From Diarylruthenium Complexes to *ortho*-Metallated Ketones: a Mechanistic and Crystal Structure Study†

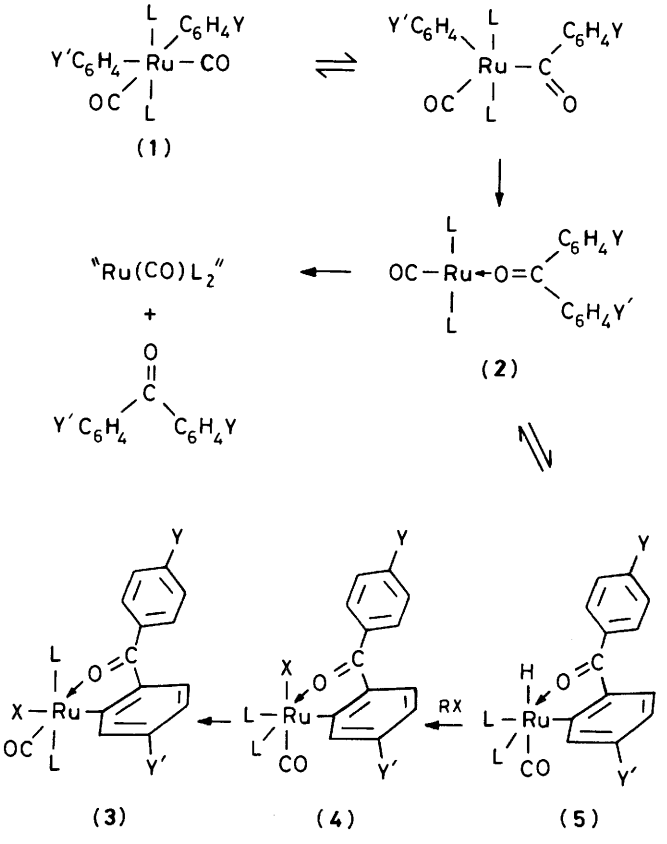
Zbigniew Dauter, Roger J. Mawby,*Colin D. Reynolds, and David R. Saunders
Department of Chemistry, University of York, York YO1 5DD

In the presence of $CHCl_3$, CCl_4, or EtI, diaryl complexes $[Ru(CO)_2(C_6H_4Y\text{-}4)(C_6H_4Y'\text{-}4)L_2]$ (Y = Y' = Me, L = PMe_2Ph or $AsMe_2Ph$; Y = Y' = Cl, L = PMe_2Ph; Y = Me, Y' = Cl, L = PMe_2Ph) are converted in solution into products $[Ru(CO)\{C_6H_3Y'C(O)C_6H_4Y\}XL_2]$, where X = Cl or I. The structure of $[Ru(CO)\{C_6H_3MeC(O)C_6H_4Me\}Cl(PMe_2Ph)_2]$, complex (**3a**), has been determined by *X*-ray crystallography. The proposed mechanism involves a two-step combination of aryl and carbonyl ligands to give $[Ru(CO)\{OC(C_6H_4Y\text{-}4)(C_6H_4Y'\text{-}4)\}L_2]$, followed by insertion of the metal into a C–H bond in one of the arene rings and reaction of the resulting hydrido-complex with the halogen-containing compound. Probably as a result of the stereochemistry of the insertion step, the product $[Ru(CO)\{C_6H_3Y'C(O)C_6H_4Y\}XL_2]$ is initially obtained as an isomer with mutually *cis* L ligands; this then rearranges to the isolated product with *trans* L ligands. The iodide ligand in the complex $[Ru(CO)\{C_6H_3MeC(O)C_6H_4Me\}I(PMe_2Ph)_2]$ can be displaced by Me_3CNC, and the complete organic ligand in complex (**3a**) is transferred from ruthenium to mercury on treatment with $HgCl_2$.

Recently we reported[1] that complexes $[Ru(CO)_2R(R')(PMe_2Ph)_2]$, containing two σ-bonded organic ligands R and R', decomposed intramolecularly in $CHCl_3$ or Me_2CO solution at room temperature to give ketones RR'CO. In $CHCl_3$ solution, however, the yield of $(4\text{-}MeC_6H_4)_2CO$ from the decomposition of $[Ru(CO)_2(C_6H_4Me\text{-}4)_2(PMe_2Ph)_2]$ fell steadily as the reaction temperature was increased, with an accompanying rise in the yield of a new ruthenium(II) complex, $[Ru(CO)\{C_6H_3MeC(O)C_6H_4Me\}Cl(PMe_2Ph)_2]$. In this paper we give further examples of reactions of this type, and describe the results of a study of the mechanism of the reactions. Details are also given of the crystal structure of $[Ru(CO)\{C_6H_3MeC(O)C_6H_4Me\}Cl(PMe_2Ph)_2]$.

Results and Discussion

The Preparation and Characterization of Complexes $[Ru(CO)\{C_6H_3Y'C(O)C_6H_4Y\}XL_2]$.—Our earlier studies had led to the conclusion that ketone formation in the decomposition of diaryl complexes $[Ru(CO)_2(C_6H_4Y)(C_6H_4Y')L_2]$ (L = PMe_2Ph) of structure (**1**) occurred as shown in the Scheme. Initial combination of aryl and carbonyl ligands to give $[Ru(CO)(COC_6H_4Y)(C_6H_4Y')L_2]$ was followed by combination of aryl and acyl ligands to produce the ruthenium(0) species $[Ru(CO)\{OC(C_6H_4Y\text{-}4)(C_6H_4Y'\text{-}4)\}L_2]$, shown as (**2**) in the Scheme, in which the ketone was still co-ordinated to the metal (probably through oxygen). Thus the ketone $(4\text{-}MeC_6H_4)_2CO$ was believed to be formed from $[Ru(CO)_2(C_6H_4Me\text{-}4)_2(PMe_2Ph)_2]$, complex (**1a**), by way of $[Ru(CO)\{OC(C_6H_4Me\text{-}4)_2\}(PMe_2Ph)_2]$, (**2a**).‡ In $CHCl_3$ solution the decomposition of (**1a**) also yielded $[Ru(CO)\{C_6H_3MeC(O)C_6H_4Me\}Cl(PMe_2Ph)_2]$, complex (**3a**), which possessed the structure shown as (**3**) in the Scheme, where L = PMe_2Ph, X = Cl, and Y = Y' = Me. We suggested that (**3a**) might also be formed *via* (**2a**), with an intramolecular oxidative–addition reaction to give the hydrido-complex $[Ru(CO)\{C_6H_3MeC(O)C_6H_4Me\}H(PMe_2Ph)_2]$ being



Scheme.

---

† Carbonylchlorobis(dimethylphenylphosphine)(6-*p*-toluoyl-*m*-tolyl-C^1O)ruthenium.

Supplementary data available (No. SUP 56186, 19 pp.): thermal parameters, complete bond lengths and angles. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

‡ A guide to the numbering system used for the complexes mentioned in the text is provided in Table 1.

Table 1. The numbering system used to identify complexes in the text

Complex	Number
$[Ru(CO)_2(C_6H_4Me\text{-}4)_2(PMe_2Ph)_2]$	**(1a)**
$[Ru(CO)_2(C_6H_4Me\text{-}4)_2(AsMe_2Ph)_2]$	**(1b)**
$[Ru(CO)_2(C_6H_4Cl\text{-}4)_2(PMe_2Ph)_2]$	**(1c)**
$[Ru(CO)_2(C_6H_4Me\text{-}4)(C_6H_4Cl\text{-}4)(PMe_2Ph)_2]$	**(1d)**
$[Ru(CO)\{OC(C_6H_4Me\text{-}4)_2\}(PMe_2Ph)_2]$	**(2a)***
$[Ru(CO)\{C_6H_3MeC(O)C_6H_4Me\}Cl(PMe_2Ph)_2]$	**(3a)**
$[Ru(CO)\{C_6H_3MeC(O)C_6H_4Me\}I(PMe_2Ph)_2]$	**(3a′)**
$[Ru(CO)\{C_6H_3MeC(O)C_6H_4Me\}Cl(AsMe_2Ph)_2]$	**(3b)**
$[Ru(CO)\{C_6H_3MeC(O)C_6H_4Me\}I(AsMe_2Ph)_2]$	**(3b′)**
$[Ru(CO)\{C_6H_3ClC(O)C_6H_4Cl\}I(PMe_2Ph)_2]$	**(3c′)**
$[Ru(CO)\{C_6H_3ClC(O)C_6H_4Me\}I(PMe_2Ph)_2]$	**(3d′)**
$[Ru(CO)(CNCMe_3)\{C_6H_3MeC(O)C_6H_4Me\}(PMe_2Ph)_2]I$	**(6a′)**

* This complex was not observed: the evidence for its intermediacy in the decomposition of **(1a)** came solely from the mechanistic studies.

Table 2. Infrared spectra (cm^{-1}) of complexes[a]

	ν(C–O)	
Complex	carbonyl ligand	acyl group
(3a)	1 924	1 585
(3a′)	1 928	1 590
(3b)	1 926	1 580
(3b′)	1 930	1 585
(3c′)	1 935	1 585
(3d′)	1 927	1 595
(6a′)[b]	1 962	1 585

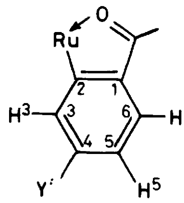
[a] In $CHCl_3$ solution. Only bands due to C–O stretching modes are listed. [b] This spectrum included a band at 2 170 cm^{-1} for the isocyanide ligand.

followed by exchange of hydrogen and chlorine between the ruthenium complex and solvent.[1]

Complex **(1a)** also decomposed in propanone solution at 318 K to yield the ketone $(4\text{-}MeC_6H_4)_2CO$, but in the absence of a chlorine-containing compound **(3a)** was of course not formed. When, however, the propanone contained a small amount of $CHCl_3$ or CCl_4, complex **(3a)** *was* obtained. Similarly the iodo-complex $[Ru(CO)\{C_6H_3MeC(O)C_6H_4Me\}I(PMe_2Ph)_2]$, **(3a′)**, was formed when **(1a)** was heated at 318 K in propanone containing a little EtI, and the related complex $[Ru(CO)\{C_6H_3MeC(O)C_6H_4Me\}I(AsMe_2Ph)_2]$, **(3b′)**, was obtained in this way from $[Ru(CO)_2(C_6H_4Me\text{-}4)_2(AsMe_2Ph)_2]$, **(1b)**. We were unable to obtain a crystalline product from the decomposition of **(1b)** in $CHCl_3$ solution, but the similarities between the i.r. and n.m.r. spectra of the material obtained and those of **(3b′)** left little doubt that it was the analogous chloro-derivative $[Ru(CO)\{C_6H_3MeC(O)C_6H_4Me\}Cl(AsMe_2Ph)_2]$, **(3b)**.

Decomposition of $[Ru(CO)_2(C_6H_4Cl\text{-}4)_2(PMe_2Ph)_2]$, complex **(1c)**, in propanone solution containing EtI was considerably slower than that of **(1a)** and **(1b)**. After heating under reflux for 1 week, purification by column chromatography and fractional crystallization yielded a small quantity of $[Ru(CO)\{C_6H_3ClC(O)C_6H_4Cl\}I(PMe_2Ph)_2]$, complex **(3c′)**. We also wished to determine the nature of the product obtained by similar treatment of $[Ru(CO)_2(C_6H_4Me\text{-}4)(C_6H_4Cl\text{-}4)(PMe_2Ph)_2]$, complex **(1d)**. Again the decomposition was rather slower than that of **(1a)** and **(1b)**, but a solid product **(3d′)** was obtained and shown by elemental analysis to be of the type $[Ru(CO)\{C_6H_3Y'C(O)C_6H_4Y\}I(PMe_2Ph)_2]$ (Y = Me, Y′ = Cl; or Y = Cl, Y′ = Me).

Details of the i.r., ^1H n.m.r., and (in some instances) ^{13}C n.m.r. spectra of the complexes $[Ru(CO)\{C_6H_3Y'C(O)C_6H_4Y\}XL_2]$ are given in Tables 2, 3, and 4 respectively. The i.r. spectra all contained bands attributable to the C–O stretching modes of the carbonyl ligand and the acyl group in the organic ligand. In the ^1H n.m.r. spectra of all four complexes $[Ru(CO)\{C_6H_3MeC(O)C_6H_4Me\}XL_2]$ [**(3a)**, **(3a′)**, **(3b)**, and **(3b′)**] separate singlet resonances were observed for the two methyl groups in the organic ligand. One (at δ 2.37—2.38) varied very little in position and was similarly placed to that (δ 2.43) for free $(4\text{-}MeC_6H_4)_2CO$, so it was assigned to the free 4-methylphenyl group in the complexes. The other (at δ 2.09—2.18) was therefore assigned to the methyl substituent in the *ortho*-metallated ring. The only resonance in this region of the spectrum for **(3d′)** was at δ 2.39, which we took as evidence that the true structure of this complex was $[Ru(CO)\{C_6H_3ClC(O)C_6H_4Me\}I(PMe_2Ph)_2]$.



The resonances for the ring protons in the *ortho*-metallated ring (numbered as shown above) were identified by comparison of their chemical shifts and proton–proton coupling constants with those for *ortho*-metallated rings in other complexes.[2] The position of the H^5 resonance (a doublet of doublets due to coupling with H^6 and H^3) was significantly affected by the nature of the substituent Y′, being at δ 6.48—6.51 for Y′ = Me but at δ 6.66 for Y′ = Cl in complex **(3c′)**. Thus the fact that the H^5 resonance for **(3d′)** was at δ 6.63 was further evidence that the *ortho*-metallated ring in this complex was the one containing the chloro-substituent.

The collection of resonances for the carbon atoms in the six-membered rings of the ketone ligand in complexes **(3a)**, **(3a′)**, **(3b)**, and **(3b′)** was complicated in appearance but very similar in all four cases [except for the triplet splittings of some of the resonances for **(3a)** and **(3a′)** due to coupling to the ^{31}P nuclei]. In assigning the resonances, we made use of spectra recorded under conditions of weak noise decoupling and also of a fully proton-coupled spectrum of **(3a)**, and in addition we compared chemical shift values with those for the corresponding carbon atoms in 4-methylbenzoyl complexes[3] and in free $(4\text{-}MeC_6H_4)_2CO$. At the low-field end of the ^{13}C n.m.r. spectra there were three resonances, one at *ca.* δ 199 and the other two near δ 205. All three appeared in the weak noise spectra (showing that the carbon atoms concerned were not bonded to hydrogen) and, in the case of **(3a)** and **(3a′)**, exhibited triplet splittings due to coupling to the ^{31}P nuclei. We assigned these resonances to C^2 (the ruthenium-bonded carbon atom in the *ortho*-metallated ring) and to the carbon atoms in the carbonyl ligand and acyl group. The triplet splitting for one of the three resonances [at δ 204.2 for **(3a)** and δ 205.4 for **(3a′)**] was markedly smaller [$|^3J(P\text{–}C)| = 2.3$ Hz] than those for the other two, suggesting that this resonance was due to the acyl carbon atom, one bond further from phosphorus than the other two. Further evidence came from the proton-coupled spectrum of **(3a)**. Here the resonance at δ 206.0 appeared the same as in the decoupled spectrum, and it was therefore assigned to the

Table 3. Proton n.m.r. spectra of complexes[a]

Complex	δ/p.p.m.	Assignment	Coupling constant/Hz	Assignment
(3a)[b]	7.29 (d, 1)	H^6	8.6	$|^3J(\text{H-H})|$
	6.96[c,d]	$C_6\mathit{H}_4Me$		
	6.51 (dd, 1)	H^5	8.6, 2.0	$|^3J(\text{H-H})|$, $|^4J(\text{H-H})|$
	2.38 (s, 3)	$C_6H_4\mathit{Me}$		
	2.15 (s, 3)	$C_6H_3\mathit{Me}$		
	1.69 (t, 6)	$P\mathit{Me}_2Ph$	7.3	$|^2J(\text{P-H}) + {}^4J(\text{P-H})|$
	1.59 (t, 6)	$P\mathit{Me}_2Ph$	7.0	$|^2J(\text{P-H}) + {}^4J(\text{P-H})|$
(3a′)	7.29 (d, 1)	H^6	7.8	$|^3J(\text{H-H})|$
	7.15 (br, 1)	H^3		
	6.99[c,d]	$C_6\mathit{H}_4Me$		
	6.48 (dd, 1)	H^5	7.8, 1.3	$|^3J(\text{H-H})|$, $|^4J(\text{H-H})|$
	2.38 (s, 3)	$C_6H_4\mathit{Me}$		
	2.09 (s, 3)	$C_6H_3\mathit{Me}$		
	1.80 (t, 6)	$P\mathit{Me}_2Ph$	7.2	$|^2J(\text{P-H}) + {}^4J(\text{P-H})|$
	1.67 (t, 6)	$P\mathit{Me}_2Ph$	7.0	$|^2J(\text{P-H}) + {}^4J(\text{P-H})|$
(3b)	7.70 (d, 1)	H^6	8.0	$|^3J(\text{H-H})|$
	7.47[d]	H^3		
	7.12[c,d]	$C_6\mathit{H}_4Me$		
	6.51 (dd, 1)	H^5	8.0, 2.0	$|^3J(\text{H-H})|$, $|^4J(\text{H-H})|$
	2.37 (s, 3)	$C_6H_4\mathit{Me}$		
	2.18 (s, 3)	$C_6H_3\mathit{Me}$		
	1.48 (s, 6)	$As\mathit{Me}_2Ph$		
	1.42 (s, 6)	$As\mathit{Me}_2Ph$		
(3b′)	7.44[d]	H^3		
	7.38 (d, 1)	H^6	8.0	$|^3J(\text{H-H})|$
	7.10[c,d]	$C_6\mathit{H}_4Me$		
	6.50 (dd, 1)	H^5	8.0, 2.0	$|^3J(\text{H-H})|$, $|^4J(\text{H-H})|$
	2.37 (s, 3)	$C_6H_4\mathit{Me}$		
	2.15 (s, 3)	$C_6H_3\mathit{Me}$		
	1.61 (s, 6)	$As\mathit{Me}_2Ph$		
	1.51 (s, 6)	$As\mathit{Me}_2Ph$		
(3c′)	7.41 (dt, 1)	H^3	2.0, 1.0	$|^4J(\text{H-H})|$,$|^4J(\text{P-H})|$
	7.21 (d, 1)	H^6	8.8	$|^3J(\text{H-H})|$
	7.04[c]	C_6H_4Cl		
	6.66 (dd, 1)	H^5	8.8, 2.0	$|^3J(\text{H-H})|$, $|^4J(\text{H-H})|$
	1.91 (t, 6)	$P\mathit{Me}_2Ph$	7.3	$|^2J(\text{P-H}) + {}^4J(\text{P-H})|$
	1.67 (t, 6)	$P\mathit{Me}_2Ph$	6.8	$|^2J(\text{P-H}) + {}^4J(\text{P-H})|$
(3d′)[e]	7.28 (d, 1)	H^6	8.7	$|^3J(\text{H-H})|$
	7.16 (br, 1)	H^3		
	6.63 (dd, 1)	H^5	8.7, 2.0	$|^3J(\text{H-H})|$, $|^4J(\text{H-H})|$
	2.39 (s, 3)	$C_6H_4\mathit{Me}$		
	1.86 (t, 6)	$P\mathit{Me}_2Ph$	7.2	$|^2J(\text{P-H}) + {}^4J(\text{P-H})|$
	1.71 (t, 6)	$P\mathit{Me}_2Ph$	7.0	$|^2J(\text{P-H}) + {}^4J(\text{P-H})|$
(6a′)	7.60 (br, 1)	H^3		
	7.58 (d, 1)	H^6	8.1	$|^3J(\text{H-H})|$
	7.26[c]	$C_6\mathit{H}_4Me$		
	6.90 (dd, 1)	H^5	8.1, 2.0	$|^3J(\text{H-H})|$, $|^4J(\text{H-H})|$
	2.44 (s, 3)	$C_6H_3\mathit{Me}$		
	2.39 (s, 3)	$C_6H_4\mathit{Me}$		
	1.64 (t, 6)	$P\mathit{Me}_2Ph$	7.0	$|^2J(\text{P-H}) + {}^4J(\text{P-H})|$
	1.61 (s, 9)	$CNCMe_3$		
	1.39 (t, 6)	$P\mathit{Me}_2Ph$	7.0	$|^2J(\text{P-H}) + {}^4J(\text{P-H})|$

[a] In $CDCl_3$ solution. Phenyl-proton resonances in PMe_2Ph and $AsMe_2Ph$ ligands omitted. Multiplicities and relative areas are given in parentheses after the chemical shift values: br indicates a broad resonance with incompletely resolved fine structure. [b] Resonance due to H^3 obscured. [c] Centre of an A_2B_2 pattern. [d] Partly obscured. [e] $C_6\mathit{H}_4Me$ resonance pattern largely obscured.

carbonyl ligand. The resonance at δ 204.2 for the acyl carbon atom was (as expected) slightly broadened due to small couplings to aryl ring protons, while the remaining resonance (at δ 199.1) was more markedly affected, which confirmed its assignment to C^2 in the *ortho*-metallated ring.

The Mechanism of Formation of (**3a**) *and Related Complexes.*—We found that ^{31}P n.m.r. spectroscopy was a convenient means of monitoring the decomposition of complex (**1a**). The reaction was carried out at 323 K in $CDCl_3$ solution, and spectra were recorded at regular intervals. As the singlet

Table 4. Carbon-13 n.m.r. spectra of complexes[a]

	(**3a**)	(**3a**′)	(**3b**)	(**3b**′)	(**6a**′)[b]
RuCO	206.0[c]	206.6[c]	205.4	206.3	202.4[c]
RuOC	204.2[d]	205.4[d]	205.2	205.9	208.9[d]
C_6H_3Me: C^1	139.4	138.6	140.2	139.5	139.7
C^2	199.1[e]	199.8[e]	198.1	198.7	193.5[e]
C^3	140.4[f]	140.4[f]	141.3	141.3	140.4
C^4	133.7	133.5	134.3	133.7	132.8
C^5	121.3	121.6	121.7	121.9	124.5
C^6	133.6	133.0	133.8	133.7	134.9
C_6H_3*Me*	21.9	22.0	22.0	22.0	22.3
C_6H_4Me: C^1	142.7	143.2	142.0	142.1	145.4
C^2, C^6	129.3	129.3	129.3	129.2	129.9
C^3, C^5	128.5	128.4	128.5	128.4	129.3
C^4	141.7	142.0	142.0	142.1	145.4
C_6H_4*Me*	21.5	21.5	21.6	21.6	21.7
E*Me*$_2$Ph[g]	13.2, 12.6	16.5, 15.2	8.4, 7.9	11.5, 10.4	15.7, 12.6

[a] In $CDCl_3$ solution. Chemical shifts are given on the δ scale. Except where otherwise indicated, resonances were singlets. Phenyl-carbon resonances in PMe_2Ph and $AsMe_2Ph$ ligands omitted. [b] Resonances for the Me_3CNC ligand were at δ 30.4, 58.5, and *ca.* 144. [c] Triplet: $|^2J(P–C)|$ = *ca.* 15 Hz. [d] Triplet: $|^3J(P–C)|$ = *ca.* 2 Hz. [e] Triplet: $|^2J(P–C)|$ = *ca.* 10 Hz. [f] Triplet: $|^3J(P–C)|$ = *ca.* 1 Hz. [g] For E = P, resonances were triplets with $|^1J(P–C) + {}^3J(P–C)|$ = *ca.* 31 Hz.

resonance at δ 3.87 due to (**1a**) decreased in area, small resonances appeared in the regions δ 17.5—19.2 and −1.21 to 0.94. Once the decomposition of (**1a**) was complete, these resonances did not alter significantly in size or position, and we attributed them to the ruthenium co-product of the formation of free $(4\text{-}MeC_6H_4)_2CO$. From the start of the decomposition, however, two further resonances appeared at δ 22.94 and −4.50. These were clearly due to two inequivalent phosphorus nuclei in a single complex, since they were at all stages roughly equal in size and they exhibited identical doublet splittings [$|^2J(P–P)|$ = 17.9 Hz]. These two doublets reached a maximum size and then weakened, ultimately disappearing completely. The singlet resonance at δ 7.60 due to complex (**3a**), which was not visible in the early stages of the decomposition, steadily increased in size as the doublets weakened. From these results we concluded that there was one long-lived intermediate on the route from (**1a**) to (**3a**), and that it was positioned *after* the point at which the pathways to free ketone and to (**3a**) diverged, and hence was *not* complex (**2a**).*

The decomposition of complex (**1a**) in $CDCl_3$ solution at 323 K was also studied by ^1H n.m.r. spectroscopy. Resonances at δ 5.24 and 2.43, attributable respectively to $CDHCl_2$ and to the methyl protons in free $(4\text{-}MeC_6H_4)_2CO$, grew steadily from the start of the reaction, as did a doublet [$|^2J(P–H)|$ = 9.6 Hz] at δ 1.23 and others at *ca.* δ 1.9, believed to be due to the ruthenium co-product of ketone formation. After the resonances due to complex (**1a**) had disappeared, none of these resonances increased any further in area. Also visible in these spectra were resonances attributable to the intermediate first observed in the ^{31}P spectra. These included four doublet resonances of equal area, two [both with $|^2J(P–H)|$ = 9.6 Hz] at δ 1.11 and 1.14, and two virtually superimposed at δ 1.76 [$|^2J(P–H)|$ = 7.8 Hz]. This pattern is characteristic for the methyl protons in a pair of inequivalent mutually *cis* PMe_2Ph ligands, where the metal–phosphorus bonds do not lie in planes of symmetry through the complex.[4,5] The spectrum of the intermediate also included a singlet at δ 2.30, whose area and chemical shift were as expected for a methyl substituent in an arene ring, and from the way in which the area of the peak at δ 2.43 [initially assigned (see above) solely to free $(4\text{-}MeC_6H_4)_2CO$] varied with time it was realized that the peak consisted of coincident $4\text{-}MeC_6H_4$ methyl-proton resonances for free ketone and for the intermediate. All the resonances attributable to the intermediate reached a maximum size and thereafter weakened, eventually disappearing completely. The resonances for complex (**3a**), which [in contrast to those for $CDHCl_2$, for $(4\text{-}MeC_6H_4)_2CO$ and its ruthenium co-product, and for the intermediate] were *not* visible in the early stages of the reaction, steadily grew as those due to the intermediate decreased in area.

Thus the ^1H n.m.r. results confirmed that the intermediate was not (**2a**), since it clearly did not lie on the pathway to free ketone. As mentioned above, we envisaged that the next step in the route from (**2a**) to (**3a**) involved the insertion of the ruthenium into a C–H bond of one of the aromatic rings in the ketone ligand, giving the hydrido-complex $[Ru(CO)\{C_6H_3MeC(O)C_6H_4Me\}H(PMe_2Ph)_2]$. This also could not be the long-lived intermediate, since the proton resonance for $CDHCl_2$ had started to appear right from the beginning of the reaction, and no more was formed as the intermediate was converted into (**3a**). In addition, throughout the reaction we observed no resonance in the part of the ^1H n.m.r. spectrum associated with hydride ligands in ruthenium(II) complexes.[6] Evidently the exchange of hydrogen and chlorine between complex and solvent had already occurred when the intermediate was reached, and we concluded that the intermediate must in fact be an *isomer* of (**3a**) in which the two PMe_2Ph ligands were mutually *cis* rather than *trans*, and that the final slow step in the route to complex (**3a**) was simply an isomerization.

In order to determine the complete stereochemistry of the intermediate, we attempted to obtain its ^{13}C n.m.r. spectrum in $CDCl_3$ solution. Decomposition of complex (**1a**) at 323 K was monitored by ^{31}P n.m.r. spectroscopy until little of (**1a**) remained and the concentration of the intermediate was at its highest. The solution was then cooled to 250 K and held at this temperature (ensuring that the reaction was effectively halted) while ^{13}C spectra were recorded. Spectra were recorded under the normal conditions of full proton decoupling, under weak noise conditions, and finally with full proton coupling. The solution was then returned to 323 K for 8 h. After this period the ^{31}P spectrum indicated that complex (**1a**) had completely disappeared, the concentration of the intermediate had decreased, and that of (**3a**) had increased. After cooling to 250 K the proton-decoupled ^{13}C n.m.r. spectrum of the solution was recorded again. Due to the inevitable presence of more than one species the spectra were very complicated, but comparison of the two proton-decoupled spectra with one another and with those of (**1a**) and (**3a**) allowed three important resonances, at δ 200.0, 206.1, and 208.8, to be attributed to the intermediate. All three appeared in the weak noise spectrum, and they were assigned (by comparison of decoupled and coupled spectra) to C^2 in the *ortho*-metallated ring, the carbonyl ligand, and the acyl group respectively. The resonance at δ 200.0 exhibited two doublet splittings of very different sizes [$|^2J(P–C)|$ = 80.5 and 12.3 Hz], indicating that C^2 in the *ortho*-metallated ring was *trans* to one PMe_2Ph ligand and *cis* to the other, while that at δ 206.1 was a doublet of doublets with $|^2J(P–C)|$ = 18.3 and 8.6 Hz, values characteristic of a carbonyl ligand *cis* to two PMe_2Ph ligands.[7] The resonance at δ 208.8 was a doublet [$|^3J(P–C)|$ = 8.3 Hz], suggesting that the acyl group was *trans* to one PMe_2Ph ligand and *cis* to the other, with the *cis* ^{31}P nucleus causing a splitting too small to be detected.

---

* A referee has asked us to note that it is conceivable that the observed 'intermediate' does not lie on the direct pathway from (**1a**) to (**3a**). If this were the case, the observed species would have to be in equilibrium with some other compound which *did* lie on the pathway but was present in too low a concentration to be detected.

We concluded, therefore, that the intermediate possessed the structure shown as (**4**) in the Scheme, where L = PMe_2Ph, X = Cl, and Y = Y′ = Me. The probable reason for the initial formation of this isomer of $[Ru(CO)\{C_6H_3MeC(O)C_6H_4Me\}Cl(PMe_2Ph)_2]$ is that the insertion of the ruthenium into a C–H bond of one of the aromatic rings of the ketone in complex (**2a**) would be expected to be a concerted process, resulting in a *fac* arrangement of the bond to the acyl oxygen atom and the newly formed Ru–C and Ru–H bonds in the hydrido-complex $[Ru(CO)\{C_6H_3MeC(O)C_6H_4Me\}H(PMe_2Ph)_2]$, shown as (**5**) in the Scheme, where L = PMe_2Ph and Y = Y′ = Me. Subsequent exchange of hydrogen and chlorine between the complex and solvent, if it proceeded with retention of configuration around the metal, would then yield the observed isomer, (**4**), of $[Ru(CO)\{C_6H_3MeC(O)C_6H_4Me\}Cl(PMe_2Ph)_2]$. The isomerization of (**4**) to (**3**) may simply serve to reduce crowding in the molecule. We have observed other cases in which ruthenium(II) complexes containing mutually *cis* PMe_2Ph ligands rearrange in this way.[5] One possible mechanism would involve dissociation of the acyl oxygen atom, rearrangement of the resulting five-co-ordinate intermediate to allow the PMe_2Ph ligands to become mutually *trans*, and re-entry of the acyl oxygen *trans* to CO, which has a greater *trans*-directing effect than a halide ligand in these complexes.[5]

A study by ^{31}P n.m.r. spectroscopy was also made of the decomposition at 318 K of complex (**1a**) in $(CD_3)_2CO$ solution containing iodoethane. A similar long-lived intermediate [presumably (**4**), where L = PMe_2Ph, X = I, and Y = Y′ = Me] was observed on the route to (**3a′**).

In the Scheme, the insertion of the ruthenium into the C–H bond [(**2**) → (**5**)] is shown as a reversible step, as it is in the case of the reactions (1) (RH = arene) first studied by Chatt and

$$[Ru(RH)(Me_2PCH_2CH_2PMe_2)_2] \rightleftharpoons [RuR(H)(Me_2PCH_2CH_2PMe_2)_2] \quad (1)$$

Davidson.[8] We attempted to obtain evidence for this reversibility by studying the decomposition of complex (**1a**) in the absence of a halogen-containing compound. Unfortunately (**1a**) was not very soluble in pure $(CD_3)_2CO$, and in ^1H n.m.r. spectra of the reaction mixture no resonance was visible above the noise level in the region characteristic of hydrido-complexes of ruthenium(II). In the ^{31}P spectra, however, in addition to the cluster of resonances associated with the ruthenium co-product of ketone formation (stronger here than in the presence of iodoethane), we observed a pair of weak doublet resonances, both with $|^2J(P-P)| = 18.3$ Hz, at δ 21.97 and −4.30, which could have been due to the hydrido-complex (**5**). Once the resonance due to complex (**1a**) had disappeared, these resonances decreased steadily in size. Since we knew that decomposition of (**1a**) in pure $(CD_3)_2CO$ ultimately gave the ketone $(4-MeC_6H_4)_2CO$ in high yield, these results were certainly compatible with an equilibrium between (**2**) and (**5**), with the quantity of (**5**) in solution decreasing as (**2**) decomposed to give free ketone.

Dissociation of ketone from complex (**2**) is shown in the Scheme as an irreversible step. This was confirmed by two experiments: decomposition of (**1a**) in Me_2CO solution in the presence of EtI and $(4-ClC_6H_4)_2CO$ yielded (**3a′**) but not (**3c′**), and decomposition of (**1c**) in the presence of EtI and $(4-MeC_6H_4)_2CO$ gave (**3c′**) but not (**3a′**).

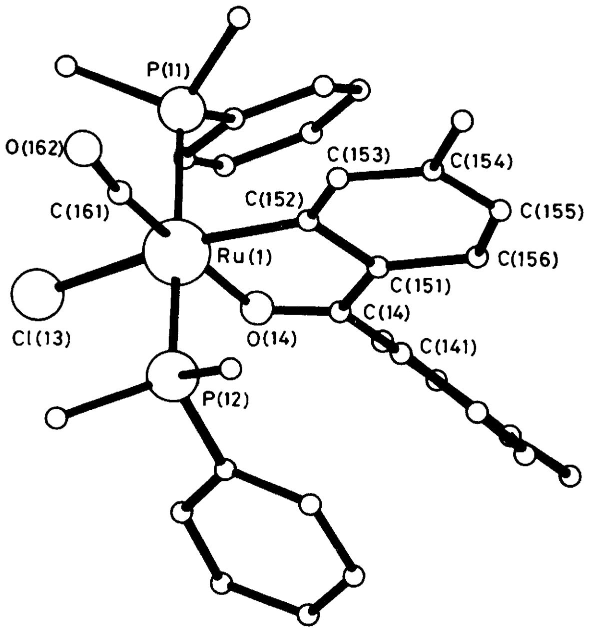


Figure. Structure of complex (**3a**) in the solid state

Reactions of Complexes (**3a**) *and* (**3a′**).—It seemed possible that the bond to the acyl oxygen atom in these complexes might break under quite mild conditions, leaving the organic ligand bound to the metal only through carbon, and freeing a co-ordination site for occupation by some other ligand. No reaction occurred, however, when CO was passed through refluxing solutions of (**3a**) and (**3a′**) in $CHCl_3$ for several days, and similarly negative results were obtained when (**3a′**) was treated with PMe_2Ph. A product, (**6a′**), *was* obtained on heating (**3a′**) with Me_3CNC, but measurement of the conductivity of a propanone solution of (**6a′**) showed that it was a 1:1 electrolyte. From analytical and spectroscopic data (see Tables 2—4) it was clear that the complex was $[Ru(CO)(CNCMe_3)\{C_6H_3MeC(O)C_6H_4Me\}(PMe_2Ph)_2]I$, formed by substitution of the halide ligand in (**3a′**), and that the ketone ligand was still chelated to the metal.

McGuiggan and Pignolet[9] reported that the ketone ligand in the complex $[Ru(CO)\{C_6H_4C(O)Me\}Cl(PPh_3)_2]$, which they obtained from $[Ru(CO)Cl(O_2CMe)(PPh_3)_2]$ and MePhCO, could be cleaved from the metal by treatment with benzoic acid. In contrast, complex (**3a**) did not react with benzoic acid even on prolonged heating in benzene solution. The organic ligand in (**3a**) was, however, transferred from ruthenium to mercury by treating a propanone solution of (**3a**) with $HgCl_2$. The solution became colourless, and subsequent purification procedures yielded a small quantity of a solid whose mass spectrum contained the expected set of peaks for the various isotopic combinations in the molecular ion $[Hg\{C_6H_3MeC(O)C_6H_4Me\}Cl]^+$ and also peaks corresponding to the fragments $[C_8H_6OHgCl]^+$ and $[C_8H_7O]^+$ resulting from cleavage either side of the acyl group. This technique was then used to confirm that the complex (**3d′**) was $[Ru(CO)\{C_6H_3ClC(O)C_6H_4Me\}I(PMe_2Ph)_2]$ and not $[Ru(CO)\{C_6H_3MeC(O)C_6H_4Cl\}I(PMe_2Ph)_2]$. The mass spectrum of the mercury-containing product of the reaction of (**3d′**) with $HgCl_2$ contained, in addition to the peaks for the parent ion, a cluster of peaks for $[C_7H_3OHgCl_2]^+$ and a peak corresponding to $[C_8H_7O]^+$, the fragments expected for $[Hg\{C_6H_3ClC(O)C_6H_4Me\}Cl]$ rather than $[Hg\{C_6H_3MeC(O)C_6H_4Cl\}Cl]$.

Crystal Structure of Complex (**3a**).—The structure consisted of discrete molecules with no intermolecular contacts shorter than 3.29 Å. The crystal contained two independent molecules within the asymmetric unit, and the stereochemistry and atom labelling system for molecule 1 are shown in the Figure. Here

Table 5. Fractional atomic co-ordinates (× 10^4) for complex (**3a**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ru(1)	2 831(1)	831(1)	3 881(1)	Ru(2)	1 009(1)	2 693(1)	10 098(1)
P(11)	3 473(2)	530(3)	3 058(2)	P(21)	−3(2)	2 390(3)	10 402(3)
C(111)	3 270(8)	1 134(14)	2 245(9)	C(211)	−539(8)	3 354(11)	10 329(11)
C(112)	3 409(9)	−528(11)	2 770(11)	C(212)	72(9)	2 014(13)	11 272(10)
C(113)	4 373(8)	707(12)	3 399(9)	C(213)	−540(7)	1 649(13)	9 844(10)
C(114)	4 719(9)	73(11)	3 854(10)	C(214)	−573(10)	789(14)	10 043(11)
C(115)	5 399(8)	182(12)	4 133(8)	C(215)	−983(11)	209(15)	9 587(14)
C(116)	5 719(9)	886(13)	3 916(10)	C(216)	−1 341(9)	503(15)	8 927(15)
C(117)	5 338(10)	1 494(12)	3 422(10)	C(217)	−1 308(9)	1 346(16)	8 723(11)
C(118)	4 684(10)	1 406(11)	3 206(9)	C(218)	−900(8)	1 958(12)	9 185(8)
P(12)	2 144(2)	1 108(3)	4 652(3)	P(22)	2 013(2)	3 045(3)	9 809(3)
C(121)	1 675(8)	238(11)	4 870(10)	C(221)	1 993(8)	4 019(11)	9 294(10)
C(122)	1 496(8)	1 908(11)	4 324(8)	C(222)	2 706(8)	3 225(13)	10 545(9)
C(123)	2 564(9)	1 517(13)	5 461(10)	C(223)	2 327(9)	2 276(13)	9 287(12)
C(124)	2 987(9)	968(12)	5 987(13)	C(224)	2 252(10)	2 375(14)	8 588(12)
C(125)	3 374(10)	1 226(17)	6 649(13)	C(225)	2 496(12)	1 746(21)	8 199(12)
C(126)	3 343(10)	2 086(18)	6 798(11)	C(226)	2 853(11)	1 045(19)	8 548(19)
C(127)	2 928(11)	2 642(13)	6 303(14)	C(227)	2 965(12)	941(18)	9 298(17)
C(128)	2 549(10)	2 327(15)	5 660(11)	C(228)	2 689(9)	1 551(16)	9 699(11)
Cl(13)	3 091(2)	−569(3)	4 439(3)	Cl(23)	1 650(2)	1 872(3)	11 126(2)
O(14)	3 669(5)	1 274(7)	4 599(6)	O(24)	945(5)	1 577(6)	9 482(6)
C(14)	3 759(7)	2 020(12)	4 594(8)	C(24)	674(7)	1 662(12)	8 825(8)
C(141)	4 340(9)	2 437(12)	5 097(9)	C(241)	619(10)	890(11)	8 381(9)
C(142)	4 936(9)	1 985(11)	5 227(9)	C(242)	−8(8)	703(11)	7 904(10)
C(143)	5 494(9)	2 278(12)	5 670(10)	C(243)	−49(10)	−23(14)	7 486(9)
C(144)	5 471(9)	3 008(13)	6 044(9)	C(244)	524(11)	−579(13)	7 565(11)
C(145)	4 871(10)	3 455(12)	5 971(9)	C(245)	1 087(10)	−369(12)	8 033(11)
C(146)	4 318(10)	3 185(11)	5 512(10)	C(246)	1 166(8)	323(12)	8 460(10)
C(147)	6 099(8)	3 379(12)	6 571(11)	C(247)	414(9)	−1 362(12)	7 062(10)
C(151)	3 319(8)	2 541(12)	4 083(8)	C(251)	462(7)	2 459(10)	8 603(10)
C(152)	2 803(9)	2 064(11)	3 596(10)	C(252)	542(8)	3 104(11)	9 153(11)
C(153)	2 360(9)	2 475(12)	3 093(10)	C(253)	287(7)	3 883(12)	8 911(9)
C(154)	2 394(10)	3 350(13)	2 979(11)	C(254)	30(7)	4 086(12)	8 191(10)
C(155)	2 915(9)	3 814(11)	3 447(11)	C(255)	−17(7)	3 480(12)	7 647(8)
C(156)	3 369(8)	3 442(12)	3 964(9)	C(256)	202(7)	2 669(13)	7 846(8)
C(157)	1 906(9)	3 809(12)	2 426(10)	C(257)	−215(8)	4 976(11)	7 973(9)
C(161)	2 113(8)	538(12)	3 292(10)	C(261)	1 032(8)	3 657(12)	10 511(9)
O(162)	1 664(6)	347(9)	2 792(7)	O(262)	1 008(6)	4 368(7)	10 726(6)

Table 6. Selected bond lengths (Å) and angles (°) for complex (**3a**)

	Molecule 1	Molecule 2		Molecule 1	Molecule 2
Ru–P(1)	2.346(5)	2.355(5)	Ru–O(4)	2.093(10)	2.136(11)
Ru–P(2)	2.330(5)	2.341(5)	O(4)–C(4)	1.208(23)	1.281(19)
Ru–Cl(3)	2.495(4)	2.508(4)	C(4)–C(51)	1.451(23)	1.386(25)
Ru–C(61)	1.728(16)	1.734(19)	C(51)–C(52)	1.473(23)	1.469(26)
C(61)–O(62)	1.224(20)	1.215(22)	Ru–C(52)	2.044(17)	1.987(19)
P(1)–Ru–P(2)	176.9(2)	177.9(2)	P(2)–Ru–C(61)	85.2(7)	87.9(6)
Cl(3)–Ru–C(52)	166.8(5)	166.3(6)	Cl(3)–Ru–O(4)	87.0(3)	88.0(3)
O(4)–Ru–C(61)	175.7(7)	173.6(6)	O(4)–Ru–C(52)	79.8(6)	78.6(6)
P(1)–Ru–Cl(3)	90.7(2)	92.1(2)	C(52)–Ru–C(61)	96.5(8)	95.1(8)
P(1)–Ru–O(4)	90.7(3)	91.2(3)	Cl(3)–Ru–C(61)	96.6(6)	98.2(5)
P(1)–Ru–C(52)	90.0(6)	91.2(5)	Ru–C(61)–O(62)	169.4(17)	172.5(14)
P(1)–Ru–C(61)	91.7(7)	90.0(6)	Ru–O(4)–C(4)	115.8(9)	115.4(11)
P(2)–Ru–Cl(3)	89.7(2)	88.6(2)	O(4)–C(4)–C(51)	119.9(14)	116.5(16)
P(2)–Ru–O(4)	92.4(3)	90.8(3)	C(4)–C(51)–C(52)	113.4(16)	116.3(15)
P(2)–Ru–C(52)	90.3(6)	88.5(5)	C(51)–C(52)–Ru	110.7(12)	113.1(12)

and in Table 5, where the atomic co-ordinates are listed, the first digit simply identifies each atom as belonging to molecule 1; for molecule 2 this digit is always a 2. In Table 6, which contains lists of selected bond lengths and angles for both molecules, and in the discussion below, this first digit is omitted.

The most marked deviation from regular octahedral geometry around the ruthenium was the angle O(4)–Ru–C(52), which (due to constraints imposed by the five-membered ring) was considerably less than 90°. The fused five- and six-membered rings were essentially coplanar, allowing delocalization between their π systems and between that of the five-membered ring and the appropriate *d* orbitals of the metal. Although C(41) lay almost exactly in the plane of the five-membered ring, the arene ring to which it belonged was tilted at *ca.* 43° out of this plane. Molecular models showed that a coplanar arrangement would have resulted in a severe repulsion

Table 7. Analytical data

Complex	Colour	Found (%)		Calc. (%)	
		C	H	C	H
(**1b**)	White	54.65	5.30	54.65	5.15
(**3a**)	Red	59.05	5.50	59.10	5.45
(**3a′**)	Red	51.85	4.75	51.85	4.75
(**3b′**)	Red	46.30	4.45	46.35	4.25
(**3c′**)	Red	46.15	4.00	46.05	3.75
(**3d′**)	Red	48.60	4.25	48.85	4.25
(**6a′**)*	Yellow	54.25	5.50	53.90	5.40

* % N: Found, 1.65; Calc. 1.70.

between the hydrogen atoms attached to C(56) and to the appropriate *ortho*-carbon atom in the 4-methylphenyl group.

Within the five-membered ring, bond lengths and angles were in most instances very similar to those reported for the related complex $[\overline{Ru(CO)\{C_6H_4C(O})Me\}Cl(PPh_3)_2]$.[9] There are also examples of ruthenium complexes containing similar rings involving acyl and *alkene* groups,[10,11] but in these complexes the alkene C=C bond is shorter than C(51)–C(52) in (**3a**), and the Ru–O bond is rather longer than that in (**3a**).

Experimental

Details of the instruments used to obtain i.r., n.m.r., and mass spectra have been given elsewhere.[1,12]

Preparations.—Analytical data for all new ruthenium complexes are given in Table 7. The light petroleum used in the preparative work had a boiling range of 313—333 K. Methods for the preparation of complexes (**1a**), (**1c**), and (**1d**) have been reported previously,[12] and complex (**1b**) was prepared in the same way as (**1a**), from *cis*-$[Ru(CO)_2Cl_2(AsMe_2Ph)_2]$ and $Li(C_6H_4Me\text{-}4)$ (yield 53%).

Complex (**3a**). A solution of complex (**1a**) (0.25 g) in $CHCl_3$ (50 cm^3) was heated under reflux for 18 h. The solvent was removed under reduced pressure, and the residue was recrystallized from a mixture of propanone (10 cm^3) and ethanol (25 cm^3). The product was washed with light petroleum containing 5% of ethanol (yield 46%). Complex (**3b**) was prepared from (**1b**) in the same way, but could not be isolated in a crystalline form.

Complex (**3a′**). A solution of complex (**1a**) (0.20 g) and iodoethane (2 cm^3) in propanone (50 cm^3) was heated under reflux for 16 h. Isolation and purification were carried out as in the case of (**3a**) (yield 62%). Complex (**3b′**) was similarly obtained from (**1b**) (yield 51%).

Complex (**3c′**). A solution of complex (**1c**) (0.10 g) and iodoethane (2 cm^3) in propanone (50 cm^3) was heated under reflux for 170 h. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on alumina. After elution of by-products with light petroleum, the alumina was transferred to a Soxhlet thimble, and complex (**3c′**) was extracted into propanone solution. Crystals of the product were obtained on cooling to 280 K, and were washed with light petroleum (yield 18%).

Complex (**3d′**). A solution of complex (**1d**) (0.03 g) and iodoethane (1 cm^3) in propanone (20 cm^3) was heated under reflux for 48 h. The volume of the solution was halved by evaporation under reduced pressure, and ethanol (20 cm^3) was added. Slow evaporation of solvent at 280 K yielded crystals of the product, which were washed with light petroleum (yield 59%).

Complex (**6a′**). A solution of complex (**3a′**) (0.14 g) and Me_3CNC (0.022 cm^3) in $CHCl_3$ (50 cm^3) was heated under reflux for 60 h. The solvent was removed under reduced pressure, and the residue recrystallized from propanone–ethanol (1:1) at 195 K. The product was washed with light petroleum (yield 78%).

Reaction of Complex (**3a**) *with* $HgCl_2$.—A solution of complex (**3a**) (0.03 g) and $HgCl_2$ (0.015 g) in propanone (10 cm^3) was stirred for 72 h. The solvent was removed under reduced pressure, and the residue was extracted with $CHCl_3$ (2 × 5 cm^3). Slow evaporation of the $CHCl_3$ yielded $[Hg\{C_6H_3MeC(O)C_6H_4Me\}Cl]$ as a white powder, which was washed with light petroleum. The same procedure was used for the reaction of complex (**3d′**) (0.01 g) with $HgCl_2$ (0.005 g).

Crystal-structure Determination of Complex (**3a**).—The crystals used for the determination were obtained from a mixture of propanone and ethanol. Preliminary precession photographs showed the crystals to be monoclinic, with space group $P2_1/a$. A crystal of dimensions 0.24 × 0.49 × 0.22 mm was used in the structure determination.

Crystal data. $C_{32}H_{35}ClO_2P_2Ru$, $M = 650.1$, $a = 20.722(2)$, $b = 15.987(1)$, $c = 19.427(2)$ Å, $\beta = 102.89(1)°$, $U = 6\,274.9$ Å^3, $Z = 8$ (two molecules per asymmetric unit), $D_c = 1.376$ g cm^{-3}, $F(000) = 2\,672$, $\mu(Cu\text{-}K_\alpha) = 61.25$ cm^{-1}, $\lambda = 1.5418$ Å.

Intensity data were collected on a Hilger and Watts Y290 computer-controlled four-circle diffractometer. Integrated intensities were collected up to $\theta = 51°$ using the ω—2θ scan technique. 5 970 Independent reflections were measured, of which 2 452 with $I < 2.5\sigma(I)$ were classified as unobserved. Corrections were applied for Lorentz and polarization factors but not for absorption.

The structure of (**3a**) was solved by the heavy-atom method and refined by the blocked full-matrix least-squares method, initially with isotropic and then with anisotropic thermal parameters, using the SHELX 76 program system.[13] The final R was 0.0793 for 3 518 observed reflections.

Acknowledgements

We thank the S.E.R.C. for a maintenance grant (to D. R. S.).

References

1 D. R. Saunders and R. J. Mawby, *J. Chem. Soc., Dalton Trans.*, 1984, 2133.

2 R. J. McKinney, G. Firestein, and H. D. Kaesz, *Inorg. Chem.*, 1975, **14**, 2057.

3 D. R. Saunders, M. Stephenson, and R. J. Mawby, *J. Chem. Soc., Dalton Trans.*, 1984, 539.

4 J. M. Jenkins, M. S. Lupin, and B. L. Shaw, *J. Chem. Soc. A*, 1966, 1787.

5 C. F. J. Barnard, J. A. Daniels, J. Jeffery, and R. J. Mawby, *J. Chem. Soc., Dalton Trans.*, 1976, 953.

6 J. D. Cotton, M. I. Bruce, and F. G. A. Stone, *J. Chem. Soc. A*, 1968, 2162.

7 P. R. Holland, B. Howard, and R. J. Mawby, *J. Chem. Soc., Dalton Trans.*, 1983, 231.

8 J. Chatt and J. M. Davidson, *J. Chem. Soc.*, 1965, 843.

9 M. F. McGuiggan and L. H. Pignolet, *Inorg. Chem.*, 1982, **21**, 2523.

10 S. Komiya, T. Ito, M. Cowie, A. Yamamoto, and J. A. Ibers, *J. Am. Chem. Soc.*, 1976, **98**, 3874.

11 H. Yamasaki and A. Katsuyuki, *J. Organomet. Chem.*, 1976, **122**, C54.

12 D. R. Saunders, M. Stephenson, and R. J. Mawby, *J. Chem. Soc., Dalton Trans.*, 1983, 2473.

13 G. M. Sheldrick, SHELX 76, a program system for crystal structure determination, University of Cambridge, 1976.

Received 21*st August* 1984; *Paper* 4/1455