, 185.
7 T. Blackmore, M. I. Bruce, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1974, 106; T. Blackmore, M. I. Bruce, F. G. A. Stone, R. E. Davis, and A. Garza, *J. Organomet. Chem.*, 1973, **49**, C35.
8 (*a*) E. Cesarotti, G. F. Ciani, and A. Sironi, *J. Organomet. Chem.*, 1981, **216**, 87; (*b*) E. Cesarotti, A. Chiesa, G. F. Ciani, A. Sironi, R. Vefghi, and C. White, *J. Chem. Soc., Dalton Trans.*, 1984, 653; (*c*) E. Cesarotti, M. Angoletta, N. P. C. Walker, M. B. Hursthouse, R. Vefghi, P. A. Schofield, and C. White, *J. Organomet. Chem.*, 1985, **286**, 343.
9 J. D. Edwards, S. A. R. Knox, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1976, 813; M. A. Huffman, D. A. Newman, M. Tilset, W. B. Tolman, and K. P. C. Vollhardt, *Organometallics*, 1986, **5**, 1926; R. Boese, W. B. Tolman, and K. P. C. Vollhardt, *ibid.*, p. 582.
10 U. Behrens and E. Weiss, *J. Organomet. Chem.*, 1975, **96**, 435; U. Behrens, D. Karnatz, and E. Weiss, *ibid.*, 1976, **117**, 171.
11 M. O. Albers, D. J. Robinson, A. Shaver, and E. Singleton, *Organometallics*, 1986, **5**, 2199.
12 S. A. R. Knox, R. P. Phillips, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1974, 658.
13 J. W. Faller, B. V. Johnson, and T. P. Dryja, *J. Organomet. Chem.*, 1974, **65**, 395.
14 E. W. Abel and S. Moorhouse, *J. Chem. Soc., Dalton Trans.*, 1973, 1706.
15 L. A. Oro, M. A. Ciriano, M. Campo, C. Foces-Foces, and F. H. Cano, *J. Organomet. Chem.*, 1985, **289**, 117.
16 (*a*) T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 1956, **2**, 38; (*b*) B. F. Hallam and P. L. Pauson, *J. Chem. Soc.*, 1958, 646; (*c*) R. B. King and M. Ishaq, *Inorg. Chim. Acta*, 1970, **4**, 258; (*d*) P. McArdle and A. R. Manning, *J. Chem. Soc. A*, 1969, 1498; (*e*) A. Eisenstadt, F. Frolow, and A. Efraty, *J. Chem. Soc., Chem. Commun.*, 1982, 642.
17 M. Loonat, L. Carlton, and N. J. Coville, *S. Afr. J. Chem.*, 1988, **41**, 72.
18 J. H. Noggle and R. E. Schirmer, 'The Nuclear Overhauser Effect,' Academic Press, New York, 1971.
19 D. Neuhaus, *J. Magn. Reson.*, 1983, **53**, 109.
20 K. Kinns and T. M. Saunders, *J. Magn. Reson.*, 1984, **56**, 518.
21 A. C. T. North, D. C. Phillips, and F. S. Matthews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.
22 G. M. Sheldrick, SHELX 76, in 'Computing in Crystallography,' eds. H. Schenk, R. Althof-Hazekamp, H. van Koningsveld, and G. C. Bassi, Delft University Press, 1978.
23 C. K. Johnson, ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, Tennessee, 1965.
24 J. C. A. Boeyens, N. J. Coville, and K. Soldenhoff, *S. Afr. J. Chem.*, 1984, **37**, 153.
25 R. J. Haines, A. L. du Preez, and I. L. Marais, *J. Organomet. Chem.*, 1971, **28**, 405.
26 E. A. Darling and N. J. Coville, *J. Organomet. Chem.*, 1984, **277**, 105.
27 N. J. Coville, M. O. Albers, and E. Singleton, *J. Chem. Soc., Dalton Trans.*, 1983, 947.
28 (*a*) 'Handbook of Chemistry and Physics,' 65th edn., CRC, Boca Raton, Florida, 1985, p. B258; (*b*) Liang-Nian Ji, M. E. Rerek, and F. Basolo, *Organometallics*, 1984, **3**, 740.
29 C. A. Tolman, *Chem. Rev.*, 1977, **77**, 313.
30 A. G. Sharpe, 'Inorganic Chemistry,' Longman, London, 1981, p. 161.
31 (*a*) M. Arthurs, S. M. Nelson, and M. G. B. Drew, *J. Chem. Soc., Dalton Trans.*, 1977, 797; (*b*) M. Arthurs, H. Karodia, M. Sedgwick, D. A. Morton-Blake, C. J. Cardin, and H. Parge, *J. Organomet. Chem.*, 1985, **291**, 231; (*c*) M. Arthurs, H. K. Al-Daffaee, J. Haslop, G. Kubal, M. D. Pearson, and E. Curzon, *J. Chem. Soc., Dalton Trans.*, 1987, 2615; (*d*) U. Dämmgen and H. Burger, *J. Organomet. Chem.*, 1975, **101**, 307.
32 (*a*) J. W. Faller, R. H. Crabteee, and A. Habib, *Organometallics*, 1985, **4**, 429; (*b*) T. B. Marder, J. C. Calabrese, D. C. Roe, and T. H. Tulip, *Organometallics*, 1987, **6**, 2012; (*c*) R. D. Barr, M. Green, T. B. Marder, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1984, 1261; (*d*) M. Mlekuz, P. Bougeard, B. G. Sayer, M. J. McGlinchey, C. A. Rodger, M. R. Churchill, J. W. Ziller, S-W. Kanz, and T. A. Albright, *Organometallics*, 1985, **5**, 1656; (*e*) R. T. Baker and T. H. Tulip, *ibid.*, 1986, **5**, 839.
33 K. du Plooy, unpublished work.
34 S. G. Davies, *Pure Appl. Chem.*, 1988, **60**, 13.

Received 6th *June* 1988; *Paper* 8/02248H