J. CHEM. SOC. DALTON TRANS. 1984 2133

# Reductive Elimination of Ketones from Ruthenium(II) Complexes

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Complexes $[Ru(CO)_2R_2(PMe_2Ph)_2]$ (R = aryl or alkyl) decompose at room temperature in $CHCl_3$ or $Me_2CO$ solution to yield the ketones $R_2CO$. Decomposition is intramolecular, since the complexes $[Ru(CO)_2RR'(PMe_2Ph)_2]$ yield only the unsymmetrical ketones RR'CO, and the disappearance of $[Ru(CO)_2(C_6H_4Me\text{-}4)_2(PMe_2Ph)_2]$ follows simple first-order kinetics. The acyl complex $[Ru(CO)(CNCMe_3)(COC_6H_4Me\text{-}4)(C_6H_4Me\text{-}4)(PMe_2Ph)_2]$ also decomposes in $CHCl_3$ solution to give $(4\text{-}MeC_6H_4)_2CO$, but the decomposition is inhibited by free $Me_3CNC$. It is believed that the ketones are formed by reductive elimination from $[Ru(CO)(COR)R(PMe_2Ph)_2]$. A ruthenium(0) product could not be isolated, but the ruthenium(II) complex $[\overline{Ru(CO)Cl\{C_6H_3MeC(O})C_6H_4Me\}\text{-}(PMe_2Ph)_2]$ was obtained when the decomposition of $[Ru(CO)_2(C_6H_4Me\text{-}4)_2(PMe_2Ph)_2]$ in $CHCl_3$ was carried out at higher temperatures.

In contrast to the detail in which reductive elimination from complexes of other $d^6$ metal ions (for example $Rh^{3+}$, $Ir^{3+}$, and $Pt^{4+}$) has been studied, elimination from complexes of ruthenium(II) has received little attention since the early discovery by Chatt and Davidson[1] that the compounds $[Ru(R)H(Me_2PCH_2CH_2PMe_2)_2]$ (R = aryl) were in equilibrium with arene complexes of ruthenium(0), $[Ru(RH)(Me_2PCH_2CH_2PMe_2)_2]$, although this particular system has since been investigated in more detail by Tolman *et al.*[2]

Recently we have prepared a range of ruthenium(II) complexes $[Ru(CO)_2RR'(PMe_2Ph)_2]$ containing two $\sigma$-bonded organic ligands R and R' in mutually *cis* positions.[3] These react with $Me_3CNC$ to form acyl complexes $[Ru(CO)(CNCMe_3)(COR)R'(PMe_2Ph)_2]$ in which the acyl ligand is *cis* to the other organic ligand R'.[4] We thought that the complexes $[Ru(CO)_2RR'(PMe_2Ph)_2]$ might readily eliminate RR' (and had tentatively ascribed the varying degree of decomposition which occurred during the preparation of these complexes to this type of elimination). It also seemed likely that reductive elimination of ketones RR'CO might occur from the acyl complexes $[Ru(CO)(CNCMe_3)(COR)R'(PMe_2Ph)_2]$. This paper describes our study of reductive elimination from both types of complex.

## Results and Discussion

*The Organic Product of Reductive Elimination.*—During the preparation of complexes $[Ru(CO)_2R_2(PMe_2Ph)_2]$ (R = aryl) by treatment of $[Ru(CO)_2Cl_2(PMe_2Ph)_2]$ with LiR,[3] there was always some darkening of the reaction mixture, which we had attributed to reductive elimination of $R_2$ to yield a ruthenium(0) complex. The darkening was particularly marked in the reaction with $Li(C_6H_4OMe\text{-}4)$, and on one occasion the dark coloured organic layer after hydrolysis was diluted with a mixture of ethanol and propanone and left to stand at room temperature for 80 h. A solid precipitated, which was shown by elemental analysis and $^1H$ n.m.r. spectroscopy to be the ketone $(4\text{-}MeOC_6H_4)_2CO$ rather than the diaryl $(4\text{-}MeOC_6H_4)_2$.

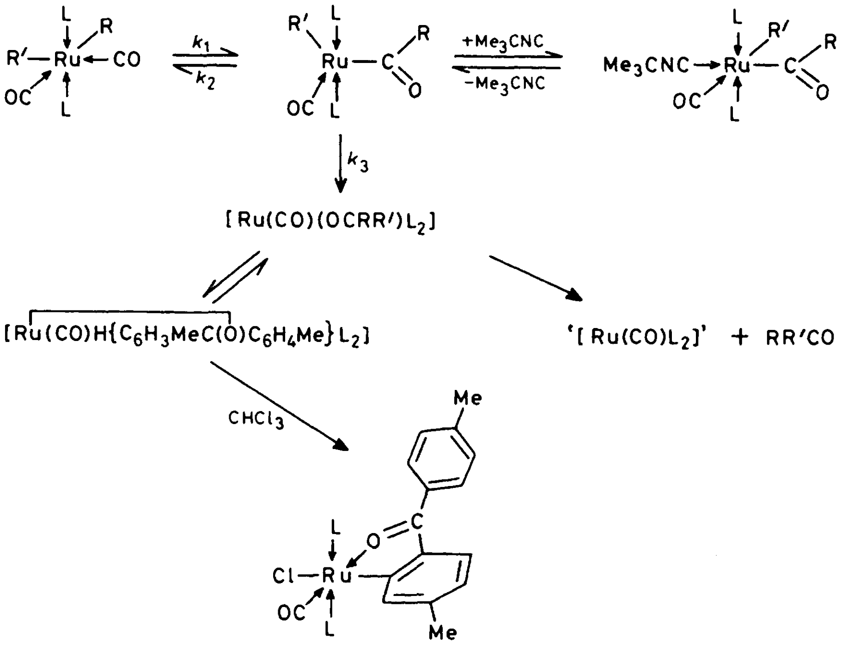
Since the only obvious source of CO for ketone formation was the carbonyl ligands bound to ruthenium, we concluded that the ketone resulted from partial decomposition of the desired product, $[Ru(CO)_2(C_6H_4OMe\text{-}4)_2(PMe_2Ph)_2]$. To confirm that this complex did decompose to yield $(4\text{-}MeOC_6H_4)_2CO$, a sample of the pure complex was left in $CHCl_3$ solution for 72 h at room temperature. Reduction in the volume of the solution by solvent evaporation resulted in the precipitation of $(4\text{-}MeOC_6H_4)_2CO$.

A more general investigation of the decomposition of complexes $[Ru(CO)_2R_2(PMe_2Ph)_2]$ was then undertaken. Solutions of $[Ru(CO)_2Ph_2(PMe_2Ph)_2]$ and $[Ru(CO)_2(C_6H_4Me\text{-}4)_2(PMe_2Ph)_2]$ in $CHCl_3$ were left at room temperature for 340 and 170 h respectively, and the solvent was then removed under reduced pressure. The pure ketones $Ph_2CO$ and $(4\text{-}MeC_6H_4)_2CO$ were obtained from the residue by thin-layer chromatography and identified by mass spectrometry; no evidence was obtained for the presence of the diaryls $Ph_2$ and $(4\text{-}MeC_6H_4)_2$. The decomposition of $[Ru(CO)_2Me_2(PMe_2Ph)_2]$ in $CDCl_3$ solution was studied by $^1H$ n.m.r. spectroscopy. Over a period of 2 000 h a singlet at $\delta$ 2.05 steadily increased in area, and this resonance was shown to be due to $Me_2CO$ by adding $Me_2CO$ to the solution and noting the immediate increase in the area of the resonance.

In several instances we had obtained spectroscopic evidence for the formation of $[Ru(CO)_2R_2(PMe_2Ph)_2]$ in the reactions of $[Ru(CO)_2Cl_2(PMe_2Ph)_2]$ with the appropriate organolithium reagents, but had been unable to isolate the products. Thus, for example, treatment of $[Ru(CO)_2Cl_2(PMe_2Ph)_2]$ with LiBu in ethoxyethane at 223 K resulted in the disappearance of the C–O stretching bands for the dichloro-complex from the i.r. spectrum of the solution, and the appearance of new bands at 1 996 and 1 928 $cm^{-1}$ {for comparison, $[Ru(CO)_2Me_2(PMe_2Ph)_2]$ in ethoxyethane exhibits C–O stretching bands at 1 995 and 1 930 $cm^{-1}$}. During hydrolysis and attempted purification, however, the organic layer rapidly darkened, and we could not isolate a solid ruthenium complex, but work-up of the organic layer yielded a colourless liquid identified by mass spectrometry as $Bu_2CO$. Similarly, the treatment of $[Ru(CO)_2Cl_2(PMe_2Ph)_2]$ with $LiCH_2CH_2CH_2CH_2Li$ yielded a solution whose i.r. spectrum included bands at 1 992 and 1 920 $cm^{-1}$; again the complex failed to survive the hydrolysis and purification procedures, but the presence of cyclopentanone in the organic layer was proved by converting it to its 2,4-dinitrophenylhydrazone derivative, which was identified by elemental analysis and by its melting point.

The decomposition of $[Ru(CO)_2(C_6H_4Me\text{-}4)_2(PMe_2Ph)_2]$ was also studied in $Me_2CO$ to determine whether ketone formation was linked specifically to the use of $CHCl_3$ as solvent; again the organic product of the decomposition was $(4\text{-}MeC_6H_4)_2CO$.

*The Mechanism of Ketone Formation.*—In order to establish that ketone formation was an intramolecular process, we examined the decomposition of complexes $[Ru(CO)_2RR'(PMe_2Ph)_2]$ containing two different organic ligands. A



(1)

**Scheme.** L = PMe$_2$Ph

CHCl$_3$ solution of [Ru(CO)$_2$(C$_6$H$_4$OMe-4)(C$_6$H$_4$Me-4)(PMe$_2$Ph)$_2$] was left at room temperature for 170 h and the solvent was then removed under reduced pressure. Thin-layer chromatography was used to separate any diaryl ketones from the remainder of the residue {previous tests had established that the $R_f$ values of (4-MeOC$_6$H$_4$)$_2$CO, (4-MeC$_6$H$_4$)$_2$CO, and (4-MeOC$_6$H$_4$)(4-MeC$_6$H$_4$)CO under the conditions used were all very similar}. A subsequent mass spectrum established that the only ketone present in significant quantity was (4-MeOC$_6$H$_4$)(4-MeC$_6$H$_4$)CO. As a further check, the decomposition of [Ru(CO)$_2$MePh(PMe$_2$Ph)$_2$] in CDCl$_3$ solution was studied by $^1$H n.m.r. spectroscopy. Over a period of 1 000 h, a singlet at $\delta$ 2.56 increased in area, and this resonance was shown to be due to the methyl protons in MePhCO. No resonance was observed at $\delta$ 2.05, so it was clear that the decomposition did not yield Me$_2$CO.

Further confirmation of the intramolecular nature of the process came from a kinetic study of the decomposition of [Ru(CO)$_2$(C$_6$H$_4$Me-4)$_2$(PMe$_2$Ph)$_2$] in CHCl$_3$ solution, in which the C–O stretching band at 2 015 cm$^{-1}$ was used to monitor the reaction. As expected for an intramolecular process, the decomposition proved to be first order in the ruthenium complex; duplicate runs carried out at 298.3 K gave rate constants of $(2.26 \pm 0.03) \times 10^{-6}$ and $(2.18 \pm 0.06) \times 10^{-6}$ s$^{-1}$, and a similar pair of runs at 303.4 K gave values of $(4.22 \pm 0.17) \times 10^{-6}$ and $(4.20 \pm 0.25) \times 10^{-6}$ s$^{-1}$.

As stated in the introduction, all the complexes [Ru(CO)$_2$RR′(PMe$_2$Ph)$_2$] mentioned above react with Me$_3$CNC to form the acyl complexes [Ru(CO)(CNCMe$_3$)(COR)R′(PMe$_2$Ph)$_2$]. The rate of reaction is independent of Me$_3$CNC concentration, and we believe that the rate-determining step involves formation of the acyl intermediates [Ru(CO)(COR)R′(PMe$_2$Ph)$_2$].[4] As shown in the Scheme, it seems probable that these species are also intermediates in ketone formation, and that the next step involves combination of the acyl ligand and the other organic ligand R′. Ketone formation is much slower than reaction with Me$_3$CNC {for example, the rate constant for the reaction of [Ru(CO)$_2$(C$_6$H$_4$Me-4)$_2$(PMe$_2$Ph)$_2$] with Me$_3$CNC in CHCl$_3$ solution at 298.3 K is $2.04 \times 10^{-4}$, as opposed to $2.22 \times 10^{-6}$ s$^{-1}$ for ketone formation}, so the simple first-order kinetics for the decomposition of [Ru(CO)$_2$(C$_6$H$_4$Me-4)$_2$(PMe$_2$Ph)$_2$] indicate that formation of the intermediate must be a reversible process. With the rate constants labelled as shown in the Scheme, $k_1$ for this complex at 298.3 K is $2.04 \times 10^{-4}$ s$^{-1}$, and the ratio $k_3/(k_2 + k_3)$ has the value 0.011.

Ketone formation was also observed when the acyl complexes [Ru(CO)(CNCMe$_3$)(COR)R′(PMe$_2$Ph)$_2$] were allowed to decompose in solution. A $^1$H n.m.r. study of the decomposition of [Ru(CO)(CNCMe$_3$)(COC$_6$H$_4$Me-4)(C$_6$H$_4$Me-4)(PMe$_2$Ph)$_2$] in CDCl$_3$ solution showed it to be slower than that of [Ru(CO)$_2$(C$_6$H$_4$Me-4)$_2$(PMe$_2$Ph)$_2$], but the product was again (4-MeC$_6$H$_4$)$_2$CO. Decomposition of the acyl complex was markedly inhibited by the addition of free Me$_3$CNC to the solution, indicating that ketone formation was preceded by loss of the isonitrile ligand to yield the same intermediate, [Ru(CO)(COC$_6$H$_4$Me-4)(C$_6$H$_4$Me-4)(PMe$_2$Ph)$_2$], as that involved in the decomposition of [Ru(CO)$_2$(C$_6$H$_4$Me-4)$_2$(PMe$_2$Ph)$_2$].

Thus it was clear that ketone elimination from [Ru(CO)(COR)R′(PMe$_2$Ph)$_2$] occurred in preference to both the elimination of RR′ from [Ru(CO)$_2$RR′(PMe$_2$Ph)$_2$] and ketone elimination from [Ru(CO)(CNCMe$_3$)(COR)R′(PMe$_2$Ph)$_2$]. Other workers have noted an apparent preference for the elimination of ketones as opposed to hydrocarbons; thus the complexes [PtMe$_2$(COMe)XL$_2$] (X = Cl or Br, L = PMe$_2$Ph or AsMe$_2$Ph), which contain both a mutually *cis* pair of methyl ligands and mutually *cis* methyl and acetyl ligands, decompose to yield propanone rather than ethane,[5] and the complexes [Co($\eta^5$-C$_5$H$_5$)Me$_2$(PPh$_3$)], [CoEt$_2$(acac)(PMe$_2$Ph)$_2$] [acac = pentane-2,4-dionate(1−)], and [Ti($\eta^5$-C$_5$H$_5$)$_2$Ph$_2$] all react with CO to yield the appropriate ketone under conditions where no reductive elimination occurs in the absence of CO.[6-8]

At first sight it is surprising that elimination of ketone occurs from [Ru(CO)(COR)R′(PMe$_2$Ph)$_2$] more readily than from [$Ru(CO)(CNCMe_3)(COR)R'(PMe_2Ph)_2$]. One might expect that the elimination reaction would be promoted both by the bulk of the isonitrile ligand and by its π-acceptor character. It may be that there are electronic factors favouring elimination from a five-co-ordinate (rather than a six-co-ordinate) complex of a $d^6$ ion, as there appear to be[9,10] for elimination of an alkane from three- rather than four-co-ordinate dialkyl complexes of the $d^8$ ion $Pd^{2+}$. Alternatively, the intermediates [$Ru(CO)(COR)R'(PMe_2Ph)_2$] may actually be six-co-ordinate, with the acyl ligand bound to ruthenium through both the carbon and the oxygen atom of the acyl group {as Roper and Wright[11] have proposed in the case of [$Ru(CO)(COC_6H_4Me\text{-}4)I(PPh_3)_2$]}. As Evitt and Bergmann[6] have suggested, this type of acyl co-ordination may serve to lower the activation energy for reductive elimination.

In an earlier paper,[3] we described how decomposition of [$Ru(CO)_2Me_2(PMe_2Ph)_2$] during its preparation could be reduced by adding CO or $PMe_2Ph$ to the reaction mixture. When CO was used, the ruthenium complex actually isolated was [$Ru(CO)_2(COMe)Me(PMe_2Ph)_2$]. We assumed that the decomposition involved reductive elimination of ethane from [$Ru(CO)_2Me_2(PMe_2Ph)_2$] and that the CO, by converting the dimethyl complex to [$Ru(CO)_2(COMe)Me(PMe_2Ph)_2$], prevented this from occurring. On this basis, however, we were unable to explain the effect of $PMe_2Ph$, since treatment of [$Ru(CO)_2Me_2(PMe_2Ph)_2$] with $PMe_2Ph$ did not result in the formation of a detectable amount of [$Ru(CO)(COMe)Me(PMe_2Ph)_3$]. It is now clear that decomposition occurs because [$Ru(CO)_2Me_2(PMe_2Ph)_2$] is in equilibrium in solution with [$Ru(CO)(COMe)Me(PMe_2Ph)_2$], which can eliminate propanone. Any species L which lowers the concentration of [$Ru(CO)(COMe)Me(PMe_2Ph)_2$] by converting it into [$Ru(CO)(COMe)MeL(PMe_2Ph)_2$] will therefore inhibit the decomposition of [$Ru(CO)_2Me_2(PMe_2Ph)_2$]. In more general terms, in the system shown by (i) and (ii), significant inhibition

$$[Ru(CO)_2RR'(PMe_2Ph)_2] \overset{K_1}{\rightleftharpoons} [Ru(CO)(COR)R'(PMe_2Ph)_2] \quad \text{(i)}$$

$$[Ru(CO)(COR)R'(PMe_2Ph)_2] + L \overset{K_2}{\rightleftharpoons} [Ru(CO)(COR)R'L(PMe_2Ph)_2] \quad \text{(ii)}$$

of decomposition will result from the use of any ligand L for which $K_2$ is reasonably large, even if (as in the case of L = $PMe_2Ph$) the value of the *product* $K_1K_2$ is small.

This is also illustrated by the effect of CO on the stability of the diaryl complexes in solution (another instance where the value of $K_1K_2$ is known to be small[3]). Thus we found that [$Ru(CO)_2(C_6H_4Me\text{-}4)_2(PMe_2Ph)_2$] could be recovered in high yield from a CO-saturated propanone solution after a period long enough to ensure total decomposition in the absence of the CO. In $CHCl_3$ solution, saturation with CO again prevented formation of $(4\text{-}MeC_6H_4)_2CO$, but a slower decomposition process occurred instead, yielding [$Ru(CO)_2(C_6H_4Me\text{-}4)Cl(PMe_2Ph)_2$]. The mechanism of this latter reaction is still under study.

*The Ruthenium-containing Product of Decomposition.*—Loss of ketone from [$Ru(CO)_2RR'(PMe_2Ph)_2$] should leave the ruthenium(0) species [$Ru(CO)(PMe_2Ph)_2$], which might be expected rapidly to form some kind of cluster complex. Unfortunately we were unable to isolate a solid complex from the decomposition reactions carried out at room temperature, although n.m.r. studies of these reactions in $CDCl_3$ solution provided some evidence for the formation of a ruthenium(0) species. A doublet resonance [$|^2J(P\text{-}H)| = 9.6$ Hz] observed at δ 1.23 and smaller peaks at *ca.* δ 1.9 were tentatively attributed to the methyl protons in the $PMe_2Ph$ ligands in such a species.

In an attempt to convert the [$Ru(CO)(PMe_2Ph)_2$] into an isolable complex, the decomposition of [$Ru(CO)_2(C_6H_4Me\text{-}4)_2(PMe_2Ph)_2$] in $CHCl_3$ solution was carried out in the presence of various reagents (alkynes, dienes, *etc.*), and a crystalline product was obtained when the decomposition was performed at 308 K in the presence of PhC≡CPh. Elemental analysis and spectroscopic data were insufficient to provide clearcut evidence as to the structure of the product, but an *X*-ray structure determination[12] showed it to be [$Ru(CO)Cl\{C_6H_3MeC(O)C_6H_4Me\}(PMe_2Ph)_2$] [complex (1) in the Scheme]. Thus it appeared that the PhC≡CPh had played no part in the reaction, and this was confirmed when the same product was obtained in the absence of the alkyne. The key to the isolation of complex (1) lay in the rather higher temperature at which the decomposition was carried out; subsequent n.m.r. studies indicated that the relative amounts of $(4\text{-}MeC_6H_4)_2CO$ and complex (1) formed varied markedly with temperature. At 298 K the ratio was *ca.* 65 : 35%, whereas at 323 K it was *ca.* 30 : 70% (at neither temperature was there any evidence of the presence of significant quantities of *other* products containing $4\text{-}MeC_6H_4$ groups).

Given the structure of complex (1), one might reasonably assume that its formation followed the breakdown of [$Ru(CO)_2(C_6H_4Me\text{-}4)_2(PMe_2Ph)_2$] into [$Ru(CO)(PMe_2Ph)_2$] and $(4\text{-}MeC_6H_4)_2CO$, and involved these two compounds and the solvent $CHCl_3$ as reactants. When, however, the decomposition of the dimethyl complex [$Ru(CO)_2Me_2(PMe_2Ph)_2$] was carried out in the presence of $(4\text{-}MeC_6H_4)_2CO$, (1) was *not* obtained, suggesting that it did not result from the reaction of *free* ketone with [$Ru(CO)(PMe_2Ph)_2$]. We concluded (see Scheme) that combination of aryl and acyl ligands in the intermediate [$Ru(CO)(COC_6H_4Me\text{-}4)(C_6H_4Me\text{-}4)(PMe_2Ph)_2$] led initially to a species [$Ru(CO)\{OC(C_6H_4Me\text{-}4)_2\}(PMe_2Ph)_2$] in which the ketone was still co-ordinated to the metal, probably through the oxygen atom. This species could then either break down into free ketone and [$Ru(CO)(PMe_2Ph)_2$] or undergo an intramolecular oxidative addition reaction to yield [$Ru(CO)H\{C_6H_3MeC(O)C_6H_4Me\}(PMe_2Ph)_2$]. Finally the hydride ligand could be replaced by chloride in a reaction with the solvent; the $CDHCl_2$ formed by this reaction in $CDCl_3$ solution was identified by both $^1H$ [δ 5.24, $|^2J(D\text{-}H)| = 1.1$ Hz] and $^{13}C$ [δ 53.6, $|^1J(C\text{-}D)| = 27.3$ Hz] n.m.r. spectroscopy.

A detailed study of the mechanism of formation of complex (1) and related complexes is in progress at present.

## Experimental

Details of the preparations of all complexes [$Ru(CO)_2RR'(PMe_2Ph)_2$] referred to in this paper have been given previously.[3] In the decomposition studies thin-layer chromatographic separation of the products was carried out using activated alumina (0.25 mm thickness) on glass, and good separation of ketones from other materials was achieved using light petroleum (b.p. 313—333 K). Spots were detected by irradiation with u.v. light (254 nm), and the ketones were recovered by extraction from the alumina with ethoxyethane.

Typical examples of the decomposition studies are given below.

*Isolation of* $(4\text{-}MeOC_6H_4)_2CO$ *from the Reaction of* [$Ru(CO)_2Cl_2(PMe_2Ph)_2$] *with* $Li(C_6H_4OMe\text{-}4)$.—The reaction between *cis*-[$Ru(CO)_2Cl_2(PMe_2Ph)_2$] and $Li(C_6H_4OMe\text{-}4)$ was carried out in ethoxyethane as described previously.[3]

After hydrolysis, the ethoxyethane layer was dried and then diluted with ethanol–propanone (1 : 1). The ethoxyethane was removed from the solution by evaporation under reduced pressure, and the solution was then left at room temperature for 80 h. The solid formed could be recrystallized from $CHCl_3$, yielding white crystals (Found: C, 74.40; H, 5.85. Calc. for $C_{15}H_{14}O_3$: C, 74.35; H, 5.85%).

*Isolation of* $(4\text{-}MeOC_6H_4)_2CO$ *from the Decomposition of* $[Ru(CO)_2(C_6H_4OMe\text{-}4)_2(PMe_2Ph)_2]$.—A solution of the ruthenium complex (0.03 g) in $CHCl_3$ (30 $cm^3$) was allowed to stand for 72 h at room temperature. The volume of the solution was then reduced under a stream of nitrogen until crystals were formed. These were filtered off and washed with ethanol (Found: C, 74.20; H, 5.85. Calc. for $C_{15}H_{14}O_3$: C, 74.35; H, 5.85%).

*Isolation of Cyclopentanone as its* 2,4-*Dinitrophenylhydrazone Derivative from the Reaction of* $[Ru(CO)_2Cl_2(PMe_2Ph)_2]$ *with* $Li(CH_2)_4Li$.—A stirred solution of *cis*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$ (0.50 g) in ethoxyethane (30 $cm^3$) at 243 K was treated dropwise with an ethoxyethane solution of $Li(CH_2)_4Li$ [13] until the i.r. spectrum of the solution indicated that all the ruthenium complex had been consumed. Water (5 $cm^3$) was then added dropwise at 273 K. After 0.1 h the water was removed by pipette and the dark brown ethoxyethane solution was dried over $MgSO_4$ and then stirred with charcoal for 24 h. After filtration, the solvent was removed under reduced pressure and the residual liquid was dissolved in a little ethanol and treated with an ethanol solution of 2,4-dinitrophenylhydrazine. On addition of water, orange crystals were formed which were filtered off and dried *in vacuo* (Found: C, 49.90; H, 4.70. N, 21.25. Calc. for $C_{11}H_{12}N_4O_4$: C, 50.00; H, 4.60; N, 21.20%). M.p. 143.0—146.0 °C (lit.[14] 144.5—146.5 °C).

*Decomposition of* $[Ru(CO)_2(C_6H_4Me\text{-}4)_2(PMe_2Ph)_2]$ *in* CO-*saturated* $CHCl_3$ *Solution*.—A CO-saturated solution of the ruthenium complex (0.10 g) in $CHCl_3$ (30 $cm^3$) was allowed to stand at room temperature for 360 h. Removal of all volatile material under a stream of CO left white crystals of $[Ru(CO)_2(C_6H_4Me\text{-}4)Cl(PMe_2Ph)_2]$ which were recrystallized from a mixture of $CHCl_3$ and ethanol (Found: C, 53.70; H, 5.30. Calc. for $C_{25}H_{29}ClO_2P_2Ru$: C, 53.60; H, 5.20%).

*Preparation of Complex* (1).—Although this was originally isolated from the decomposition of $[Ru(CO)_2(C_6H_4Me\text{-}4)_2(PMe_2Ph)_2]$ in the presence of $PhC{\equiv}CPh$, it was subsequently obtained simply by heating the diaryl complex (0.10 g) in refluxing $CHCl_3$ (30 $cm^3$) for 16 h. After removal of the solvent under reduced pressure, the residue was extracted with propanone (5 $cm^3$). The propanone solution was filtered and treated with ethanol. Slow evaporation under a stream of nitrogen resulted in the formation of red crystals, which were filtered off and washed with a mixture of ethanol and light petroleum (b.p. 313—333 K) (Found: C, 59.05; H, 5.50. Calc. for $C_{32}H_{35}ClO_2P_2Ru$: C, 59.10; H, 5.45%).

*Spectroscopic and Kinetic Studies*.—Details of the instruments used to obtain i.r. and n.m.r. spectra have been given elsewhere.[3] Mass spectra were recorded on an A.E.I. MS 30 spectrometer. For the kinetic studies, solutions of $[Ru(CO)_2(C_6H_4Me\text{-}4)_2(PMe_2Ph)_2]$ were made up under nitrogen in flasks kept in a thermostatically controlled water-bath, using spectroscopic grade $CHCl_3$ which had been purged with nitrogen. Samples were withdrawn at intervals, and their absorbance at 2 015 $cm^{-1}$ (the position of one of the C–O stretching bands for the starting material) was recorded on a Perkin-Elmer 177 spectrophotometer. Data were collected for at least 2.5 half-lives, and rate constants were obtained by least-mean-squares treatment of values for ln(absorbance) and time.

## Acknowledgements

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

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*Received* 10*th February* 1984; *Paper* 4/237