Dialkyl, Diaryl, and Alkyl Aryl Complexes of Ruthenium(II)

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Whereas HgR_2 (R = methyl or aryl) converts *trans*-[$Ru(CO)_2Cl_2(PMe_2Ph)_2$] exclusively into [$Ru(CO)_2R(Cl)(PMe_2Ph)_2$] and does not react with *cis*-[$Ru(CO)_2Cl_2(PMe_2Ph)_2$], LiR reacts with either isomer to yield [$Ru(CO)_2R_2(PMe_2Ph)_2$] and also catalyses conversion of the *trans* isomer into the *cis*. The initial attack by R^- is believed to be on a carbonyl ligand. Treatment of [$Ru(CO)_2R(Cl)(PMe_2Ph)_2$] with LiR′ yields mixed complexes [$Ru(CO)_2R(R')(PMe_2Ph)_2$]. In all cases the two organic ligands are mutually *cis*. The dimethyl complex undergoes reversible carbonylation to form mono- and di-acetyl complexes, and [$Ru(CO)_2Me(Ph)(PMe_2Ph)_2$] also forms an acetyl complex, but aryl ligands are unaffected by treatment with CO.

Reaction of the complex *trans*-[$Ru(CO)_2Cl_2(PMe_2Ph)_2$] [(1), where L = PMe_2Ph] with organomercury compounds HgR_2 (R = Me or Ph) is a convenient route to complexes [$Ru(CO)_2R(Cl)(PMe_2Ph)_2$].[1] Even when HgR_2 is added in large excess, however, there is no replacement of the remaining halide ligand to yield [$Ru(CO)_2R_2(PMe_2Ph)_2$]. In the search for a route to dialkyl and diaryl complexes, required for studies of their conversion into acyl complexes and of their readiness to undergo reductive elimination, we have investigated the use of organolithium compounds in place of HgR_2. This paper gives details of the investigation and of some reactions of the complexes obtained.

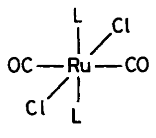
Results and Discussion

Details of the i.r. and ^1H n.m.r. spectra of the new complexes are given in Table 1, and ^{13}C n.m.r. data are in Table 2.

Preparation of Complexes.—Treatment at 263 K of a methylbenzene solution of *trans*-[$Ru(CO)_2Cl_2(PMe_2Ph)_2$] with a slight excess of LiPh in a mixture of ethoxyethane and benzene resulted in complete conversion into a new ruthenium complex, shown by elemental analysis to be [$Ru(CO)_2Ph_2(PMe_2Ph)_2$].

In a subsequent preparation of [$Ru(CO)_2Ph_2(PMe_2Ph)_2$] an insufficient quantity of LiPh was added. An i.r. spectrum of the reaction mixture revealed that the unreacted [$Ru(CO)_2Cl_2(PMe_2Ph)_2$] was now present as the *cis* isomer [(2), where L = PMe_2Ph], despite the fact that conversion of *trans*-[$Ru(CO)_2Cl_2(PMe_2Ph)_2$] into its *cis* isomer normally occurs only on heating in solution.[2] Furthermore, addition of more LiPh at this stage converted the *cis*-[$Ru(CO)_2Cl_2(PMe_2Ph)_2$] into [$Ru(CO)_2Ph_2(PMe_2Ph)_2$]. This also was unexpected, since *cis*-[$Ru(CO)_2Cl_2(PMe_2Ph)_2$], unlike the *trans* isomer, does *not* react with $HgPh_2$ or $HgMe_2$. The mechanistic implications of this will be discussed shortly, but since *trans*-[$Ru(CO)_2Cl_2(PMe_2Ph)_2$] is prepared by way of the *cis* isomer,[2] the latter was naturally used for all subsequent preparative work. Thus the diaryl complexes [$Ru(CO)_2R_2(PMe_2Ph)_2$] (R = Ph, 4-$MeOC_6H_4$, 3-MeC_6H_4, 4-MeC_6H_4, 4-FC_6H_4, or 4-ClC_6H_4) were all prepared from ethoxyethane solutions of *cis*-[$Ru(CO)_2Cl_2(PMe_2Ph)_2$] and the appropriate organolithium reagent at 273 K.

Treatment of *cis*-[$Ru(CO)_2Cl_2(PMe_2Ph)_2$] with a slight excess of LiMe in ethoxyethane solution at 258 K resulted in complete conversion into a species with i.r. bands at 1 995 and 1 918 cm^{-1}. Unfortunately the solution darkened during hydrolysis of excess of LiMe, even when the water used was carefully deoxygenated and NH_4Cl was used as a buffer. Darkening could be avoided by carrying out the reaction in the presence of a little free PMe_2Ph (subsequently removed by conversion into [PMe_3Ph]I), and in this way we were able to obtain the desired [$Ru(CO)_2Me_2(PMe_2Ph)_2$] in a pure state.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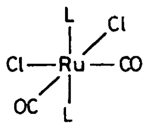
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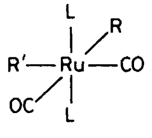
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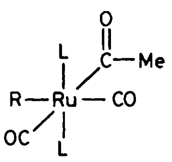
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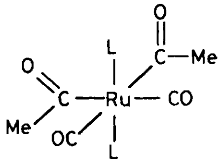
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We were also interested to see whether complexes [$Ru(CO)_2R(Cl)(PMe_2Ph)_2$] could be converted into [$Ru(CO)_2R(R')(PMe_2Ph)_2$] by reaction with LiR′. It proved possible to prepare [$Ru(CO)_2Me(Ph)(PMe_2Ph)_2$] either by treatment of [$Ru(CO)_2Me(Cl)(PMe_2Ph)_2$] with LiPh or by treating [$Ru(CO)_2Ph(Cl)(PMe_2Ph)_2$] with LiMe, but the former method gave a purer product and a higher yield. The mixed diaryl complex [$Ru(CO)_2(C_6H_4OMe\text{-}4)(C_6H_4Me\text{-}4)(PMe_2Ph)_2$] was obtained from *trans*-[$Ru(CO)_2Cl_2(PMe_2Ph)_2$] *via* [$Ru(CO)_2(C_6H_4OMe\text{-}4)Cl(PMe_2Ph)_2$], using $Hg(C_6H_4OMe\text{-}4)_2$ to accomplish the first step and $Li(C_6H_4Me\text{-}4)$ for the second step. A similar approach, using $Hg(C_6H_4Cl\text{-}4)_2$ and $Li(C_6H_4Me\text{-}4)$, yielded [$Ru(CO)_2(C_6H_4Cl\text{-}4)(C_6H_4Me\text{-}4)(PMe_2Ph)_2$].

Spectra of Complexes.— The i.r. spectra of all the complexes [$Ru(CO)_2R_2(PMe_2Ph)_2$] and [$Ru(CO)_2R(R')(PMe_2Ph)_2$] contained two bands of similar intensity in the C–O stretching region, establishing that the carbonyl ligands were mutually *cis*. In the n.m.r. spectra of the complexes, the resonances for the carbon and hydrogen atoms in the methyl substituents in the PMe_2Ph ligands were triplets, showing that these ligands were mutually *trans*.† Thus all the complexes possessed structure (3), where L = PMe_2Ph. All the ^{13}C resonances for the carbonyl ligands exhibited the expected triplet splitting

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† The ways in which phosphorus ligands can be used as stereochemical probes in ruthenium(II) complexes have been described by Shaw and co-workers.[3,4]

Table 1. Infrared [a] and ^1H n.m.r.[b] spectra of complexes

Complex	$\tilde{\nu}$(C–O)/cm^{-1}	δ/p.p.m.	Assignment
$[Ru(CO)_2Me_2(PMe_2Ph)_2]$	1 999	1.66 (t, 12)	$P\mathit{Me}_2Ph$
	1 928	−0.65 (t, 6)	RuMe
$[Ru(CO)_2Ph_2(PMe_2Ph)_2]$	2 020	1.38 (t)	$P\mathit{Me}_2Ph$
	1 954		
$[Ru(CO)_2(C_6H_4OMe\text{-}4)_2(PMe_2Ph)_2]$	2 018	3.75 (s, 6)	4-MeO
	1 948	1.33 (t, 12)	$P\mathit{Me}_2Ph$
$[Ru(CO)_2(C_6H_4Me\text{-}3)_2(PMe_2Ph)_2]$	2 018	2.20 (s, 6)	3-Me
	1 948	1.34 (t, 12)	$P\mathit{Me}_2Ph$
$[Ru(CO)_2(C_6H_4Me\text{-}4)_2(PMe_2Ph)_2]$	2 015	2.29 (s, 6)	4-Me
	1 954	1.35 (t, 12)	$P\mathit{Me}_2Ph$
$[Ru(CO)_2(C_6H_4F\text{-}4)_2(PMe_2Ph)_2]$	2 020	1.35 (t)	$P\mathit{Me}_2Ph$
	1 952		
$[Ru(CO)_2(C_6H_4Cl\text{-}4)_2(PMe_2Ph)_2]$	2 025	1.35 (t)	$P\mathit{Me}_2Ph$
	1 957		
$[Ru(CO)_2Me(Ph)(PMe_2Ph)_2]$	2 002	1.47 (t, 6)	$P\mathit{Me}_2Ph$
	1 940	1.43 (t, 6)	$P\mathit{Me}_2Ph$
		−0.31 (t, 3)	RuMe
$[Ru(CO)_2(C_6H_4OMe\text{-}4)(C_6H_4Me\text{-}4)(PMe_2Ph)_2]$	2 020	3.71 (s, 3)	4-MeO
	1 950	2.25 (s, 3)	4-Me
		1.31 (t, 12) [c]	$P\mathit{Me}_2Ph$
$[Ru(CO)_2(C_6H_4Cl\text{-}4)(C_6H_4Me\text{-}4)(PMe_2Ph)_2]$	2 013	2.27 (s, 3)	4-Me
	1 952	1.34 (t, 6)	$P\mathit{Me}_2Ph$
		1.31 (t, 6)	$P\mathit{Me}_2Ph$
$[Ru(CO)_2(COMe)Me(PMe_2Ph)_2]$	2 013	2.00 (s, 3)	COMe
	1 948	1.63 (t, 12) [c]	$P\mathit{Me}_2Ph$
	1 600	−0.33 (t, 3)	RuMe
$[Ru(CO)_2(COMe)_2(PMe_2Ph)_2]$ [d]	2 031	2.24 (s, 6)	COMe
	1 977	1.74 (t, 12)	$P\mathit{Me}_2Ph$
	1 597		
$[Ru(CO)_2(COMe)Ph(PMe_2Ph)_2]$ [d]	2 010	2.22 (s, 3)	COMe
	1 956	1.50 (t, 6)	$P\mathit{Me}_2Ph$
	1 595	1.36 (t, 6)	$P\mathit{Me}_2Ph$

[a] In $CHCl_3$ solution. Only carbonyl and acyl resonances are listed. [b] In $CDCl_3$ solution. Resonances due to aromatic ring protons are no included. Multiplicities and relative areas are given after the chemical shift values. For PMe_2Ph methyl protons, $|^2J(P-H) + {}^4J(P-H)|$ = *ca.* 7.5 Hz. Other coupling constants are given in the text. [c] Accidental superimposition of two resonances. [d] Not isolated. N.m.r. spectrum recorded at 243 K.

Table 2. Carbon-13 n.m.r. spectra of complexes [a]

				Aryl ligand					
Complex	RuCO	RuMe	RuCOMe	C^1	C^2,C^6	C^3,C^5	C^4	Substituent	$P\mathit{Me}_2Ph$
$[Ru(CO)_2Me_2(PMe_2Ph)_2]$	198.2	−8.1							13.8
$[Ru(CO)_2Ph_2(PMe_2Ph)_2]$	198.1			162.5	143.7	126.2	121.9		14.3
$[Ru(CO)_2(C_6H_4OMe\text{-}4)_2(PMe_2Ph)_2]$	198.3			150.5	143.8	112.2	155.7	54.7	14.3
$[Ru(CO)_2(C_6H_4Me\text{-}3)_2(PMe_2Ph)_2]$	198.2			162.2	140.8	134.6	122.6	21.7	14.3
					144.8	125.8			
$[Ru(CO)_2(C_6H_4Me\text{-}4)_2(PMe_2Ph)_2]$	198.3			157.5	143.5	127.3	131.0	20.9	14.2
$[Ru(CO)_2(C_6H_4F\text{-}4)_2(PMe_2Ph)_2]$ [b]	198.1			155.1	143.9	113.2	160.5		14.4
$[Ru(CO)_2(C_6H_4Cl\text{-}4)_2(PMe_2Ph)_2]$	197.8			160.0	144.5	126.3	128.7		14.4
$[Ru(CO)_2Me(Ph)(PMe_2Ph)_2]$	200.3	−7.1		160.6	141.2 [c]	126.5	122.4		15.5
	196.6								14.0
$[Ru(CO)_2(C_6H_4OMe\text{-}4)(C_6H_4Me\text{-}4)(PMe_2Ph)_2]$	198.3 [d]			150.5	143.8	112.4	155.9	54.8	14.5
				157.3	143.6	127.3	131.0	20.9	14.4
$[Ru(CO)_2(C_6H_4Cl\text{-}4)(C_6H_4Me\text{-}4)(PMe_2Ph)_2]$	198.3			160.6	144.6	126.1	128.8		14.3
	197.8			156.9	143.4	127.4	131.2	20.9	14.1
$[Ru(CO)_2(COMe)Me(PMe_2Ph)_2]$	201.3	−6.8	268.3						15.3
	195.8		50.1						14.9
$[Ru(CO)_2(COMe)_2(PMe_2Ph)_2]$ [e]	197.5		269.7						15.8
			49.7						
$[Ru(CO)_2(COMe)Ph(PMe_2Ph)_2]$ [e]	198.3		266.8	160.6	143.0	126.4	122.3		15.4
	197.6		52.4						13.9

[a] In $CDCl_3$ solution. Resonances due to PMe_2Ph phenyl-carbon atoms omitted. RuCO resonances were triplets with $|^2J(P-C)|$ *ca.* 9.5 Hz. Aryl-ligand C^1, C^2, and C^6 resonances were triplets with $|^2J(P-C)|$ *ca.* 14.0, $|^3J(P-C)|$ *ca.* 3.5 Hz: other aryl carbons showed no clear phosphorus splittings. $P\mathit{Me}_2Ph$ resonances were triplets with $|^1J(P-C) + {}^3J(P-C)|$ *ca.* 32.0 Hz. Other coupling constants are given in the text. [b] For the aryl ligands, $|^1J(F-C)| = 240.8$, $|^2J(F-C)| = 16.5$, $|^3J(F-C)| = 4.2$, and $|^4J(F-C)| = 3.4$ Hz. [c] Broad resonance: see text. [d] Accidental superimposition of two resonances. [e] Not isolated. Spectrum recorded at 243 K.

Table 3. Analytical data and yields

Complex	Analysis (%) Found C	Found H	Calculated C	Calculated H	Yield (%)
$[Ru(CO)_2Me_2(PMe_2Ph)_2]$	51.55	6.05	51.8	6.10	70
$[Ru(CO)_2Ph_2(PMe_2Ph)_2]$	61.35	5.55	61.3	5.50	67
$[Ru(CO)_2(C_6H_4OMe\text{-}4)_2(PMe_2Ph)_2]$	59.4	5.55	59.35	5.60	57
$[Ru(CO)_2(C_6H_4Me\text{-}3)_2(PMe_2Ph)_2]$	62.3	5.85	62.4	5.90	64
$[Ru(CO)_2(C_6H_4Me\text{-}4)_2(PMe_2Ph)_2]$	62.4	5.85	62.4	5.90	68
$[Ru(CO)_2(C_6H_4F\text{-}4)_2(PMe_2Ph)_2]$	57.85	4.80	57.8	4.85	56
$[Ru(CO)_2(C_6H_4Cl\text{-}4)_2(PMe_2Ph)_2]$	54.8	4.60	54.9	4.60	59
$[Ru(CO)_2Me(Ph)(PMe_2Ph)_2]$	57.1	5.65	57.15	5.75	73
$[Ru(CO)_2(C_6H_4OMe\text{-}4)(C_6H_4Me\text{-}4)(PMe_2Ph)_2]$	60.7	5.70	60.85	5.75	73
$[Ru(CO)_2(C_6H_4Cl\text{-}4)(C_6H_4Me\text{-}4)(PMe_2Ph)_2]$	58.65	5.35	58.55	5.25	72
$[Ru(CO)_2(C_6H_4Cl\text{-}4)Cl(PMe_2Ph)_2]$	49.6	4.45	49.65	4.50	72
$[Ru(CO)_2(C_6H_4OMe\text{-}4)Cl(PMe_2Ph)_2]$	52.1	5.15	52.15	5.05	82
$Hg(C_6H_4Cl\text{-}4)_2$	34.05	1.95	34.0	1.90	66
$Hg(C_6H_4OMe\text{-}4)_2$	40.35	3.60	40.55	3.40	87

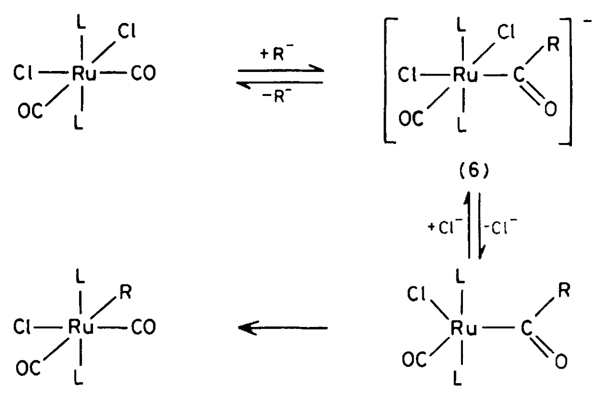
due to the two equivalent phosphorus nuclei. The resonances for the carbon and hydrogen atoms in the methyl ligands were also triplets: coupling constants for $[Ru(CO)_2Me_2(PMe_2Ph)_2]$ were $|^2J(P-C)| = 11.7$ Hz and $|^3J(P-H)| = 7.5$ Hz, the corresponding values for $[Ru(CO)_2Me(Ph)(PMe_2Ph)_2]$ being 11.0 and 8.0 Hz respectively.

In most instances the resonances for the ring protons in the aryl ligands were not particularly well resolved, but the ring-carbon atom resonances were better separated from one another and from the resonances for the phenyl-carbon atoms in the PMe_2Ph ligands. The resonances for C^1 (the carbon atom directly attached to the metal) and (for the *para*-substituted phenyl complexes) C^4 were identified by re-recording the spectra under conditions of weak noise decoupling, and the remaining resonances by comparison within the set of spectra and also with chemical shifts previously reported for other transition-metal phenyl complexes.[5] It was noticeable that the strength of the coupling to phosphorus decreased with increasing distance from the metal: the resonances for C^1, C^2, and C^6 were clear triplets, while those for C^3, C^4, and C^5 were not significantly split. For $[Ru(CO)_2(C_6H_4F\text{-}4)_2(PMe_2Ph)_2]$, there were further splittings due to the fluorine (see Table 2).

The n.m.r. spectra of the mixed complexes $[Ru(CO)_2R(R')(PMe_2Ph)_2]$ were complicated by the lower symmetry of the molecules. In such complexes the two methyl groups in a given PMe_2Ph ligand are inequivalent, as are the two carbonyl ligands, and these inequivalences were usually large enough to allow separate resonances to be observed. In the complexes containing two different aryl ligands, the separate sets of aryl-carbon resonances were identified by comparison with the spectra of the two appropriate complexes $[Ru(CO)_2R_2(PMe_2Ph)_2]$.

The orientation of the aryl ligands in $[Ru(CO)_2Me(Ph)(PMe_2Ph)_2]$ and the diaryl complexes is of some interest. The ambient-temperature ^{13}C n.m.r. spectrum of $[Ru(CO)_2Me(Ph)(PMe_2Ph)_2]$ exhibited only a very broad hump for C^2 and C^6, and in a spectrum recorded at 233 K separate sharp resonances were observed at δ 145.2 and 137.3 for the two atoms. Thus there must be a significant barrier to rotation of the phenyl ligand, as there is in the case of $[Ru(CO)(CNCMe_3)Ph(Cl)(PMe_2Ph)_2]$.[6] In solid $[Ru(CO)(CNCMe_3)Ph(Cl)(PMe_2Ph)_2]$ the phenyl ring is coplanar with the carbonyl and isonitrile ligands,[6] and it seems likely that the phenyl ring in $[Ru(CO)_2Me(Ph)(PMe_2Ph)_2]$ prefers to lie coplanar with the carbonyl ligands.

In the case of the diaryl complexes $[Ru(CO)_2R_2(PMe_2Ph)_2]$, however, it must be sterically impossible for both aryl rings to lie in the same plane as the carbonyl ligands. The ^{13}C n.m.r. spectra of these complexes revealed that C^2 and C^6 were still equivalent even at 223 K, suggesting either that the preferred orientation of the aryl rings was at right angles to the plane containing the carbonyl ligands or that the rings were still oscillating rapidly between positions either side of this orientation.



Scheme. Proposed mechanism for the conversion of *cis*-$[Ru(CO)_2Cl_2L_2]$ into $[Ru(CO)_2R(Cl)L_2]$

Mechanism of Formation of the Complexes.—We have shown that the reactions of *trans*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$ with HgR_2 proceed by way of an initial dissociation of a carbonyl ligand.[1] This mechanism must be ruled out for the reactions of *cis*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$ with LiR, since *cis*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$ is remarkably resistant to thermal dissociation of a carbonyl ligand.[2] Judging by the forcing conditions required to carry out halide exchange in the complex,[3] removal of a halide ligand must also be difficult. We believe (see Scheme, where $L = PMe_2Ph$) that the nucleophile R^- probably attacks the carbon atom of a carbonyl ligand to yield the acyl complex (6). Similar reactions have been observed for other complexes containing carbonyl ligands[7] {for example, $[W(CO)_6]$[8]}. Acyl ligands have a strong *trans*-labilising influence in ruthenium(II) complexes,[9] and loss of the chloride ligand *trans* to the newly formed acyl followed by breakdown of the acyl into separate carbonyl and alkyl or aryl ligands would yield $[Ru(CO)_2R(Cl)(PMe_2Ph)_2]$. The same sequence of steps would then allow conversion of this complex into $[Ru(CO)_2R_2(PMe_2Ph)_2]$.

We are uncertain as to the role of PMe_2Ph in preventing decompositon during the preparation of $[Ru(CO)_2Me_2(PMe_2Ph)_2]$. We expected that PMe_2Ph would convert the dimethyl complex into a more stable acetyl complex,[9] and that the dimethyl complex would be regenerated when the PMe_2Ph was removed with iodomethane. In fact $[Ru(CO)_2Me_2(PMe_2Ph)_2]$ does not appear to react with PMe_2Ph (see later).

Corbonylation Reactions of the Complexes.—Treatment of a $CHCl_3$ solution of $[Ru(CO)_2Me_2(PMe_2Ph)_2]$ with CO at room temperature resulted in fairly rapid changes in the i.r. spectrum of the solution. The terminal C–O stretching bands characteristic of the dimethyl complex were replaced by new bands of similar intensity at 2 013 and 1 948 cm^{-1}, and a band appeared in the acyl-stretching region. Companion studies in $CDCl_3$ solution revealed that the ^1H n.m.r. spectrum of the new species contained a triplet resonance $[|^3J(P-H)| = 8.0$ Hz] at δ −0.33 and a singlet at δ 2.00, each of the same area. Thus the complex contained both a methyl and an acetyl ligand {for comparison, the acetyl proton resonance for $[Ru(CO)_2(COMe)Cl(PMe_2Ph)_2]$ is a singlet at δ 2.12 [9]}. It was also clear from the spectrum that the PMe_2Ph ligands were still mutually *trans*. Thus the complex was $[Ru(CO)_2(COMe)Me(PMe_2Ph)_2]$, and it possessed structure (4), where L = PMe_2Ph and R = Me. This complex had already been isolated from a reaction of *cis*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$ and LiMe in which the hydrolysis and work-up were carried out under CO in an attempt to avoid the problems of decomposition mentioned earlier. A ^{13}C n.m.r. spectrum of the isolated sample confirmed the stereochemistry of the complex and the presence of methyl [triplet, $|^2J(P-C)| = 10.0$ Hz, at δ −6.8] and acetyl [triplet, $|^2J(P-C)| = 13.0$ Hz, at δ 268.3; singlet at δ 50.1] ligands.

On more prolonged carbonylation, the i.r. bands at 2 013 and 1 948 cm^{-1} slowly decreased in intensity as new bands appeared at 2 031 and 1 977 cm^{-1}, and the acyl C–O stretching band shifted slightly to lower energy and increased in intensity. In the ^1H n.m.r. spectrum the methyl and acetyl ligand resonances decreased in area as a new acetyl resonance appeared at δ 2.24. A new triplet resonance for the methyl protons in the PMe_2Ph ligands appeared at δ 1.74. Clearly the new complex was $[Ru(CO)_2(COMe)_2(PMe_2Ph)_2]$, of structure (5), where L = PMe_2Ph. Conversion into this diacetyl complex was, however, incomplete. As the temperature was lowered, the position of equilibrium shifted (as would be expected) towards the diacetyl complex, and ^1H and ^{13}C n.m.r. spectra recorded at 243 K revealed that this was the major species present in solution. The ^{13}C spectrum included a singlet resonance at δ 49.7 and a triplet resonance $[|^2J(P-C)| = 11.9$ Hz] at δ 269.7 for the methyl- and carbonyl-carbon atoms in the acetyl ligands. Unfortunately even low-temperature crystallisation under an atmosphere of CO failed to yield a pure sample of the complex.

None of the diaryl complexes reacted with CO at atmospheric pressure to form acyl complexes, but there was a reaction between $[Ru(CO)_2Me(Ph)(PMe_2Ph)_2]$ and CO in $CHCl_3$ solution. This did not go to completion, but the appearance of an acyl C–O stretching band at 1 595 cm^{-1} (together with new terminal C–O stretching bands at 2 010 and 1 956 cm^{-1}) in the i.r. spectrum of the solution confirmed that an acyl species was present. N.m.r. spectra recorded at 243 K showed that the equilibrium between $[Ru(CO)_2Me(Ph)(PMe_2Ph)_2]$ and the acyl complex favoured the latter quite strongly. The presence of an acetyl ligand was indicated by a singlet resonance at δ 2.22 for the methyl protons and triplet resonances at δ 266.8 $[|^2J(P-C)| = 11.9$ Hz] and 52.4 $[|^3J(P-C)| = 2.5$ Hz] for carbonyl- and methyl-carbon atoms, and it was also clear from the ^{13}C spectrum that the complex contained a phenyl (as opposed to a benzoyl) ligand. Although it was not possible to isolate the complex in a pure state, the spectroscopic data showed it to be $[Ru(CO)_2(COMe)Ph(PMe_2Ph)_2]$, with structure (4) where L = PMe_2Ph and R = Ph.

The methyl $\rightleftharpoons$ acetyl interconversions of these complexes were not as fast as that between $[Ru(CO)_2Me(Cl)(PMe_2Ph)_2]$ and $[Ru(CO)_2(COMe)Cl(PMe_2Ph)_2]$, which is too rapid at ambient temperature for sharp separate resonances to be observed for the two species in partially carbonylated solutions of $[Ru(CO)_2Me(Cl)(PMe_2Ph)_2]$.[9] Indeed decarbonylation of $[Ru(CO)_2(COMe)Me(PMe_2Ph)_2]$ in solution was extremely slow unless the solution was either heated or purged with N_2.

The dimethyl and diphenyl complexes did not react with PMe_2Ph at room temperature in $CHCl_3$ solution, and no reaction (other than slow decomposition) occurred on heating. This was particularly unexpected in the case of the dimethyl complex: monomethyl complexes $[Ru(CO)_2Me(X)(PMe_2Ph)_2]$ (X = Cl, Br, or I) react with both CO and PMe_2Ph under extremely mild conditions to form acetyl complexes {$[Ru(CO)_2(COMe)X(PMe_2Ph)_2]$ and $[Ru(CO)(COMe)X(PMe_2Ph)_3]$ respectively},[9] and yet the dimethyl complex reacts readily with CO but not at all with PMe_2Ph. Given the bulkiness of the halide ligands, the difference in behaviour between $[Ru(CO)_2Me_2(PMe_2Ph)_2]$ and $[Ru(CO)_2Me(X)(PMe_2Ph)_2]$ cannot be steric in origin, and it may be that the electron density on the ruthenium atom in $[Ru(CO)(COMe)Me(PMe_2Ph)_3]$ would be unacceptably high by virtue of the presence of four strongly σ-donating ligands. The failure of $[Ru(CO)_2Ph_2(PMe_2Ph)_2]$ to undergo carbonyl substitution and form $[Ru(CO)Ph_2(PMe_2Ph)_3]$, when $[Ru(CO)_2Ph(Cl)(PMe_2Ph)_2]$ is easily converted into $[Ru(CO)Ph(Cl)(PMe_2Ph)_3]$,[1] may perhaps be accounted for in the same way.

Experimental

Except where indicated otherwise, all operations were carried out under an atmosphere of dry nitrogen, using oxygen-free solvents. Ethoxyethane was distilled from sodium before use. The light petroleum used had a boiling point range of 313—333 K. Analytical data and yields are given in Table 3: all ruthenium complexes listed were white. Infrared spectra were recorded on a Perkin-Elmer 177 spectrophotometer, ^1H n.m.r. spectra on a Varian EM360 60-MHz spectrometer, and ^{13}C spectra on a JEOL FX-90Q spectrometer with an operating frequency (for ^{13}C) of 22.5 MHz.

Organolithium Reagents.—LiPh.[10] A solution of bromobenzene (2 cm^3) in ethoxyethane (20 cm^3) was slowly added, with stirring, to lithium chips (0.50 g) in ethoxyethane (20 cm^3). Gentle warming was sometimes required to initiate reaction. When addition was complete, stirring was continued for 2 h. The precipitate of LiBr was then allowed to settle, and the solution of LiPh was removed for immediate use. Solutions of $Li(C_6H_4OMe\text{-}4)$, $Li(C_6H_4Me\text{-}3)$, and $Li(C_6H_4Me\text{-}4)$ were obtained in the same way. In the preparation of LiMe, iodomethane was used, and the solution was heated under reflux for 1 h after addition of the iodomethane.

$Li(C_6H_4Cl\text{-}4)$.[11] A 1.6 mol dm^{-3} solution of LiBu (Aldrich, 10 cm^3) was slowly added, with stirring, to bromo-4-chlorobenzene (2.00 g) in ethoxyethane (25 cm^3). The solution was then heated under reflux for 0.1 h, allowed to cool, and used immediately. The same method was used for $Li(C_6H_4F\text{-}4)$.

Organomercury Reagents.—$Hg(C_6H_4Cl\text{-}4)_2$. A suspension of $HgCl_2$ (2.70 g) in ethoxyethane (50 cm^3) was added over 0.2

h with stirring to an ethoxyethane solution of $Li(C_6H_4Cl\text{-}4)$ (*ca.* 0.025 mol). The solution was stirred overnight and then treated with $CHCl_3$ (500 cm^3) and water (250 cm^3). After separation, the aqueous layer was extracted with a further 250 cm^3 of $CHCl_3$. The combined organic layers were dried over Na_2SO_4. Removal of the solvent under reduced pressure left a microcrystalline product which was washed with ethoxyethane. The same method was used to prepare $Hg(C_6H_4\text{-}OMe\text{-}4)_2$.

Ruthenium Complexes.—Details of the preparations of *trans*- and *cis*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$,[2] $[Ru(CO)_2Me(Cl)(PMe_2Ph)_2]$, and $[Ru(CO)_2Ph(Cl)(PMe_2Ph)_2]$ [1] have been given elsewhere. The complexes $[Ru(CO)_2(C_6H_4Cl\text{-}4)Cl(PMe_2Ph)_2]$ and $[Ru(CO)_2(C_6H_4OMe\text{-}4)Cl(PMe_2Ph)_2]$ were prepared in the same way as the phenyl complex, using the appropriate organomercury reagents.

$[Ru(CO)_2Ph_2(PMe_2Ph)_2]$. A stirred solution of *cis*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$ (0.50 g) in ethoxyethane (30 cm^3) at 273 K was treated dropwise with an ethoxyethane solution of LiPh, the reaction being monitored by i.r. spectroscopy. When no *cis*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$ remained, water (5 cm^3) was added dropwise, still at 273 K. After 0.1 h the water was removed by pipette. The ethoxyethane solution was dried over $MgSO_4$, and the solvent was then removed under reduced pressure. The residue was crystallised from a mixture of ethanol and propanone and washed with light petroleum containing a little ethanol. All the other symmetrical diaryl complexes were prepared in this way.

$[Ru(CO)_2Me_2(PMe_2Ph)_2]$. A stirred solution of *cis*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$ (0.20 g) and PMe_2Ph (0.05 g) in ethoxyethane (20 cm^3) at 258 K was treated dropwise with an ethoxyethane solution of LiMe until no *cis*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$ remained. After hydrolysis at 273 K, the ethoxyethane solution was treated with iodomethane (3 cm^3) while being dried over $MgSO_4$. The drying agent and $[PMe_3Ph]I$ were filtered off and washed with ethoxyethane (40 cm^3). The filtrate and washings were combined and treated with ethanol (15 cm^3). Slow evaporation under N_2 resulted in crystallisation. The product was washed with a mixture of light petroleum and ethanol.

$[Ru(CO)_2Me(Ph)(PMe_2Ph)_2]$. This was prepared from $[Ru(CO)_2Me(Cl)(PMe_2Ph)_2]$ and LiPh, using the technique described above for the diphenyl complex, except that crystallisation was from a mixture of ethanol and trichloromethane and was carried out at 253 K. The crystals were washed with ethanol.

$[Ru(CO)_2(C_6H_4OMe\text{-}4)(C_6H_4Me\text{-}4)(PMe_2Ph)_2]$. This was prepared from $[Ru(CO)_2(C_6H_4OMe\text{-}4)Cl(PMe_2Ph)_2]$ and $Li(C_6H_4Me\text{-}4)$, using the technique described for the diphenyl complex. The same organolithium reagent was used to convert $[Ru(CO)_2(C_6H_4Cl\text{-}4)Cl(PMe_2Ph)_2]$ into $[Ru(CO)_2(C_6H_4Cl\text{-}4)(C_6H_4Me\text{-}4)(PMe_2Ph)_2]$.

$[Ru(CO)_2(COMe)Me(PMe_2Ph)_2]$. A stirred solution of *cis*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$ (0.20 g) in ethoxyethane (40 cm^3) at 263 K was treated dropwise with an ethoxyethane solution of LiMe until no *cis*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$ remained. From the point where water (5 cm^3) was added to hydrolyse any excess of LiMe, CO was passed through the organic layer. The layers were separated, trichloromethane (15 cm^3) was added to the organic layer, and this was dried over $MgSO_4$. The CO flow was continued for 2 h after filtering off the $MgSO_4$, and crystallisation was then achieved by adding ethanol (15 cm^3) and allowing solvent to evaporate under a slow stream of N_2. The crystals were washed with a mixture of light petroleum and ethanol. Analysis figures for carbon were persistently low (*e.g.* Found: C, 49.95; H, 5.80. Calc. for $C_{21}H_{28}O_3P_2Ru$: C, 51.3; H, 5.75%). This appeared to be due to incomplete combustion of CO lost rapidly as the complex reverted to $[Ru(CO)_2Me_2(PMe_2Ph)_2]$ on heating. When analysis was carried out without adding WO_3 (used to improve combustion), the figures obtained were close to those calculated for loss of 1 mol of CO per mol of complex (Found: C, 48.85; H, 5.75. Calc.: C, 48.9; H, 5.75%).

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