Journal of Organometallic Chemistry, 272 (1984) 189–205
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

SYNTHESIS OF MONOHYDRIDOHEXAMETHYLBENZENERUTHENIUM(II) COMPLEXES CONTAINING GROUP V DONOR LIGANDS. ISOMERISM ARISING FROM CYCLOMETALLATION OF A TERTIARY PHOSPHINE AT ALIPHATIC AND AROMATIC CARBON ATOMS *

MARTIN A. BENNETT *, TAI-NANG HUANG and JOZEF L. LATTEN

Research School of Chemistry, The Australian National University, Box 4, G.P.O., Canberra, A.C.T. 2601 (Australia)

(Received May 9th, 1984)

Summary

The η-hexamethylbenzenehydridoruthenium(II) complexes $RuHCl(\eta\text{-}C_6Me_6)L$ (L = PPh_3 (**11**), $AsPh_3$ (**12**), $P(C_6H_4\text{-}p\text{-}F)_3$ (**14**), $P(C_6H_4\text{-}p\text{-}Me)_3$ (**15**), $P(C_6H_4\text{-}p\text{-}OMe)_3$ (**16**), P-t-$BuPh_2$(**17**), P-i-$PrPh_2$(**18**), P-i-Pr_3 (**19**), PCy_3 (**20**) and P-t-$BuMe_2$ (**21**)) have been made by heating $[RuCl_2(\eta\text{-}C_6Me_6)]_2$, the ligand and sodium carbonate in propan-2-ol. The triarylphosphine complexes **11**, **14** and **15** react with methyllithium to give aryl *ortho*-metallated hydridoruthenium(II) complexes such as $RuH(o\text{-}C_6H_4PPh_2)(\eta\text{-}C_6Me_6)$ (**22**) and **19** similarly gives the isopropyl cyclometallated complex $RuH(CH_2CHMeP\text{-}i\text{-}Pr_2)(\eta\text{-}C_6Me_6)$ (**29**) as a mixture of diastereomers. Reaction of **17** with methyllithium gives initially the t-butyl cyclometallated complex $RuH(CH_2CMe_2PPh_2)(\eta\text{-}C_6Me_6)$ (**25**) which isomerizes by a first order process ($k \sim 0.2\ h^{-1}$ in C_6D_6 or THF-d_8 at 50 °C) to the aryl *ortho*-metallated complex $RuH(o\text{-}C_6H_4P\text{-}t\text{-}BuPh)(\eta\text{-}C_6Me_6)$ (**26**). The similarly generated isopropyl cyclometallated complex $RuH(CH_2CHMePPh_2)(\eta\text{-}C_6Me_6)$ (**27**) has not been isolated in a pure state owing to rapid isomerization to $RuH(o\text{-}C_6H_4P\text{-}i\text{-}PrPh)(\eta\text{-}C_6Me_6)$ (**28**); both **27** and **28** exist as a pair of diastereomers. The formation of the cyclometallated complexes and the isomerizations are thought to involve intermediate 16-electron ruthenium(0) complexes $Ru(\eta\text{-}C_6Me_6)L$.

Introduction

We reported briefly several years ago that when the η-hexamethylbenzeneruthenium(II) complex $RuCl_2(\eta\text{-}C_6Me_6)(PPh_3)$ ** is heated with propan-2-ol

* Dedicated to Prof. S. Otsuka.

** Abbreviations: Me, methyl; i-Pr, isopropyl; Cy, cyclohexyl.

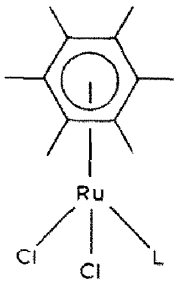
0022-328X/84/$03.00

and aqueous sodium carbonate, one of the chloride ligands is replaced by hydride to give $RuHCl(\eta\text{-}C_6Me_6)(PPh_3)$ [1]. Compounds of this type represent possible precursors to highly reactive, 16-electron ruthenium(0) fragments of general formula $Ru(\eta\text{-}C_6Me_6)(PR_3)$. Recently, the isolectronic rhodium(I) and iridium(I) species $M(\eta\text{-}C_5Me_5)(PMe_3)$ (M = Rh, Ir) have been generated by photoinduced elimination of dihydrogen from the dihydrides $MH_2(\eta\text{-}C_5Me_5)(PMe_3)$ and have been shown to oxidatively add the C–H bonds of alkanes and arenes [2–4]. Similar behaviour has been found for the 16-electron fragment $Ir(\eta\text{-}C_5Me_5)(CO)$ formed by photolysis of $Ir(\eta\text{-}C_5Me_5)(CO)_2$ [5]. The complex $RhH(Me)(\eta\text{-}C_5Me_5)(PMe_3)$, made by hydride reduction of $[RhMe(\eta\text{-}C_5Me_5)(THF)(PMe_3)]PF_6$ at $-40\,^{\circ}C$, has also been shown to lose methane on reaction with C_6D_6 to give $RhD(C_6D_6)(\eta\text{-}C_5Me_5)(PMe_3)$, and presumably the highly reactive species $Rh(\eta\text{-}C_5Me_5)(PMe_3)$ is an intermediate in this reaction [4]. During the course of our work, it was reported [6] that photolysis of either $RuH_2(\eta\text{-}C_6H_6)(P\text{-}i\text{-}Pr_3)$ or $RuH_2(\eta\text{-}C_6Me_6)(PMe_3)$ in aromatic solvents affords hydridoaryl complexes $RuH(aryl)(\eta\text{-}C_6H_6)(P\text{-}i\text{-}Pr_3)$ and $RuH(aryl)(\eta\text{-}C_6Me_6)(PMe_3)$, respectively. In cyclohexane, irradiation of $RuH_2(\eta\text{-}C_6H_6)(P\text{-}i\text{-}Pr_3)$ does not give a hydridocyclohexyl derivative, rather the presumed intermediate $Ru(\eta\text{-}C_6H_6)(P\text{-}i\text{-}Pr_3)$ undergoes cyclometallation to give a hydrido ruthenium(II) complex $RuH(CH_2CHMeP\text{-}i\text{-}Pr_2)(\eta\text{-}C_6H_6)$. In this paper we describe the synthesis of a series of monohydrido-η-hexamethylbenzene complexes $RuHCl(\eta\text{-}C_6Me_6)$-(ligand) and present evidence for the generation from them of the unsaturated fragments $Ru(\eta\text{-}C_6Me_6)$(ligand).

Results and discussion

Cleavage of the chloride bridges of $[RuCl_2(\eta\text{-}C_6Me_6)]_2$ with various Group V donor ligands (L) gives monomeric compounds $RuCl_2(\eta\text{-}C_6Me_6)L$ (L = PPh_3 (**1**), $AsPh_3$ (**2**), $SbPh_3$ (**3**), $P(C_6H_4\text{-}p\text{-}F)_3$ (**4**), $P(C_6H_4\text{-}p\text{-}Me)_3$ (**5**), $P(C_6H_4\text{-}p\text{-}OMe)_3$ (**6**), P-i-$PrPh_2$ (**7**), P-t-$BuPh_2$ (**8**), P-i-Pr_3 (**9**) and P-t-$BuMe_2$ (**10**)) as orange or red, air-stable solids. The preparation of the triisopropylphosphine and diphenyl-t-butylphosphine complexes requires a fourfold excess of ligand, whereas the other members of the series can be made satisfactorily by use of the stoichiometric quantity of ligand. The corresponding complexes containing tricyclohexylphosphine (PCy_3) and di-t-butylphenylphosphine (P-t-Bu_2Ph) could not be made from $[RuCl_2(\eta\text{-}C_6Me_6)]_2$ and the ligands, even when the latter were in large excess.

The IR spectra of the complexes (Table 1) in the solid state show the two ν(Ru–Cl) bands in the region 260–300 cm^{-1} expected for a piano-stool structure. The triphenylphosphine complex has been prepared independently by Werner and Kletzin [7], who have also made the corresponding diphenylmethylphosphine and trimethylphosphine compounds. The ^1H NMR spectra of complexes **1**–**7** and **10** (Table 1) show a singlet due to the methyl protons of hexamethylbenzene in addition to the resonances arising from the Group V donor ligand, and the $^{31}P\{^1H\}$ NMR spectra of the tertiary phosphine complexes **1**, **4**, **5**, **6**, **7** and **9** show just the expected singlet. In the case of the P-t-$BuPh_2$ complex (**8**), the ^1H NMR spectrum in CD_2Cl_2 shows a resonance at δ 1.99 ppm due to $[RuCl_2(\eta\text{-}C_6Me_6)]_2$ of about 20% of the intensity of the singlet at δ 1.53 ppm due to the complex. In the $^{31}P\{^1H\}$ NMR spectrum recorded in $CDCl_3$ there is a small singlet at δ 17.9 ppm assignable to free



(1 – 10)

(L = PPh_3 (1), $AsPh_3$ (2), $SbPh_3$ (3), $P(C_6H_4\text{-}p\text{-}F)_3$ (4), $P(C_6H_4\text{-}p\text{-}Me)_3$ (5), $P(C_6H_4\text{-}p\text{-}OMe)_3$ (6), P-i-$PrPh_2$ (7), P-t-$BuPh_2$ (8), P-i-Pr_3 (9), P-t-$BuMe_2$ (10))

P-t-$BuPh_2$ (lit. δ 17.3 ppm [8]) in addition to the main singlet at δ 24.0 ppm due to the complex. The $^{31}P\{^1H\}$ NMR spectrum of **9** in $CDCl_3$ has three singlets at δ 37.0, 28.6 and 20.7 ppm in an approximate ratio of 2/2/1, the last of which is due to free P-i-Pr_3 (lit. δ 19.4 ppm, solvent not specified [9]). Addition of this ligand causes a slight increase in the relative intensity of the peak at δ 28.6 ppm. In contrast, the $^{31}P\{^1H\}$ NMR spectrum of the benzene complex $RuCl_2(\eta\text{-}C_6H_6)$(P-i-$Pr_3$) in $CDCl_3$ shows only the expected singlet at δ 40.3 ppm [10]. Although the nature of the species present in solutions of **9** has not been studied further, the results suggest that $RuCl_2(\eta\text{-}C_6Me_6)L$ complexes containing bulky tertiary phosphines are sterically crowded, thus accounting for our failure to make the corresponding PCy_3 and P-t-Bu_2Ph complexes.

When $RuCl_2(\eta\text{-}C_6Me_6)(PPh_3)$ is heated with sodium carbonate dissolved in aqueous propan-2-ol, the yellow hydrido complex $RuHCl(\eta\text{-}C_6Me_6)(PPh_3)$ (**11**) precipitates in ca. 35% yield. A better yield (ca. 60%) is obtained by heating a mixture of $[RuCl_2(\eta\text{-}C_6Me_6)]_2$, an approximately threefold excess of triphenylphosphine and anhydrous Na_2CO_3 in anhydrous propan-2-ol. This method also works well for triphenylarsine, triphenylstibine and tri-*p*-fluorophenylphosphine and for bulky tertiary phosphines having a cone angle greater than that of PPh_3 (145°). In this way the complexes $RuHCl(\eta\text{-}C_6Me_6)L$ (L = $AsPh_3$ (**12**), $SbPh_3$ (**13**), $P(C_6H_4\text{-}p\text{-}F)_3$ (**14**), P-t-$BuPh_2$ (**17**), P-i-$PrPh_2$ (**18**), P-i-Pr_3 (**19**) and PCy_3 (**20**)) were formed as yellow or orange crystalline solids in yields of 35–70%. Attempts to prepare the analogous hydride containing P-t-Bu_2Ph were unsuccessful. When present in large excess, tri-*p*-tolylphosphine and tri-*p*-anisylphosphine readily displace coordinated hexamethylbenzene, so the hydride complexes of these ligands are best made either from $RuCl_2(\eta\text{-}C_6Me_6)L$ or from $[RuCl_2(\eta\text{-}C_6Me_6)]_2$ and four mols of ligand per mol of dimer. Complex $RuHCl(\eta\text{-}C_6Me_6)\{P(C_6H_4\text{-}p\text{-}OMe)_3\}$ (**16**) proved difficult to purify and the $^{31}P\{^1H\}$ NMR spectrum showed the presence of impurities, including $RuCl_2(\eta\text{-}C_6Me_6)\{P(C_6H_4\text{-}p\text{-}OMe)_3\}$. The complex $RuHCl(\eta\text{-}C_6Me_6)$(P-

(Continued on p. 194)

TABLE 1

SPECTROSCOPIC DATA FOR COMPLEXES $RuCl_2(\eta\text{-}C_6Me_6)L$

L	IR	NMR		
	ν(Ru–Cl) (cm^{-1}) [a]	δ(P) (ppm) [b]	$\delta(C_6Me_6)$ (ppm) [c]	Other (ppm) [c]
PPh_3 (**1**)	295, 280	30.4	1.70	6.8–7.6(m, C_6H_5)
$AsPh_3$ (**2**)	308, 295		1.82	6.8–7.6(m, C_6H_5)
$SbPh_3$ (**3**)	280, 265		1.84	6.8–7.6(m, C_6H_5)
$P(C_6H_4\text{-}p\text{-}F)_3$ (**4**)	295, 280	28.0	1.84	6.4–7.7(m, C_6H_4)
$P(C_6H_4\text{-}p\text{-}Me)_3$ (**5**)	290, 275	28.0	2.04	1.76(s, C_6H_4Me), 7.0–7.2, 7.5–7.8(m, C_6H_4Me)
$P(C_6H_4\text{-}p\text{-}OMe)_3$ (**6**)	295, 275	26.0	1.78	3.8(s, OMe), 6.7–6.9, 7.5–7.8(m, C_6H_4)
P-i-$PrPh_2$ (**7**)	295, 275	27.7	1.63	0.83[dd, ^3J(PH) 15, $3J$(HH) 7, $CHMe_2$], 3.46[m, $CHMe_2$], 7.3–7.5, 7.8–8.1(m, C_6H_5)
P-t-$BuPh_2$ (**8**)	291, 280(brsh)	24.0(br), 17.9 [d]	1.99, 1.53	1.04[d, ^3J(PH) 13, CMe_3], 7.3–7.5, 8.1–8.4(m, C_6H_5)
P-i-Pr_3 (**9**)	296, 282(brsh)	37.0, 28.6, 20.7 [d]	2.00 [d]	1.1–1.5(m, $CHMe_2$), 2.3–2.9(m, $CHMe_2$) [d]
P-t-$BuMe_2$ (**10**)	296(br)	25.1 [d]	2.06 [d]	1.19[d, ^3J(PH) 13.2, CMe_3], 1.38[d, ^2J(PH) 9.8, PMe] [d]

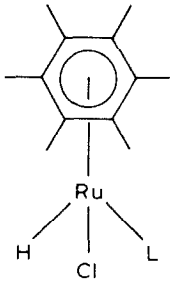
[a] Measured in polythene discs. [b] In CD_2Cl_2 at 28°C except where indicated otherwise; δ(P) in ppm. [c] In CD_2Cl_2 except where indicated otherwise, to high frequency (taken as positive) of external 85% H_3PO_4 couplings in Hz. [d] In $CDCl_3$.

TABLE 2

SPECTROSCOPIC DATA FOR COMPLEXES $RuHCl(\eta\text{-}C_6Me_6)L$

L	IR		NMR			
	ν(Ru–H) (cm^{-1}) [a]	ν(Ru–Cl) (cm^{-1}) [b]	δ(P) (ppm) [c]	δ(Ru–H)(ppm) [^2J(PH)] (Hz) [c]	$\delta(C_6Me_6)$ (ppm) [c]	Other (ppm) [c]
PPh_3 (**11**)	1935 [d]	295	57.1	−8.34(56)	1.70	6.9–7.1, 7.7–8.0(m, C_6H_5)
$AsPh_3$ (**12**)	1925	296		−7.32	1.78	6.9–7.1, 7.8–7.9(m, C_6H_5)
$SbPh_3$ (**13**)	1900	298		−7.16	1.89	7.0–7.2, 7.8–7.9(m, C_6H_5)
$P(C_6H_4\text{-}p\text{-}F)_3$ (**14**)	1955	302	55.9	−8.56(55)	1.62	6.6–6.8, 7.5–7.7(m, C_6H_4) [e]
$P(C_6H_4\text{-}p\text{-}Me)_3$ (**15**)	1955	302	55.9	−8.21(54)	1.76	2.00(s, C_6H_4Me), 6.9–7.0, 7.8–8.0(m, C_6H_4Me)
$P(C_6H_4\text{-}p\text{-}OMe)_3$ (**16**)	1920	292	52.5	−8.21(55)	1.79	3.22(s, OMe), 6.7–6.8, 7.8–8.0(m, C_6H_4)
P-t-$BuPh_2$ (**17**)	1965	292	69.8	−8.54(56)	1.58	1.25[d, ^3J(PH) 14, CMe_3], 6.9–8.5(m, C_6H_5)
P-i-$PrPh_2$ (**18**)	1940	295	64.4	−8.49(50)	1.64	0.80[dd, ^3J(PH) 14.9, ^3J(HH) 7], 1.10[dd, ^3J(PH) 18.6, ^3J(HH) 6.8](CHMe_2), 3.65[m, C$H$$Me_2$], 7.0–7.3, 7.8–8.1(m, C_6H_5)
P-i-Pr_3 (**19**)	1980	295	68.9	−9.13(52)	1.89	1.17–1.20[overlapping dd, ^3J(HH) 7, ^3J(PH) 12, CHMe_2], 2.05–2.55[m, C$H$$Me_2$]
PCy_3 (**20**)	2010	287	58.9	−9.18(55)	1.94	1.0–2.3(br m, C_6H_{11})
P-t-$BuMe_2$ (**21**)	1960	298	33.1	−9.52(58)	1.88	1.01[d, ^2J(PH) 9.8, PMe], 1.06[d, ^3J(PH) 13.2, CMe_3], 1.34[d, ^2J(PH) 8.8, PMe]

[a] KBr disc. [b] Polythene disc. [c] Measured in C_6D_6. [d] In KBr disc and CH_2Cl_2 solution. [e] δ(F) −116.1 ppm relative to $CFCl_3$.



(**11** – **21**)

(L = PPh_3 (**11**), $AsPh_3$ (**12**), $SbPh_3$ (**13**), $P(C_6H_4\text{-}p\text{-}F)_3$ (**14**), $P(C_6H_4\text{-}p\text{-}Me)_3$ (**15**), $P(C_6H_4\text{-}p\text{-}OMe)_3$ (**16**), P-t-$BuPh_2$ (**17**), P-i-$PrPh_2$ (**18**), P-i-Pr_3 (**19**), PCy_3 (**20**), P-t-$BuMe_2$ (**21**))

t-$BuMe_2$) (**21**) was prepared satisfactorily by heating $RuCl_2(\eta\text{-}C_6Me_6)$(P-t-$BuMe_2$) (**10**) with Na_2CO_3/propan-2-ol.

The IR spectra of the hydrido complexes show a band of medium intensity in the range 1920–1980 cm^{-1} due to ν(Ru–H) and a band at ca. 300 cm^{-1} assignable to ν(Ru–Cl) (Table 2). The value of ν(Ru–H) for the PCy_3 complex is exceptionally high (2010 cm^{-1}). In the ^1H NMR spectra of the tertiary phosphine complexes (Table 2) the hydride resonance appears as a doublet [^2J(PH) ca. 50 Hz] in the range δ −7 to −10 ppm; in the triphenylarsine and triphenylstibine complexes the hydride resonance is a singlet as expected. Since the metal atom in $RuHCl(\eta\text{-}C_6Me_6)L$ is a chiral centre, the P–CH_3 groups in **21** (L = P-t-$BuMe_2$) and the isopropylmethyl groups in **18** (L = P-i-$PrPh_2$) and **19** (L = P-i-Pr_3) should be diastereotopic. In agreement, the P–CH_3 resonances of **21** are a pair of doublets and the isopropylmethyl resonances of **18** and **19** appear as two equally intense doublets of doublets owing to coupling with the methine proton and with ^{31}P. The $^{31}P\{^1H\}$ NMR spectra of the tertiary phosphine complexes $RuHCl(\eta\text{-}C_6Me_6)L$ show a singlet which is generally ca. 30 ppm to higher field than that of the corresponding $RuCl_2(\eta\text{-}C_6Me_6)L$ complexes, though in the case of L = P-t-$BuMe_2$ the shift is only 8 ppm.

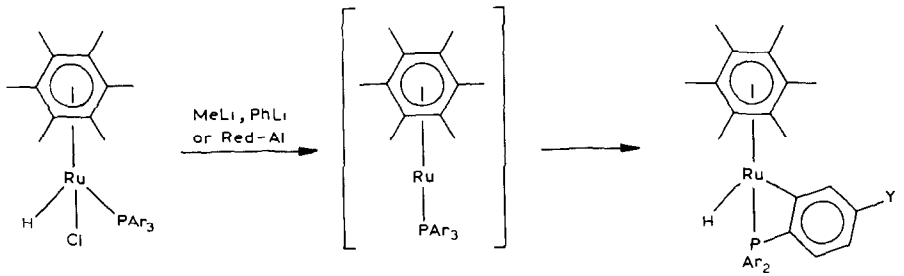
Reaction of **11** with methyllithium gives, after methanolysis, a yellow-green, crystalline compound of empirical formula $Ru(\eta\text{-}C_6Me_6)(PPh_3)$ (**22**) in ca. 50% yield. The mass spectrum shows a monomer parent-ion peak and the IR spectrum exhibits bands characteristic of *ortho*-metallated triphenylphosphine [11–13] at 1550, 1410 and 720 cm^{-1}, in addition to a band at 1940 cm^{-1} due to ν(Ru–H). The ^1H NMR spectrum shows a singlet due to C_6Me_6 and a doublet hydride resonance at δ −7.58 ppm (^2J(PH) 41 Hz), the chemical shift being to lower field and the magnitude of the P–H coupling being less than in the starting hydride **11**. The singlet in the $^{31}P\{^1H\}$ NMR spectrum of **22** is at δ −8.4 ppm, ca. 65 ppm to higher field than for **11**; this upfield shift is characteristic of four-membered rings contain-

ing phosphorus [14]. These data are in accord with the *ortho*-metallated structure $RuH(o\text{-}C_6H_4PPh_2)(\eta\text{-}C_6Me_6)$ for **22**.

The complexes $RuHCl(\eta\text{-}C_6Me_6)\{P(C_6H_4\text{-}p\text{-}F)_3\}$ (**14**) and $RuHCl(\eta\text{-}C_6Me_6)\text{-}\{P(C_6H_4\text{-}p\text{-}Me)_3\}$ (**15**) also react with methyllithium to give the analogous cyclometallated complexes **23** and **24**. The ^{19}F NMR spectrum of **23** shows three resonances arising from the fluorine atom in the *ortho*-metallated ring and the fluorine atoms in the diastereotopic non-metallated rings. The ^1H NMR spectrum of **24** shows two *p*-tolyl methyl resonances in a 2/1 ratio, probably due to the accidentally isochronous methyl protons in the non-metallated rings and those in the *ortho*-metallated ring respectively.

Complex **22** is also formed on reaction of **11** with phenyllithium or with a large excess of Red-Al, $Na[AlH_2(OCH_2CH_2OMe)_2]$, at room temperature. The reactions of **11** with MeLi or PhLi probably give initially hydrido(methyl) or hydrido(phenyl) complexes of ruthenium(II), $RuHR(\eta\text{-}C_6Me_6)(PPh_3)$ (R = Me, Ph), although these could not be detected even when the reactions were carried out at −78°C. They must readily lose methane or benzene to give the highly reactive ruthenium(0) species $Ru(\eta\text{-}C_6Me_6)(PPh_3)$, which rapidly isomerizes by intramolecular attack on the C–H bonds of the triphenylphosphine ligand (Scheme 1). This idea is supported

SCHEME 1. Formation of *ortho*-metallated complexes (Ar = C_6H_4-*p*-Y; Y = H (**22**), F (**23**), Me (**24**)).



by the observation that **22** is also formed by $NaBH_4$ reduction of the methylruthenium(II) complex $RuMe(O_2CCF_3)(\eta\text{-}C_6Me_6)(PPh_3)$ [7]. However another species is also formed in this reaction which is being studied further.

The reaction of $RuHCl(\eta\text{-}C_6Me_6)(PPh_3)$ (**11**) with methyllithium can be compared with the corresponding reaction of $RuHCl(PPh_3)_3$ [13]. In the latter case, a yellow compound believed to be the hydrido(methyl) complex $RuH(Me)(PPh_3)_2\text{-}(Et_2O)_2$ can be isolated at 0°C, but this readily eliminates methane in THF to give the *ortho*-metallated complex $RuH(o\text{-}C_6H_4PPh_2)(PPh_3)(THF)_2$.

It is also noteworthy that the iridium(I) fragment $Ir(\eta\text{-}C_5Me_5)(PPh_3)$, when generated by photolysis of $IrH_2(\eta\text{-}C_5Me_5)(PPh_3)$ in benzene, gives approximately equal amounts of $IrH(o\text{-}C_6H_4PPh_2)(\eta\text{-}C_5Me_5)$ and $IrH(Ph)(\eta\text{-}C_5Me_5)(PPh_3)$ [2]. The latter must be less prone than the analogous $Ru(\eta\text{-}C_6Me_6)$ compound to undergo reductive elimination to give the cyclometallated product.

When $RuHCl(\eta\text{-}C_6Me_6)(P\text{-}t\text{-}BuPh_2)$ (**17**) is allowed to react with methyllithium at −78°C and the mixture is worked up as soon as possible, a white hydrido complex is isolated in ca. 60% yield. Analytical and spectroscopic data (Table 3) show that this compound is $RuH(CH_2CMe_2PPh_2)(\eta\text{-}C_6Me_6)$ (**25**) in which the

TABLE 3

IR, ^1H AND ^{31}P NMR DATA FOR CYCLOMETALLATED COMPLEXES

Complex	IR		NMR			
	ν(Ru–H) (cm^{-1}) [a]	*Ortho*-metallation bands (cm^{-1}) [a]	δ(P) (ppm) [b]	δ(Ru–H) (ppm) [^2J(PH)] (Hz) [b]	δ(C_6Me_6) (ppm) [b]	Other (ppm) [b]
RuH(*o*-$C_6H_4PPh_2$)(η-C_6Me_6) (**22**)	1940	1550,1410, 720	−8.4	−7.58(41)	1.95	6.7–8.1(m, C_6H_4 and C_6H_5)
RuH{*o*-C_6H_3-*p*-F)P(C_6H_4-*p*-F)$_2$}-(η-C_6Me_6) (**23**)	1903		−6.8	−7.92(40)	1.84	6.7–8.0(m, C_6H_3 and C_6H_4) [c]
RuH{*o*-C_6H_3-*p*-Me)P(C_6H_4-*p*-Me)$_2$}-(η-C_6Me_6) (**24**)	1905	1555,1410, 730	−8.9	−7.56(40)	2.03	2.04(s, C_6H_4*Me*), 2.33(s, C_6H_3*Me*), 6.7–8.0(m, C_6H_3Me and C_6H_4Me)
RuH($CH_2CMe_2PPh_2$)(η-C_6Me_6) (**25**)	1960		26.3 [d]	−8.82(46) [e]	1.97	1.02[dd,^2J(H^AH^B) 7.3, ^3J(PH) ca.4, CH^AH^B] [d], 1.33[d,^3J(PH) 15.6], 1.35[d,^3J(PH) 14.2](CMe$_2$), 1.39[m,^3J(PH) ca.29, ^3J($H^{Ru}H$) ca.3, CH^AH^B] [d], 7.0–7.8(m, C_6H_5)
RuH(*o*-C_6H_4P-t-BuPh)(η-C_6Me_6) (**26**)	1955	1555,1413 728	13.1 [d]	−7.96(40)	1.93	1.23[d, ^3J(PH) 14.2, CMe_3], 6.7–8.0(m, C_6H_4 and C_6H_5)
RuH($CH_2CHMePPh_2$)(η-C_6Me_6) (**27a**) and (**27b**)	1910		12.5,9.0 [d]	−8.17(45) [e] −8.90(49) [f]	1.93,2.01	
RuH(*o*-C_6H_4P-i-PrPh)(η-C_6Me_6) (**28a**) and (**28b**)	1973	1557,1413, 728	4.2 (**28a**) −1.9 (**28b**)	−8.03(41)	1.93 (**28a**) 2.11 (**28b**)	1.16[dd,^3J(PH) 15.6, ^3J(HH) 7.8], 1.20[dd,^3J(PH) 16.6, ^3J(HH) ca.7] (CH*Me*$_2$), 6.5–7.6(m,C_6H_4 and C_6H_5)
RuH(CH_2CHMeP-i-Pr_2)(η-C_6Me_6) (**29**)	1900		33.4,21.0 (2/1 ratio)	−9.47(47) [e] −9.91(46) [g] (1/2 ratio)	2.10	0.15–0.3, 0.8–2.0(m,CH*Me*$_2$ and CH_2), 2.6–2.9, 3.2–3.4(m,CH)

[a] KBr disc [b] Measured in C_6D_6, except where indicated otherwise. [c] δ(F) −108.8, −109.2, −110.6 ppm relative to $CFCl_3$. [d] In toluene-d_8 at −10 °C. [e] Additional small H–H couplings present. [f] Additional splitting of ca. 3 Hz observed owing to coupling with one of methylene protons (H^B). [g] Additional splitting of ca. 2.5 Hz observed owing to coupling with one of methylene protons.

t-butyl methyl group has been metallated. There are no bands in the IR spectrum attributable to *ortho*-metallated arylphosphines, although there is a ν(Ru–H) band at 1960 cm^{-1}. The hydride resonance in the ^1H NMR spectrum appears as a doublet of doublets at δ −8.82 ppm owing to coupling with one of the methylene protons as well as with phosphorus (^2J(PH) 46 Hz, ^3J(HH) ca. 3 Hz). The remaining t-butyl-methyl groups are diastereotopic, as expected, appearing as a pair of doublets at δ 1.35 ppm (^3J(PH) 14.2 Hz) and δ 1.33 ppm (^3J(PH) 15.6 Hz). The diastereotopic methylene protons form a complex pattern which simplifies to an AB quartet when decoupled from both ^{31}P and Ru–*H* (see Table 3 for chemical shifts and coupling constants). In the $^{13}C\{^1H\}$ NMR spectrum (Table 4) there are four resonances arising from the tertiary carbon atom, the methylene carbon atom and the diastereotopic methyl carbon atoms, in addition to the usual aromatic and hexamethylbenzene carbon signals; with the exception of one of the methyl carbon atoms, all ^{13}C nuclei associated with the chelate ring are coupled to ^{31}P. The $^{31}P\{^1H\}$ NMR spectrum consists of a singlet which is shifted 44 ppm upfield of that due to **17** consistent with the presence of a four-membered ring.

If **17** is treated with methyllithium and the reaction mixture is subsequently heated to 70 °C for 4 h, a dark brown solution is formed from which, after methanolysis, a yellow *ortho*-metallated aryl hydrido complex RuH(o-C_6H_4P-t-BuPh)(η-C_6Me_6) (**26**), isomeric with **25**, is isolated in ca. 40% yield. The IR spectrum shows a ν(Ru–H) band at 1955 cm^{-1} and bands typical of an *ortho*-metallated phenyl group at 1555, 1413 and 728 cm^{-1}. The ^1H NMR spectrum of **26** shows just a doublet at δ 1.23 ppm (^3J(PH) 14.2 Hz) for the t-butyl protons and a doublet hydride resonance at δ −8.0 ppm (^2J(PH) 40 Hz). The singlet in the $^{31}P\{^1H\}$ NMR spectrum is ca. 57 ppm upfield of that in **17**, suggesting that **26**, like **25**, contains a four-membered ring.

If the reaction between **17** and methyllithium is carried out at room temperature, a mixture of **25** and **26** is formed, but if the solution is allowed to stand at room temperature for several days the hydride resonance of **25** disappears and that of **26** increases. The isomerization (Scheme 2) is conveniently monitored by following the decay of the peak at δ 26.3 ppm due to **25** and the appearance of the peak at δ 13.1 ppm due to **26** in the $^{31}P\{^1H\}$ NMR spectrum. In both C_6D_6 and THF-d_8 at 50 °C a second product characterized by a ^{31}P NMR singlet at δ 7.9 ppm is formed as **25**

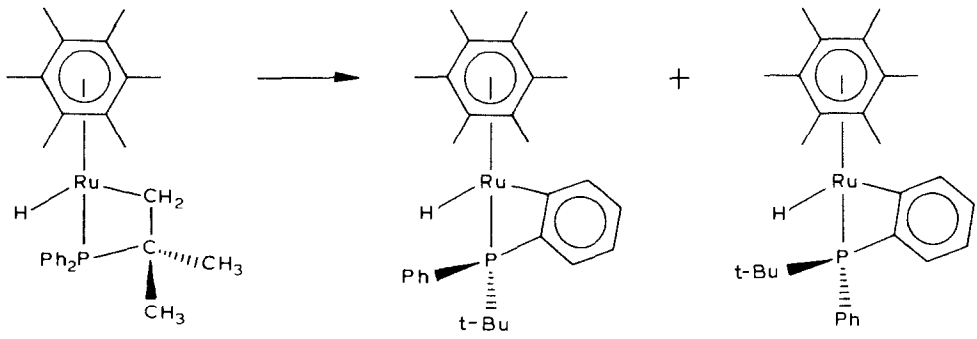
TABLE 4

^{13}C NMR DATA FOR CYCLOMETALLATED COMPLEXES [a]

Complex	$\delta(C_6Me_6)$ (ppm) [^2J(PC)] (Hz)	$\delta(C_6\mathit{Me}_6)$ (ppm)	Other [J(PC)Hz] (Assignment) [b]
22	96.8(2.9)	17.0	
23	97.4(0)	16.9	
24	96.5(2.9)	17.1	22.7(0)(C_6H_3-*p*-Me), 21.2(0)(C_6H_4-*p*-*Me*)
25	94.8(0)	17.0	54.6(35.2)(CMe$_2$), 30.9(2.9), 30.7(0)(C*Me*$_2$), 11.4(42.5)(CH_2)
27	96.3(2.9)	17.0	28.0(5.9)(C*Me*$_3$)
28	96.3(0)	17.0	28.9(22.0)(CHMe$_2$), 20.8(4.4), 18.9(0)(CH*Me*$_2$)
29a/29b	93.2(0), 93.0(0)	17.8, 17.7	17–46(CHMe$_2$, CH_2)

[a] Measured in C_6D_6. [b] Aryl carbon resonances appeared in the region δ 120 ppm.

SCHEME 2. Isomerization of t-butyl cyclometallated complex to diasteromeric aryl *ortho*-metallated complexes.



(25) (26a) (26b)

disappears, its concentration being about 10% that of the main product. In **26** both ruthenium and phosphorus are chiral centres, so that a pair of diastereomers **26a** and **26b** can exist. We suggest that the major isomer (δ(P) 13.1 ppm) has structure **26a** in which the phenyl group on phosphorus points towards the C_6Me_6 ring and that the minor isomer (δ(P) 7.9 ppm) has structure **26b** in which the more bulky t-butyl group points towards the C_6Me_6 ring. The minor isomer is evidently removed during the preparative work-up and we have not attempted to isolate it.

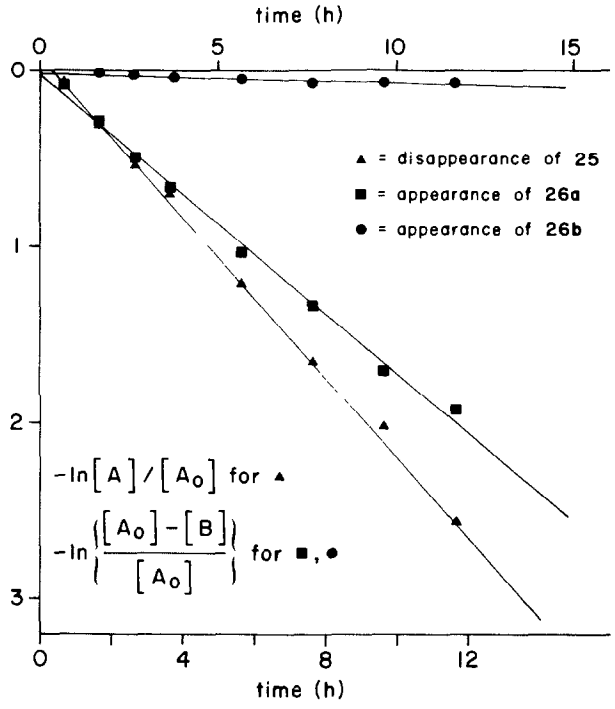
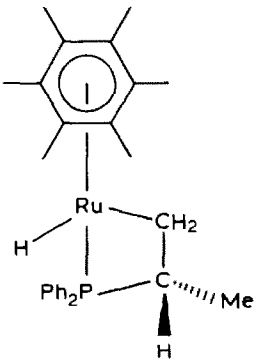
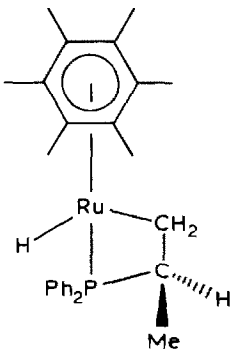


Fig. 1. First order rate plot for the isomerization of $\overline{RuH(CH_2CMe_2PPh_2)(\eta\text{-}C_6Me_6)}$ (**25**) to $\overline{RuH(o\text{-}C_6H_4P\text{-}t\text{-}BuPh)(\eta\text{-}C_6Me_6)}$ (diastereomeric mixture of **26a** and **26b**).

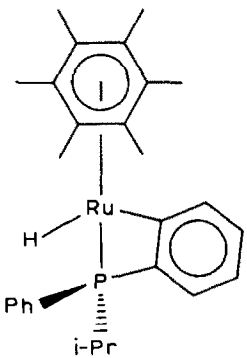
The disappearance of **25** follows first order behaviour (Fig. 1), the rate constants at 50 °C being equal within experimental error in C_6D_6 and THF-d_8 (0.23 ± 0.03 h^{-1} and 0.19 ± 0.04 h^{-1} respectively). The rates of formation of the diastereomers of **26** are also first order in complex, the rate constants being 0.17 ± 0.03 h^{-1} (C_6D_6) and 0.13 ± 0.01 h^{-1} (THF-d_8) for **26a** and $5.7 \pm 7.7.10^{-3}$ h^{-1} (C_6D_6) and $6.6 \pm 1.3.10^{-3}$ h^{-1} (THF-d_8) for **26b**.

The solid obtained from the reaction of RuHCl(η-C_6Me_6)(P-i-$PrPh_2$) (**18**) with methyllithium, even at low temperature, shows three hydride resonances in its ^1H NMR spectrum, a doublet at δ −8.03 ppm (^2J(PH) 41 Hz), an approximate doublet of triplets at δ −8.17 ppm (^2J(PH) 45 Hz) and a doublet of doublets at δ −8.90 ppm (^2J(PH) 49 Hz, ^3J(HH) ca. 2 Hz). On heating the sample at 60 °C in toluene for 4 h, the last two resonances disappear and they are therefore assigned to the diastereomers of the isopropyl cyclometallated product (**27a** and **27b**), in this case,

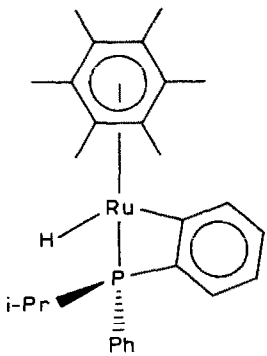




the chiral centres are at ruthenium and at the methine carbon atom. The presence of these two isomers is also evident from the presence of singlets at δ 12.5 and 9.0 ppm in the $^{31}P\{^1H\}$ NMR spectrum. The IR spectrum of the product isolated after isomerization is complete has bands characteristic of Ru–H and of aryl cyclometallation. Its $^{31}P\{^1H\}$ NMR spectrum shows two singlets at δ 4.2 and −1.9 ppm, the



(28a)



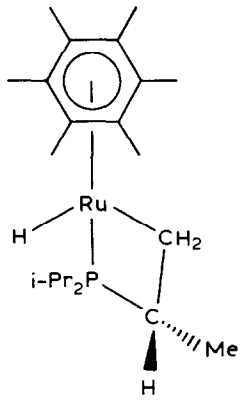
(28b)

ratio of the peak heights being about 10/1. These are assigned to the diastereomers **28a** and **28b** which arise from the chiral centres at ruthenium and phosphorus. Attempts to separate these diastereomers or to obtain **27a/27b** free from **28a/28b** have not been successful since, qualitatively, the isomerization of **27** to **28** occurs more rapidly than that of **25** to **26**. The isopropyl methyl groups in **28a** are diastereotopic and appear as a pair of doublets of doublets (Table 3); those of **28b** could not be located.

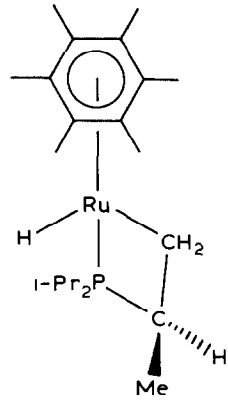
Cyclometallation of a wide range of tertiary phosphines has been established for many metals [15]. However, there are relatively few examples of cyclometallation at two different sites of a tertiary phosphine and isomerization from one to another does not seem to have been demonstrated. Vrieze et al. [16] have reported that when $[IrCl(C_8H_{14})_2]_2$ (C_8H_{14} = cyclooctene) is heated with P-t-Bu_2-n-Pr in the presence of γ-picoline, isomers of the type IrHCl(γ-pic)(PC) can be isolated in 55 and 20% yield in which the n-propyl and t-butyl groups respectively have been metallated. The corresponding reaction with P-t-Bu_2-n-Bu gives predominantly t-butyl metallated product. Depending on reaction conditions, metallation of t-$Bu_2PC_6H_4$-*p*-OMe by platinum(II) can occur either at the methoxyl carbon atom or at oxygen, the methyl group being eliminated as methyl halide in the latter case [17]. There is also evidence for competitive cyclometallation from H–D exchange studies on coordinated tertiary phosphines, although the reported behaviour seems to be markedly dependent on both the ligand and the metal. The complex Pt_2Cl_4(P-t-$BuPh_2)_2$ undergoes H-D exchange in CH_3CO_2D/D_2O in both the *ortho*-positions of the phenyl groups and the t-butyl group, the former being ca. 50 times faster than the latter, whereas in the corresponding P-n-$PrPh_2$ and P-n-Pr_2Ph complexes exchange occurs exclusively in the terminal methyl groups [18]. In contrast, P-n-$PrPh_2$ under D_2 gas in the presence of $RuHCl(PPh_3)_3$ incorporates deuterium into the *ortho*-positions of the aromatic rings and into the α-, β- and γ-positions, the exchange at the methyl group being as rapid as *ortho*-exchange [19].

Our results show that the primary C–H bonds of t-butyl and isopropyl groups in tertiary phosphines are metallated more rapidly by Ru(η-C_6Me_6) than are the corresponding aromatic C–H bonds, although the aryl cyclometallated complexes are thermodynamically the more stable. The isomerization clearly requires that the metallation of the aliphatic C–H bonds is reversible and it must proceed via the 16-electron ruthenium(0) intermediate Ru(η-C_6Me_6)L (L = P-t-$BuPh_2$, P-i-$PrPh_2$).

In an attempt to find further evidence for this intermediate, the reaction of RuHCl(η-C_6Me_6)(P-i-Pr_3) (**19**) with methyllithium was examined. The yellow solid, isolated in 46% yield after recrystallization from n-hexane, has the empirical formula Ru(η-C_6Me_6)(P-i-Pr_3) and shows a ν(Ru–H) band at 1900 cm^{-1} in its IR spectrum. There are two hydride resonances in the ^1H NMR spectrum at δ −9.47 and −9.91 ppm, the former being a broad doublet (^2J(PH) 47 Hz), the latter a doublet of doublets (^2J(PH) 46 Hz, ^3J(HH) 2.5 Hz), and there are two singlets in a ratio of ca. 2/1 in the $^{31}P\{^1H\}$ NMR spectrum. These data are consistent with the presence of a pair of diastereomeric cyclometallation products RuH(CH_2CHMeP-i-Pr_2)(η-C_6Me_6), **29a** and **29b**. The ^1H NMR spectrum in the isopropyl region is very complex (Table 3) because each diastereomer has inequivalent isopropyl groups and inequivalent methylene protons. As mentioned in the Introduction, the analogous η-benzene compound has recently been isolated by photolysis of RuH_2(η-C_6H_6)(P-i-Pr_3) in cyclohexane and is reported to react with benzene to give the hydridophenyl



(29a)



(29b)

$RuH(C_6H_5)(\eta\text{-}C_6H_6)(P\text{-}i\text{-}Pr_3)$ [6]. In contrast, the η-hexamethylbenzene complex **29** is inert towards aromatic solvents, as is evident from the fact that toluene can be used to extract it from the reaction of **19** with methyllithium. Ligands such as $P\text{-}i\text{-}Pr_3$, PPh_3, CO (1 atm) and C_2H_4 (1 atm) also do not react with **29**, presumably because steric strain is most effectively relieved by formation of the cyclometallated complex.

Experimental

All manipulations were carried out in an atmosphere of purified nitrogen or argon using conventional Schlenk and syringe techniques. Diethyl ether, THF and toluene were freshly distilled from sodium benzophenone ketyl, and propan-2-ol was distilled from calcium hydride before use. Tertiary phosphines were either prepared by standard methods or were used as received from commercial suppliers. Methyllithium was bought from Ega Chemie and was standardized before use [20]. The complex $[RuCl_2(\eta\text{-}C_6Me_6)]_2$ was prepared by a literature procedure [21].

The following instruments were used for spectroscopic measurements: ^1H NMR: Varian HA 100, Jeol FX 200, Bruker CXP 200; $^{31}P\{^1H\}$ NMR: Bruker B-KR 322 S (24.29 MHz), Bruker CXP 200 (80.98 MHz); ^{13}C NMR: Jeol FX 200 (50.10 MHz); ^{19}F NMR: Bruker CXP 200 (188.15 MHz); IR: Perkin–Elmer 683 (4000–200 cm^{-1}), Hitachi F1S-3 (400–30 cm^{-1}); Mass spectra: VG Micromass 7070F (70 eV). Analyses and molecular weight determinations (Table 5) were carried out by the ANU Microanalytical Unit.

Preparation of $RuCl_2(\eta\text{-}C_6Me_6)L$ ($L = PPh_3$ (1), $AsPh_3$ (2), $SbPh_3$ (3), $P(C_6H_4\text{-}p\text{-}F)_3$ (4), $P(C_6H_4\text{-}p\text{-}Me)_3$ (5), $P(C_6H_4\text{-}p\text{-}OMe)_3$ (6), $P\text{-}i\text{-}PrPh_2$ (7), $P\text{-}t\text{-}BuMe_2$ (10))

A mixture of $[RuCl_2(\eta\text{-}C_6Me_6)]_2$ (0.30 g, 0.45 mmol) and the ligand (ca. 1 mmol) was suspended in propan-2-ol (50 ml) and heated to reflux for 2 h. The solution was evaporated to dryness under reduced pressure and the residue was recrystallized from chloroform/n-hexane, or dichloromethane/diethyl ether in the case of **10**, yielding red crystals of the product. Yields were 92% (**1**), 85% (**2**), 82% (**3**), 87% (**4**), 92% (**5**), 94% (**6**), 88% (**7**) and 71% (**10**).

TABLE 5

ANALYTICAL AND MOLECULAR WEIGHT DATA

Complex	Analysis (found (calcd.) (%))				Mol wt [a]
	C	H	Cl	P	
$C_{30}H_{33}Cl_2PRu$ (**1**)	60 5	5 5	12 1	5 5	592
	(60.4)	(5 5)	(11 7)	(5.2)	(596)
$C_{30}H_{33}Cl_2AsRu$ (**2**)	55.9	5.3		12.3 (As)	602
	(56 25)	(5.15)		(11 7)	(640)
$C_{30}H_{33}Cl_2SbRu$ (**3**)	51.3	4.7		16 8 (Sb)	682
	(52.5)	(4.8)		(17.8)	(687)
$C_{30}H_{30}Cl_2F_3PRu$ (**4**)	55.5	4.8	11 3	4 9	636
	(55.4)	(4.6)	(10.8)	(4.8)	(650)
$C_{33}H_{37}Cl_2PRu$ (**5**)	62.3	6.85	10.7	4 7	691
	(62.1)	(6 1)	(11.0)	(4.9)	(638)
$C_{33}H_{37}Cl_2O_3PRu$ (**6**)	57.8	5.6	10 1	4.8	681
	(57 7)	(5.7)	(10.2)	(4.5)	(686)
$C_{30}H_{39}Cl_2PRu$ (**7**)	57 5	6 1	12.4	5 4	564
	(57.65)	(6.2)	(12.45)	(5.5)	(562)
$C_{31}H_{41}Cl_2PRu$ (**8**)	57.5	6 4	12 3	5.5	
	(58 3)	(6 5)	(12 3)	(5.4)	
$C_{21}H_{39}Cl_2PRu$ (**9**)	51.0	8 0	14 3	6.35	
	(51 0)	(7.95)	(14.3)	(6.3) [b]	
$C_{18}H_{33}Cl_2PRu$ (**10**)	48 25	7.2	15.5	6.9	
	(48.0)	(7.35)	(15.7)	(6 85)	
$C_{30}H_{39}ClPRu$ (**11**)	63.25	6.1	6.8	5.6	562
	(64.1)	(6 0)	(6 3)	(5 5)	
$C_{30}H_{39}ClAsRu$ (**12**)	59.1	5.4	5 9	12.6 (As)	
	(59.5)	(5.65)	(5 85)	(12 4)	
$C_{30}H_{39}ClSbRu$ (**13**)	54.9	5 3	5.2	18.55 (Sb)	
	(55.2)	(5.25)	(5.4)	(18 65)	
$C_{30}H_{36}ClF_3PRu$ (**14**)	58.2	5.1	5.9	5.3	616
	(58.5)	(5.1)	(5.75)	(5.0) [c]	
$C_{33}H_{42}ClPRu$ (**15**)	66.4	6.7	5.5	5 6	604
	(65 6)	(6.7)	(5.9)	(5 1)	
$C_{33}H_{42}ClO_3PRu$ (**16**)	60.15	6.25	5.2	4.8	652
	(60.8)	(6 2)	(5.4)	(4.75)	
$C_{32}H_{35}ClPRu$ (**17**)	61 45	7.1	6.1	5 65	542
	(62.0)	(7.1)	(6.5)	(5.7)	
$C_{27}H_{41}ClPRu$ (**18**)	60.9	6.7	6.9	6 1	528
	(61.4)	(6.9)	(6 7)	(5.9)	
$C_{21}H_{45}ClPRu$ (**19**)	55.0	8.8	6.85	7.7	460
	(54.8)	(8.8)	(6.7)	(7.4)	
$C_{30}H_{57}ClPRu$ (**20**)	62.3	9.0	6.1	5.6	580
	(62 1)	(9.0)	(6.1)	(5.3)	
$C_{18}H_{54}ClPRu$ (**21**)	52.9	8.5	8.6	7.65	418
	(51.7)	(8.2)	(8.5)	(7 2)	
$C_{30}H_{33}PRu$ (**22**)	68.7	6.5		6.2	526
	(68.55)	(6 3)		(5.9)	
$C_{30}H_{31}F_2PRu$ (**23**)	61.7	5.3		6.0	580
	(62.2)	(5.2)		(5.3) [d]	
$C_{32}H_{37}PRu$ (**24**)	69.2	6.9		5 6	568
	(69.8)	(6.9)		(5 5)	
$C_{28}H_{37}PRu$ (**25**)	67.05	7.8		5 9	506
	(66.5)	(7.4)		(6.1)	
$C_{26}H_{37}PRu$ (**26**)	67 1	7.6		5.9	506
	(66.5)	(7.4)		(6 1)	

TABLE 5 (continued)

Complex	Analysis (found (calcd.) (%))				Mol. wt. [a]
	C	H	Cl	P	
$C_{26}H_{35}PRu$ (**28**)	66.1 (66.0)	7.3 (7.2)		6.2 (6.3)	492
$C_{21}H_{39}PRu$ (**29**)	59.75 (59.55)	9.5 (9.3)		7.4 (7.3)	424

[a] Molecular weights for **1–6** determined by vapour pressure osmometry in CH_2Cl_2 at 30 °C, those for **10** and **14–29** refer to the parent ion ($^{102}Ru^{35}Cl$) observed in the 70 eV mass spectrum. Complexes **11** and **12** did not show parent ions. [b] Ru: found, 20.4; calcd. 20.4%. [c] F: found, 9.0; calcd. 9.25%. [d] F: found 9.2; calcd. 9.8%.

Preparation of $RuCl_2(\eta\text{-}C_6Me_6)(P\text{-}t\text{-}BuPh_2)$ (8)

A suspension of $[RuCl_2(\eta\text{-}C_6Me_6)]_2$ in propan-2-ol (30 ml) was heated with a fourfold excess of P-t-$BuPh_2$ for 4 h. The solvent was removed under reduced pressure and the residue was recrystallized from chloroform/ether giving orange crystals of **8** in 56% yield.

Preparation of $RuCl_2(\eta\text{-}C_6Me_6)(P\text{-}i\text{-}Pr_3)$ (9)

This was prepared similarly to **8**. The solution formed at the end of the reaction was allowed to cool and, after being filtered, it was set aside overnight in a freezer. The precipitate was filtered and washed with ether to give fine orange crystals of **9** in 26% yield.

Preparation of $RuHCl(\eta\text{-}C_6Me_6)(PPh_3)$ (11)

A mixture of $[RuCl_2(\eta\text{-}C_6Me_6)]_2$ (0.61 g, 0.92 mmol), anhydrous sodium carbonate (0.55 g, 5.18 mmol) and triphenylphosphine (1.32 g, 5.03 mmol) was suspended in propan-2-ol (30 ml) and heated to reflux for 15 h. The yellow-brown solution was allowed to cool and was evaporated to dryness under reduced pressure. The residue was extracted with toluene (ca. 60 ml) and the solution was filtered. Evaporation under reduced pressure and addition of n-hexane gave **11** as a fine yellow, microcrystalline powder (0.66 g, 1.17 mmol, 64%).

Similarly prepared (yields in parentheses) were: $RuHCl(\eta\text{-}C_6Me_6)(AsPh_3)$ (**12**) (71%), $RuHCl(\eta\text{-}C_6Me_6)[P(C_6H_4\text{-}p\text{-}F)_3]$ (**14**) (68%), $RuHCl(\eta\text{-}C_6Me_6)(P\text{-}t\text{-}BuPh_2)$ (**17**) (60%), $RuHCl(\eta\text{-}C_6Me_6)(P\text{-}i\text{-}PrPh_2)$ (**18**) (65%), $RuHCl(\eta\text{-}C_6Me_6)(P\text{-}i\text{-}Pr_3)$ (**19**) (58%) and $RuHCl(\eta\text{-}C_6Me_6)(PCy_3)$ (**20**) (57%).

The complex $RuHCl(\eta\text{-}C_6Me_6)[P(C_6H_4\text{-}p\text{-}Me)_3]$ (**15**) was prepared in 46% yield similarly to **11** by use of only a 6% excess of tri-*p*-tolylphosphine over $[RuCl_2(\eta\text{-}C_6Me_6)]_2$ in the reaction mixture.

The complex $RuHCl(\eta\text{-}C_6Me_6)(SbPh_3)$ (**13**) was prepared in 59% yield similarly to **11** but with a heating time of only 3 h. Prolonged heating caused the product to decompose.

Preparation of $RuHCl(\eta\text{-}C_6Me_6)(P\text{-}t\text{-}BuMe_2)$ (21)

A suspension of $RuCl_2(\eta\text{-}C_6Me_6)(P\text{-}t\text{-}BuMe_2)$ (**10**) (2.62 g, 5.79 mmol) and

anhydrous sodium carbonate (2.03 g, 19.1 mmol) in propan-2-ol (50 ml) was heated to reflux for 15 h. The yellow solution was allowed to cool and was evaporated to dryness under reduced pressure. The residue was extracted with toluene, filtered, and the solution was reduced in volume. Addition of n-hexane gave large, deep brown crystals of **21** (1.80 g, 4.30 mmol, 74%).

Preparation of $RuHCl(\eta\text{-}C_6Me_6)[P(C_6H_4\text{-}p\text{-}OMe)_3]$ (16)

This was carried out similarly to that of **21**, the suspension being heated to reflux for 60 h. After removal of solvent, the residue was suspended in toluene, and the solution was filtered through Filter-Aid. The filtrate was evaporated under reduced pressure and n-hexane was added to give fine yellow crystals of **16** in 21% yield.

Preparation of $\overline{RuH(o\text{-}C_6H_4PPh_2)}(\eta\text{-}C_6Me_6)$ (22)

A suspension of $RuHCl(\eta\text{-}C_6Me_6)(PPh_3)$ (**11**) (0.53 g, 0.94 mmol) in toluene (10 ml) was cooled to −78 °C and treated dropwise with a 1.45 *M* solution of methyllithium in ether (1.7 ml, 2.5 mmol). The solution was allowed to stir at room temperature for 2 h. The yellow-brown solution was again cooled to −78 °C and methanol (2 ml) was added dropwise. The thick slurry was allowed to warm to room temperature and the resulting pale yellow solution was evaporated to dryness under reduced pressure. The residue was recrystallized from toluene/n-hexane to give fine, yellow-green crystals of **22** (0.28 g, 0.54 mmol, 58%). An analytical sample was obtained by recrystallization from THF/n-hexane.

Similarly prepared (yields in parentheses) were: $\overline{RuH(o\text{-}C_6H_3\text{-}p\text{-}F)P(C_6H_4\text{-}p\text{-}F)_2}(\eta\text{-}C_6Me_6)$ (**23**) (45%), $\overline{RuH(o\text{-}C_6H_3\text{-}p\text{-}Me)P(C_6H_4\text{-}p\text{-}Me)_2}(\eta\text{-}C_6Me_6)$ (**24**) (67%) and $\overline{RuH(CH_2CHMe)P(i\text{-}Pr)_2}(\eta\text{-}C_6Me_6)$ (diastereomeric mixture of **29a** and **29b**) (46%), the last being recrystallized from n-hexane at −78 °C.

Preparation of $\overline{RuH(o\text{-}C_6H_4P\text{-}t\text{-}BuPh)}(\eta\text{-}C_6Me_6)$ (26) and $\overline{RuH(o\text{-}C_6H_4P\text{-}i\text{-}PrPh)}(\eta\text{-}C_6Me_6)$ (28)

These were prepared similarly to **22** from **17** and **18** respectively except that after the methyllithium had been added the solutions were allowed to come to room temperature and then heated at 60–70 °C for 4 h. The products were isolated in the usual way from the resulting dark brown to black solutions. The yields of **26** and **28** were 41% and 38% respectively.

Preparation of $\overline{RuH(CH_2CMe_2PPh_2)}(\eta\text{-}C_6Me_6)$ (25)

A suspension of $RuHCl(\eta\text{-}C_6Me_6)(P\text{-}t\text{-}BuPh_2)$ (**17**) (0.32 g, 0.59 mmol) in ether (10 ml) was cooled to −78 °C and treated dropwise with a 1.60 *M* solution of methyllithium (1.0 ml, 1.6 mmol). The yellow suspension was stirred in an ice-bath for 3 h, then cooled to −78 °C again and treated dropwise with methanol (1 ml). The suspension was evaporated to dryness under reduced pressure while being maintained at ice-bath temperature. The residue was extracted with cold toluene and the extract was evaporated to dryness under reduced pressure at ice-bath temperature. The pale yellow solid residue was recrystallized from THF/n-hexane by cooling to −78 °C to give **25** as an off-white powder (0.17 g, 0.33 mmol, 55%).

Isomerization of $RuH(CH_2CMe_2PPh_2)(\eta\text{-}C_6Me_6)$ *(25) to* $RuH(o\text{-}C_6H_4P\text{-}t\text{-}BuPh)(\eta\text{-}C_6Me_6)$ *(26)*

A solution containing **25** (70–100 mg) in C_6D_6 or THF-d_8 (2.6 ml) in a 10 mm NMR tube was sealed in vacuo. Its 80.98 MHz $^{31}P\{^1H\}$ NMR spectrum was recorded at 50 °C, spectra being accumulated for 30 min with a pulse repetition rate of 1.0 s, an acquisition time of 0.82 s and a spectral width of 5000 Hz. Integrals of peak areas were used to determine the relative amounts of the three species **25**, **26a** and **26b** present. Rate constants were determined from a least squares fit, the errors quoted being 90% confidence limits [22].

There was no observable NOE difference between the ^{31}P resonances of **25** and **26a/26b** in C_6D_6 at 50 °C. The difference in T_1's would result in a 3% error in the measurement of peak areas under the experimental conditions.

Acknowledgments

We thank Johnson–Matthey for a loan of ruthenium trichloride.

References

1 M.A. Bennett, Tai-Nang Huang, A.K. Smith and T.W. Turney, J. Chem. Soc., Chem. Commun., (1978)582.
2 A.H. Janowicz and R.G. Bergman, J. Am. Chem. Soc., 104(1982)352; 105(1983)3929.
3 W.D. Jones and F.J. Feher, J. Am. Chem. Soc., 104(1982)4240.
4 W.D. Jones and F.J. Feher, Organometallics, 2(1983)562.
5 J.K. Hoyano and W.A.G. Graham, J. Am. Chem. Soc., 104(1982)3723.
6 H. Kletzin and H. Werner, Angew. Chem. Int. Ed. Engl., 22(1983)873.
7 H. Werner and H. Kletzin, J. Organomet. Chem., 228(1982)289.
8 B.E. Mann, C. Masters, B.L. Shaw, R.M. Slade and R.E. Stainbank, Inorg. Nucl. Chem. Lett., 7(1971)881.
9 S.O. Grim and W. McFarlane, Nature, 208(1965)995.
10 H. Werner and H. Kletzin, J. Organomet. Chem., 243(1983)C59.
11 M.A. Bennett and D.L. Milner, J. Am. Chem. Soc., 91(1969)6983.
12 R.J. McKinney, R. Hoxmeier and H.D. Kaesz, J. Am. Chem. Soc., 97(1975)3059.
13 D.J. Cole-Hamilton and G. Wilkinson, J. Chem. Soc., Dalton Trans., (1977)797.
14 P.E. Garrou, Chem. Rev., 81(1981)229.
15 I. Omae, Coord. Chem. Rev., 32(1980)235.
16 S. Hietkamp, D.J. Stufkens and K. Vrieze, J. Organomet. Chem., 139(1977)189.
17 C.E. Jones, B.L. Shaw and B.L. Turtle, J. Chem. Soc., Dalton Trans., (1974)992.
18 A.A. Kiffen, C. Masters and L. Raynand, J. Chem. Soc., Dalton Trans., (1975)853.
19 U. Klabunde, unpublished work cited by G.W. Parshall, Organo-transition Metal Chemistry, Proc. 1st Jpn-Amer Seminar, 1974, Y. Ishii and M. Tsutsui (Eds.), Plenum, 1975, p.127.
20 H. Gilman and F.K. Cartledge, J. Organomet. Chem., 2(1964)447.
21 M.A. Bennett, Tai-Nang Huang, T.W. Matheson and A.K. Smith, Inorg. Synth., 21(1982)74.
22 C.J. Brookes, I.G. Bettley and S.M. Loxston, Mathematics and Statistics for Chemists, Wiley, 1969.