Preparative, Carbon-13 and Phosphorus-31 Nuclear Magnetic Resonance Studies on Dicarbonyl Complexes of Ruthenium(II) and Ruthenium(I) Containing Tertiary Mono-t-butyl- or Di-t-butyl-phosphines †

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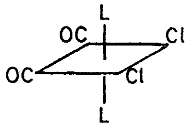
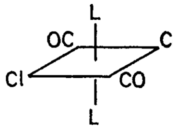
Some new complexes of the types *cis*-$[RuCl_2(CO)_2(PR_2Bu^t)_2]$ (*trans*-phosphines but COs and Cls *cis*) (R = Me, Et, Pr^n, Bu^n, Ph, or *p*-tolyl), *cis*-$[RuCl_2(CO)_2(PRBu^t{}_2)_2]$ (R = Me or Pr^n), and *trans*-$[RuCl_2(CO)_2(PR_2Bu^t)_2]$ (R = Et, Pr^n, or Bu^n) are described. ^{31}P N.m.r. data for these and other dicarbonylruthenium–tertiary phosphine complexes are given. There is a linear correlation between the chemical shift of the free phosphine, δ_{free}, and the co-ordination shift, Δ, on complexation for the complexes *trans*-$[RuCl_2(CO)_2L_2]$. This linear relationship does not apply to the complexes *cis*-$[RuCl_2(CO)_2L_2]$, possibly because of conformational effects. The ^{13}C n.m.r spectra have been recorded for a number of the complexes *cis*-$[RuCl_2(CO)_2L_2]$ and a linear relationship between the ^{13}C chemical shift of the carbonyl and the force constant for the C–O stretching vibration is reported. Treat-~~ment of *cis*-$[RuCl_2(CO)_2(PPr^n{}_2Bu^t)_2]$ with KOH in 2-methoxyethanol gives $[RuHCl(CO)_2(PPr^n{}_2Bu^t)_2]$. The~~ benzenediazonium cation is shown to insert into the ruthenium–hydrogen bond of $[RuHCl(CO)_2(PPr^n{}_2Bu^t)_2]$ to produce the phenyldi-imide complex $[RuCl(NH{=}NPh)(CO)_2(PPr^n{}_2Bu^t)_2]BF_4$. Binuclear ruthenium(I) complexes $[RuX(CO)_2L]_2$ [X = Cl, Br, I, or OAc; L = $PBu^t{}_2Ph$ or $PBu^t{}_2(p\text{-tolyl})$] with a ruthenium–ruthenium bond and a bent bridging system are also described. For X = Cl, phosphorus–phosphorus nuclear spin–spin coupling of *ca.* 80 Hz is transmitted through the ruthenium–ruthenium bond. The bridging system in $[RuCl(CO)_2L]_2$ is cleaved by Cl_2 to give $[Ru_2Cl_4(CO)_4L_2]$, which undergo bridge-splitting reactions to give mononuclear complexes $[RuCl_2(CO)_2QL]$ (Q = pyridine or PMe_2Ph) or easy reduction back to $[RuCl(CO)_2L]_2$. I.r., ^1H, and ^{31}P n.m.r. data are given and discussed.

HEREIN we report the preparation of some new complexes of ruthenium(II) and ruthenium(I) carbonyls with tertiary mono-t-butyl- or di-t-butyl-phosphine ligands. We have previously shown that bulky phosphine ligands such as these generate unusual chemical and n.m.r. effects.[1-5] The unusual chemistry seems to be largely associated with steric effects. The work with the tertiary mono-t-butylphosphines PBu^tR_2 (R = Me, Et, Pr^n, Bu^n, Ph, and *p*-tolyl) is described first.

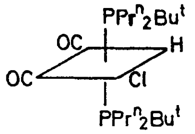
When alcoholic solutions of ruthenium trichloride are treated with carbon monoxide and a tertiary phosphine (L) is added to the resultant solution, complexes of the types $[RuCl_2(CO)_2L_2]$ are readily formed for L = PEt_3, PMe_2Ph, PEt_2Ph, *etc.*[6-10] If the ruthenium trichloride is treated with carbon monoxide in boiling ethanol then the complex $[RuCl_2(CO)_2L_2]$ is orange and of configuration (II) which we shall call *trans* but treatment with carbon monoxide under more vigorous conditions gives an isomer of configuration (I), which is white and which we shall call *cis*. The *trans*-complexes when heated isomerize completely to the *cis*-complexes.[6,7] We find that the mono-t-butyl-phosphines show behaviour similar to that of less bulky phosphines such as PEt_3, PMe_2Ph, *etc.*, *e.g.* when ruthenium trichloride is treated with carbon monoxide for 16 h in boiling 2-methoxyethanol solution and PBu^tMe_2 is added to the resultant pale yellow solution *cis*-$[RuCl_2(CO)_2(PBu^tMe_2)_2]$ is formed in high yield. We have similarly prepared new complexes *cis*-$[RuCl_2(CO)_2L_2]$ with other mono-t-butylphosphines, L = PBu^tEt_2, $PBu^tPr^n{}_2$, $PBu^tBu^n{}_2$, PBu^tPh_2, or $PBu^t(p\text{-tolyl})_2$; with di-t-butylphosphines, *i.e.* L = $PBu^t{}_2Me$ or $PBu^t{}_2Pr^n$; and also with L = $PMePh_2$ and $PEtPh_2$ (see Table 1 for analytical and other data). The complex *cis*-$[RuCl_2(CO)_2(PBu^tPr^n{}_2)_2]$ was also prepared by treating ruthenium trichloride with $PBu^tPr^n{}_2$ (4 mol) in boiling 2-methoxyethanol for $1\frac{1}{4}$ h followed by treatment with carbon monoxide. Treatment of ruthenium trichloride in boiling 2-methoxyethanol with carbon monoxide over a shorter period ($2\frac{1}{2}$ h) followed by addition of the appropriate tertiary phosphine gave a mixture of *cis*- and *trans*-$[RuCl_2(CO)_2L_2]$ (L = PBu^tEt_2, $PBu^tPr^n{}_2$, or $PBu^tBu^n{}_2$). The mixture of isomers was separated by chromatography on Keiselgel G, the *trans*-isomer, configuration (II) being eluted first with benzene (see Table 1).



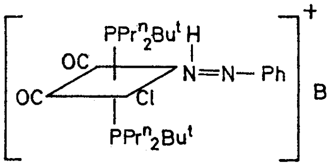
(I)



(II)



(III)



(IV)

The i.r. and ^1H n.m.r. data (Table 1) indicate that the white complexes have configuration (I) (*cis*).[7,9] Thus there are two i.r. bands due to $\nu(C{\equiv}O)$ (1950—2057 cm^{-1}),

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† No reprints available.

[1] A. J. Cheney, B. E. Mann, B. L. Shaw, and R. M. Slade, *Chem. Comm.*, 1970, 1176.

[2] C. Masters and B. L. Shaw, *J. Chem. Soc.* (*A*), 1971, 3679.

[3] B. E. Mann, C. Masters, and B. L. Shaw, *J. Chem. Soc.* (*A*), 1971, 1104.

[4] B. E. Mann, C. Masters, B. L. Shaw, and R. E. Stainbank, *Chem. Comm.*, 1971, 1103.

[5] C. Masters, B. L. Shaw, and R. E. Stainbank, *Chem. Comm.*, 1971, 209.

[6] J. Chatt, B. L. Shaw, and A. E. Field, *J. Chem. Soc.*, 1964, 3466.

[7] M. S. Lupin and B. L. Shaw, *J. Chem. Soc.* (*A*), 1968, 741.

[8] T. A. Stephenson and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1966, **28**, 945.

[9] J. M. Jenkins, M. S. Lupin, and B. L. Shaw, *J. Chem. Soc.* (*A*), 1966, 1787.

[10] M. I. Bruce and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1967, 1238.

two due to ν(Ru–Cl) (*ca.* 300 cm^{-1}) and the ^{1}H n.m.r. t-butyl pattern consists of a triplet showing that J(P–P) is large and the phosphines are mutually *trans*.[11] The yellow *trans*-complexes as expected show a 1 : 2 : 1 triplet t-butyl ^{1}H n.m.r. pattern and only one i.r. band due to ν(C≡O) [7] but there are two strong bands in the region 300—350 cm^{-1} and we are unable to determine which of these is due to the ruthenium–chlorine stretch. Similarly the complexes *trans*-$[RuCl_2(CO)_2L_2]$ with L = PEt_3 or PEt_2Ph show two very intense absorptions in the region 300—350 cm^{-1} and a definite assignment to ν(Ru–Cl) was not made. There is no doubt that the stereochemistry of these complexes is *trans* since in addition to the i.r. and n.m.r. evidence they have zero, or almost zero, dipole moments.[6] The *trans*-complexes (II) are thermally unstable and isomerize readily on heating to the *cis*-complexes; [6,7] thus attempted replacement of Cl by Br or I by metathesis causes isomerization *trans* ⟶ *cis*. The complex *trans*-$[RuCl_2(CO)_2(PBu^tPr^n_2)_2]$ does not react with $PBu^tPr^n_2$ to give $[RuCl_2(CO)(PBu^tPr^n_2)_3]$ as do the corresponding *trans*-dicarbonyl complexes with less bulky tertiary phosphine ligands and only *cis*-$[RuCl_2(CO)_2(PBu^tPr^n_2)_2]$ was isolated from the mixture. The *cis*-dicarbonyl complexes are extremely stable thermally and very inert to substitution. Replacement of chlorine with bromine or iodine by metathesis with lithium bromide or sodium iodide could not be achieved completely even in boiling 2-methoxyethanol for many hours. The complexes *cis*-$[RuCl_2(CO)_2L_2]$ (L = PEt_3 or PEt_2Ph) do not form hydrido-carbonyl complexes on boiling with alcohols in the presence of base.[6] We find that *cis*-$[RuCl_2(CO)_2(PBu^tPr^n_2)_2]$ when treated with potassium hydroxide in boiling 2-methoxyethanol gives $[RuHCl(CO)_2(PBu^tPr^n_2)_2]$ (Table 1). Possibly the relief of steric strain on replacing Cl by H is the driving force behind this conversion. The ^{1}H n.m.r. spectrum of the t-butyl groups of this complex appear as a triplet at τ 8·84 indicative of mutually *trans*-phosphines, with $|^{3}J(\text{P–H}) + {}^{5}J(\text{P–H})| = 13{\cdot}4$ Hz and the hydride resonance occurs as a triplet at τ 15·29 with ^{2}J(P–H) = 19·9 Hz, showing the hydride ligand to be *cis* to both phosphine ligands. The i.r. spectrum (Table 2) shows three bands at *ca.* 2000 cm^{-1} but we are unable to assign ν(C≡O) and ν(Ru–H). The far-i.r. spectrum showed one strong band at 281 cm^{-1} characteristic of chlorine *trans* to carbonyl.[7] From these data we assign configuration (III) to this complex. It reacts with hydrogen chloride evolving hydrogen, regenerating *cis*-$[RuCl_2(CO)_2(PBu^tPr^n_2)_2]$.

TABLE 1

Analytical, spectroscopic, and other weight data for the complexes *cis*- and *trans*-$[RuCl_2(CO)_2L_2]$ (L = tertiary phosphine), and $[RuHCl(CO)_2(PPr^n_2Bu^t)_2]$ and $[RuCl(PhN_2H)(CO)_2(PPr^n_2Bu^t)_2]BF_4$

				Analytical data [a]					I.r. data				
									ν(C≡O) cm^{-1}			^{1}H N.m.r. data [c]	
$[RuCl_2(CO)_2L_2]$	Configuration	Colour	Yield %	C	H	Cl	M [a,b]	M.p.	Nujol	Chloroform	ν(Ru–Cl) cm^{-1}	τ(Bu^t)	' J '
L = PMe_2Bu^t	I	Pale yellow	70	36·35(36·2)	6·55(6·5)	15·1(15·25)	459(464)	179 [d]	2025, 1958	2037, 1976	308vs, 283vs	8·77(t) [e]	14·3
PEt_2Bu^t	I	White	74	41·6(41·55)	7·2(7·35)	13·5(13·6)		195 [d]	2025, 1957	2033, 1969	302vs, 277vs	8·69(t)	13·5
$PPr^n_2Bu^t$	I	White	85	45·5(45·85)	8·05(8·0)	12·25(12·3)	547(576)	137—139	2025, 1957	2033, 1969	310s, 282s	8·69(t)	13·2
$PBu^n_2Bu^t$	I	White	86	49·4(49·4)	8·45(8·55)	11·2(11·2)	587(632)	73—76	2025, 1955	2031, 1965	308s, 281vs	8·71(t)	13·3
PPh_2Bu^t	I	White	80	56·15 (57·3)	5·35(5·35)		727(713)	225—235	2050, 1984	2049, 1984	304s, 282s	8·61(t)	14·8
P(*p*-tolyl)$_2$Bu^t	I	White	87	58·65(59·35)	6·2(6·05)	9·0(9·2)	765(769)	245—268 [f]	2035, 1972	2049, 1978	297s, 275s	8·61(t) [g]	14·7
$PMeBu^t_2$	I	White	82	43·8(43·8)	7·65(7·7)	13·2(12·95)	541(549)	230—245	2020, 1950	2037, 1970	309vs, 277vs	8·54(t) [h]	13·2
$PPr^nBu^t_2$	I	White	91	47·45(47·7)	8·3(8·35)	11·55(11·75)		210—230 [f]	2027, 1957	2033, 1969	309vs, 279vs	8·52(t)	12·5
$PMePh_2$	I	White	57	53·15(53·5)	4·2(4·15)	11·0(11·3)	613(628)	224—228	2049, 1984	2053, 1988	307s, 284s	7·70(t) [i]	8·6
$PEtPh_2$	I	White	81	54·95(54·9)	4·65(4·6)	10·85(10·8)	651(656)	250—259	2057, 1980	1056, 1992	308vs, 280vs		
PEt_2Bu^t	II	Yellow	33	41·6(41·55)	7·6(7·35)	13·4(13·6)		168 [d]	1981	1992	346s?, 323m?	8·66(t)	13·5
$PPr^n_2Bu^t$	II	Yellow	34	45·6 (45·85)	7·9(8·0)	12·15(12·3)	550(576)	120—139	1984	1989	345vs?, 327vs?	8·67(t)	14·0
$PBu^n_2Bu^t$	II	Yellow	25	49·3(49·4)	8·5(8·55)	11·3(11·2)		82—88	1986	1990	341vs?, 323s?	8·68(t)	13·5
$[RhCl(CO)_2(PPr^n_2Bu^t)_2]$		White	70	48·8(48·9)	8·55(8·4)	6·7(6·55)	523(541)	160—164 [f]	2939, 1949br, 1921 [j]	2933, 1957, 1932sh [j]	281s	8·84(t) [k]	13·4
$[RuCl(PhN_2H)(CO)_2(PPr^n_2Bu^t)_2]BF_4$		Fawn	67	46·25(45·8)	7·3(7·15)	4·7(4·85) [l]		142—145 [m]	2061, 1996	2066, 2008	300vs	8·66(tr) [n]	15·0

[a] Theoretical values in parentheses. [b] In chloroform solution. [c] ^{1}H N.m.r. spectra recorded at *ca.* 35° and 60 MHz in $CDCl_3$ solution. τ-values ±0·02, J-values ±0·5 Hz; ' J ' = $|^{3}J(\text{P–H}) + {}^{5}J(\text{P–H})|$. [d] Sublimes. [e] Methyl groups at τ 8·39(t); $|^{3}J(\text{P–H}) + {}^{4}J(\text{P–H})|$ 7·8 Hz. [f] With decomposition. [g] *p*-Tolyl methyl groups at τ 7·69 (s). [h] Methyl groups at τ 8·24(t) $^{2}J(\text{P–H}) + {}^{4}J(\text{P–H})|$ 7·0 Hz. [i] Values given are for the methyl groups; ' J ' = $|^{2}J(\text{P–H}) + {}^{4}J(\text{P–H})|$. [j] One of these bands is probably assignable to ν(Ru–H). [k] Spectrum recorded in benzene solution. Hydride resonance at τ 15·29; ^{2}J(P–H) 19·9 Hz. [l] Nitrogen, 4·1(3·8)%. [m] With gas evolution. [n] Aromatic protons at τ 2·16 (singlet). N–*H* proton at τ −3·57 (broadened singlet). ν(N–H) tentatively assigned at 3378vw (Nujol), 3365vw,br ($CHCl_3$) cm^{-1}.

In recent years it has been reported that many metal hydride complexes react with arenediazonium salts to produce arylazo- or aryldi-imide-complexes.[12-16] We find that $[RuHCl(CO)_2(PPr^n_2Bu^t)_2]$ (III) reacts with benzenediazonium tetrafluoroborate in acetone solution, to give a phenyldi-imide complex of ruthenium, $[RuCl(NH{=}NPh)(CO)_2(PPr^n_2Bu^t)_2]BF_4$ (IV) (Table 1)]. This complex is pale yellow, soluble in polar solvents, and a 1 : 1 electrolyte in nitrobenzene solution. Its ^{1}H n.m.r. spectrum (Table 1) shows a triplet for the t-butyl groups at τ 8·66, $|^{3}J(\text{P–H}) + {}^{5}J(\text{P–H})|$ 15·0 Hz; a singlet at τ 2·16 for the phenyl protons; and a broadened singlet at τ −3·57, assigned to the proton attached to the ruthenium-bonded nitrogen atom. Very low τ-values for the nitrogen-bound protons of phenyldi-imide complexes have been reported by Parshall [14] and Eisenberg.[12] The i.r. spectrum (Table 1) shows two strong bonds at 2061 and 1996 cm^{-1} due to mutually *cis*-carbonyl groups, and bands due to the tetrafluoroborate anion. We cannot unequivocally assign a band due to ν(N=N) but

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[11] B. E. Mann, B. L. Shaw, and R. M. Slade, *J. Chem. Soc.* (*A*), 1971, 2976.

[12] L. Toniolo and R. Eisenberg, *Chem. Comm.*, 1971, 455.

[13] J. A. McCleverty and R. N. Whiteley, *Chem. Comm.*, 1971, 1159.

[14] G. W. Parshall, *J. Amer. Chem. Soc.*, 1965, **87**, 2133.

[15] G. W. Parshall, *J. Amer. Chem. Soc.*, 1967, **89**, 1822.

[16] M. L. H. Green, T. R. Sanders, and R. N. Whiteley, *Z. Naturforsch.*, 1968, **23b**, 106.

we tentatively assign ν(N–H) at 3378 cm^{-1}. The far-i.r. spectrum (Table 1) contains a strong band at 300 cm^{-1} assigned to the ruthenium–chlorine stretching vibration *trans* to carbonyl. These data indicate the complex to be of configuration (IV).

N.M.R. Studies on Complexes of the Types [RuCl$_2$(CO)$_2$(PBu^{t}R$_2$)$_2$] *(I) and (II)*.—In a number of papers we have reported accurate ^{31}P n.m.r. shifts of tertiary phosphine–transition metal complexes. We found that most tertiary phosphines with t-butyl groups have ^{31}P shifts at less positive or more negative values (relative to 85% H$_3$PO$_4$) than tertiary phosphines such as PEt$_3$, PBu$^n{}_3$, PMe$_2$Ph, PPh$_3$, *etc.* and hence we were able to study the effects of co-ordination on tertiary phosphines with a larger range of chemical shifts than previously. It was found that for many types of complexes, *e.g. cis-* or *trans-*[MCl$_2$L$_2$] (M = Pd or Pt), *trans-*[MCl(CO)L$_2$], *mer-*[MCl$_3$L$_3$] (M = Rh or Ir), *etc.* there is a linear relationship between the ^{31}P chemical shift of the free tertiary phosphine, δ_{free}, and the change in ^{31}P chemical shift on co-ordination, Δ.[3,11,17,18] We also found by ^{1}H and ^{31}P n.m.r. spectroscopy that bulky phosphines such as tertiary mono- or di-t-butyl phosphines give complexes which can exist as conformers in solution because of restricted rotation about the phosphorus–metal bond. Sometimes the conformers are sufficiently long-lived to be observed at room temperature but in other cases, *e.g. trans-*[RhCl(CO)(PBu$^t{}_2$Et)$_2$] rotation is fairly rapid at 20° giving a broad ^{31}P resonance but essentially stops at −60° when the spectra of three conformers are observed (in these spectra the protons were decoupled by ' random noise ').[18,19] The ^{31}P shifts of these conformers can be very different, *e.g.* two conformers of *trans-*[RhCl(CO)(PBu$^t{}_2$Me)$_2$] differ by 16 p.p.m.[19] If the tertiary phosphine has substituents which differ greatly in bulk then there may be big differences between the populations of the various conformers and the linear relationship between δ_{free} and Δ may not hold.[18] We have now investigated the ^{31}P shifts of *cis-* and *trans-*[RuCl$_2$(CO)$_2$L$_2$] including the complexes described in this paper and many described previously, see Table 2. There is a reasonably good linear relationship between δ_{free} and Δ for complexes of the type *trans-*[RuCl$_2$(CO)$_2$L$_2$], *i.e.* $\Delta = -(29{\cdot}9 \pm 1{\cdot}2) - (0{\cdot}308 \pm 0{\cdot}051)\ \delta_{\text{free}}$. For the corresponding *cis*-complexes the linear relationship does not hold. We suggest that in the *cis*-complexes there are big changes in the various conformer populations with different phosphines and consequently there is no linear correlation between Δ and δ_{free} but in the more symmetrical *trans*-complexes the differences in conformer populations are smaller and less important and there is a linear relationship.

TABLE 2

Phosphorus-31 n.m.r. data for complexes of types *trans-* and *cis-*[RuCl$_2$(CO)$_2$L$_2$], measured in CH$_2$Cl$_2$

trans-[RuCl$_2$(CO)$_2$L$_2$]			*cis-*[RuCl$_2$(CO)$_2$L$_2$]		
L	$\delta_{\text{H}_3\text{PO}_4}$	Δ_{obs}	L	$\delta_{\text{H}_3\text{PO}_4}$	Δ_{obs}
PMe$_2$Ph	2·90	−44·65	PMe$_2$Bu^t	−28·3	−57·0
			PMePh$_2$	−11·5	−39·1
PBu$^n{}_2$Ph	−10·62	−36·64	PPr$^n{}_2$Ph	−7·7	−35·1
PEt$_3$	−16·38	−36·49	PBu$^n{}_2$Ph	−8·2	−34·2
PEt$_2$Ph	−15·92	−33·51	PEt$_3$	−15·7	−35·8
PBu^{t}Pr$^n{}_2$	−27·40	−36·14	PEt$_2$Ph	−13·0	−30·6
PBu^{t}Bu$^n{}_2$	−28·07	−32·45	PEtPh$_2$	−19·7	−32·0
PBu^{t}Et$_2$	−32·41	−25·55	PPr$^n{}_2$Bu^t	−32·3	−41·1
			PPh$_3$	−17·4	−24·4
			PBu$^n{}_2$Bu^t	−32·7	−37·1
			PEt$_2$Bu^t	−36·1	−29·2
			PBu^t(*p*-tolyl)$_2$	−28·5	−13·3
			BPu^{t}Ph$_2$	−30·2	−12·9
			PBu$^t{}_2$Pr^n	−45·6	−19·2
			PHBu$^t{}_2$	−53·2	−34·2

We have also examined the ^{13}C n.m.r. spectra of a number of these complexes, see Table 3. There are several features of interest. It has been well established that for metal complexes containing two tertiary phosphine ligands with methyl or t-butyl groups then, when the tertiary phosphines are mutually *trans*, the methyl or t-butyl resonances are triplets {*i.e.* $|^2J(\text{P–P})|$ is large} but when they are mutually *cis* then the resonances are doublets {*i.e.* $|^2J(\text{P–P})|$ is small}.[11] This method is not easily applicable to groups giving more complex ^{1}H n.m.r. patterns as the spectra cannot be interpreted readily. The restriction does not apply to ^{13}C n.m.r. spectroscopy thus an n-butyl group gives a triplet for the α- and γ-carbons and singlets for the β- and δ-carbons (Table 3). Similarly all the carbons of a phenyl group with the exception of the *p*-carbon appear as triplets. Thus ^{13}C n.m.r. spectroscopy would appear to offer a general way of determining when tertiary phosphines are mutually *trans*. It is interesting to note that in alkyl groups attached to phosphorus $|^xJ(^{31}\text{P–C–}^{13}\text{C}) + {}^{x+2}J(^{31}\text{P–M–P–C–}^{13}\text{C})|$ is measurable for the α- and γ-carbon atoms (*i.e.* $x = 1$ or 3) but small and unresolved for the β-carbon atom (*i.e.* $x = 2$). We have found this to be so for all the transition metal–tertiary phosphine complexes so far examined and facilitates the assignment of β-carbon resonances.

It has been reported that for complexes of the type W(CO)$_5$L, a linear relationship exists between the ^{13}C chemical shift of the carbonyl and the force constant for the C–O stretching vibration.[20] We also find a linear relationship between the ^{13}C chemical shift of the carbonyl and the force constant for the C–O stretching vibration as calculated by the Cotton–Kraihanzel method.[21]

Complexes with PBu$^t{}_2$Ph *or* PBu$^t{}_2$(p-*tolyl*).—As seen from the work described above tertiary mono-t-butyl phosphines and also PBu$^t{}_2$Me and PBu$^t{}_2$Pr^n behave like ' normal ' or typical phosphines in that complexes of type [RuCl$_2$(CO)$_2$L$_2$] can be prepared. However, molecular models show that some of these complexes are extremely crowded and with yet more bulky phosphines complexes

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[17] B. E. Mann, C. Masters, B. L. Shaw, R. M. Slade, and R. E. Stainbank, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 881.

[18] B. E. Mann, C. Masters, and B. L. Shaw, *J.C.S. Dalton*, 1972, 704.

[19] B. E. Mann, C. Masters, B. L. Shaw, and R. E. Stainbank, *Chem. Comm.*, 1971, 1103.

[20] O. A. Gansow, B. Y. Kimura, G. R. Dobson, and R. A. Brown, *J. Amer. Chem. Soc.*, 1971, **93**, 5922.

[21] F. A. Cotton and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, 1962, **84**, 4432.

of this type should not exist. In agreement with this we find that when ruthenium trichloride is treated with carbon monoxide in boiling 2-methoxyethanol and then either PBu^t_2Ph or PBu^t_2(*p*-tolyl) added, orange diamagnetic ruthenium(I) complexes $[RuCl(CO)_2(PBu^t_2R)]_2$ are formed in high yield (Table 4). Molecular weight measurements show these complexes to be binuclear and the i.r. spectra (Table 4) show two bands due to ν(Ru–Cl) and three due to ν(C≡O). The ^1H n.m.r. pattern of the t-butyl groups consists of a 1 : 2 : 1 triplet with a very broad central peak, suggesting an intermediate value of $|J(P–P)|$. The structure of the complex $[RuCl(CO)_2\{PBu^t_2(p\text{-tolyl})\}]_2$ has been determined by single crystal *X*-ray diffraction[22] and is shown in (V). The Ru–Ru distance of 2·63 Å is shorter than those found in other bi- and poly-nuclear complexes of ruthenium (2·73 Å in $[(\pi-C_5H_5)Ru(CO)_2]_2$;[23] 2·77—2·81 Å in $[C_{12}H_{16}Ru_4(CO)_{10}]$;[24] 2·85 Å in $[Ru_3(CO)_{12}]$[25]). This observation, the non-planarity of the bridge system {the dihedral angle between the $RuCl_2(CO)_2$ planes being 92°} and the requirements of the rare-gas rule lead to the postulation of a bent metal–metal bond, formed from the overlap of essentially octahedral metal hybrid orbitals. Only very few other binuclear complexes of ruthenium(I) have been reported, notably $[(\pi-C_5H_5)Ru(CO)_2]_2$[26] and $[RuI_2(NO)L_2]_2$[27] (L = py, $AsMePh_2$, or ½ bipy).

TABLE 3

22·62 MHz ^{13}C N.m.r. data for some complexes of the type *cis*-$[MCl_2(CO)_2L_2]$ measured in CH_2Cl_2, with white noise decoupling of the protons. Shifts (p.p.m.) are reported with respect to $SiMe_4$, with increasing frequency taken as being positive. The coupling constant to phosphorus is given in parentheses (in Hz). The force constant and frequency for the C–O stretch is also given for CH_2Cl_2 solution

			n-Alkyl				t-Bu		Phenyl					
M	L	CO	α-C	β-C	γ-C	δ-C	C	Me	*p*-C	*o*-C	*m*-C	*p*-C	*k*/ mdyn Å⁻¹	ν(C≡O)/cm⁻¹
Ru	PEt_3	195·4(10·6)	16·9(28·2)[a]	8·0(3)[a]									16·36	2045, 1980
Ru	PEt_2Ph	193·9(11·0)	16·0(28·4)[a]	7·6(3)[a]					133·9(41·0)[a]	131·2(7·6)[a]	129·2(8·4)[a]	130·6	16·46	2053, 1984
Ru	$PEtPh_2$	193·7(10·6)	18·1(28·0)[a]	7·8(*ca.* 0)[a]					[b]	134·0(10·2)[a]	129·1(8·8)[a]	131·2	16·56	2058, 1992
Ru	PPh_3	[b]							[b]	135·3(10·4)[a]	129·0(9·6)[a]	131·5		
Ru	PEt_2Bu^t	197·4(10·9)	15·8(24·0)[a]	10·0(*ca.* 0)[a]			34·6(22·8)[a]	28·3					16·26	2041, 1971
Ru	$PBu^n_2Bu^t$	197·3(11·0)	22·8(22·6)[a]	27·1(*ca.* 0)[a]	25·4(12·1)[a]	18·4	34·4(22·8)[a]	28·3					16·24	2039, 1971
Ru	$PMeBu^t_2$	198·3(10·7)	5·7(23)[a]				31·1(24·4)[a]	38·9					16·21	2037, 1969
Os	$PPr^n_2Bu^t$	177·6(7·3)	24·2(27·2)[a]	19·0(*ca.* 0)[a]	16·3(13·6)[a]		34·3(27·4)[a]	28·0						

[a] $|J(P–C) + J(P–C')|$ quoted. [b] Not found.

TABLE 4

Analytical, spectroscopic, m.p., and molecular weight data for the complexes $[RuX(CO)_2L]_2$ [X = Cl, Br, I, or OAc; L′ = PBu^t_2Ph; L″ = PBu^t_2(*p*-tolyl)], $[Ru_2Cl_4(CO)_4L_2]$ [L′ = PBu^t_2Ph; L″ = PBu^t_2(*p*-tolyl)], and the products obtained from the bridge-splitting reactions of $[Ru_2Cl_4(CO)_4L_2]$.

			Analytical data [a]					I.r. data			N.m.r. data [c]		
								ν(C≡O)					
Compound	Colour	% Yield	C	H	Halogen	*M* [a,b]	M.p.	Nujol	Chloroform	ν(Ru–halogen)	τ(Bu^t)	*J*(P–Bu^t)	τ(tolyl-Me)
$[RuCl(CO)_2L']_2$	Orange	72	46·4 (46·3)	5·65 (5·6)	8·6 (8·55)		217—235°[d]	2016vs, 1978s, 1942vs	2024, 1988, 1949	313m, 283s	8·56tr	13·6[e]	
$[RuCl(CO)_2L'']_2$	Orange	82	48·1 (47·6)	6·05 (5·9)	8·5 (8·25)	882 (858)	208—217[d]	2020s, 1981s, 1954s, 1943s	2024, 1984, 1949	312m, 277s	8·52tr	13·6[e]	7·62
$[L'(CO)_2RuCl_2Ru(CO)_2L'']$	Orange	75	47·0 (47·0)	5·7 (5·75)	8·7 (8·4)		190—199[d]	2030, 1982, 1956s, 1948s	2032, 1988, 1952	308m, 273s	8·50[f]	13·9[e]	7·58
$[RuBr(CO)_2L'']_2$	Orange	82	43·3 (43·15)	5·55 (5·3)	16·95 (16·9)	919 (946)	217—225[d]	2021s, 1979s, 1953s, 1941s	2028, 1990, 1953	196s, 187s	8·53tr	13·6[e]	7·65
$[RuI(CO)_2L']_2$	Red	90	38·1 (37·95)	4·35 (4·6)	24·9 (25·05)	986 (1012)	186—192[d]	2010s, 1984s, 1972m, 1949s, 1944s	2020, 1984, 1951	157m, 147msh	8·52tr	13·5[e]	
$[RuI(CO)_2L'']_2$	Red	78	39·35 (39·25)	5·05 (4·85)	24·1 (24·4)	1011 (1041)	201—206	2018vs, 1976s, 1953vs	2023, 1984, 1951	160m, 152m	8·47tr	13·6[e]	7·62
$[Ru(OAc)(CO)_2L'']_2$	Yellow	69	50·3 (50·45)	6·25 (6·25)			180—193[d]	2015vs, 1971s, 1936vs	2016, 1972, 1942		8·53tr	12·7[e]	7·62
$[Ru_2Cl_4(CO)_4L'_2]$	Light yellow	98	42·2 (42·65)	5·0 (5·15)			240—246[d]	2055vs, 1993vs		318vs, 271vs, 242s			
$[Ru_2Cl_4(CO)_4L'']$	Light yellow	82	44·1 (44·0)	5·25 (5·45)	15·8 (15·25)		233—237[d]	2065vs, 1994vs		318vs, 271s, 242m			
$[RuCl_2(CO)_2(py)L']$[f]	White	84	47·4 (47·65)	5·2 (5·35)	13·7 (13·4)[h]	543 (529)	200—205 240—250[d]	2058vs, 1985vs	2049, 1980	305vs, 284vs	8·32(d)	14·0[i]	
$[RuCl_2(CO)_2(py)L'']$	White	58	48·5 (48·6)	5·5 (5·55)	13·5 (13·05)		232—245[d]	2058vs, 1979vs	2051, 1984	301vs, 276vs	8·33(d)	13·8[i]	7·60
$[RuCl_2(CO)_2(PMe_2Ph)L']$	White	49	48·7 (49·0)	5·75 (5·8)	11·85 (12·05)	532 (588)	156—162	2045vs, 1977vs	2049, 1984	303vs, 273vs	8·39(d)[j]	12·9	

[a] Theoretical values in parentheses. [b] Recorded in chloroform solution. [c] Spectra recorded at *ca.* 35° and 60 MHz in $CDCl_3$ solution. τ-Values ±0·02, *J*-values ±0·5 Hz. (d) = doublet; tr = intermediate coupling pattern approximating to a triplet. [d] With decomposition. [e] '*J*' = $|^3J(P–H) + {}^6J(P–H)|$. [f] Multiplet (see text). [g] Acetate methyls at τ 8·13. ν(C≡O) at 1572s and 1434s cm⁻¹ (Nujol). [h] Nitrogen = 2·9(2·65)%. [i] '*J*' = $^3J(P–H)$. [j] PMe_2Ph-methyls at τ 7·84 ddl; $^2J(P–H)$ 11·1 Hz, $^4J(P–H)$ 2·0 Hz.

In order to establish the strength of the phosphorus–phosphorus coupling the complex $(L'(CO)_2RuCl_2Ru(CO)_2L'')$ [L′ = PBu^t_2Ph; L″ = PBu^t_2(*p*-tolyl)], configuration (V) was prepared by heating an equimolar mixture of $[RuCl(CO)_2PBu^t_2Ph]_2$ and $[RuCl(CO)_2PBu^t_2(p\text{-tolyl})]_2$ under reflux in toluene. The product has similar near- and far-i.r. spectra to the starting materials, *i.e.* three carbonyl stretching vibrations and two metal–chlorine stretching frequencies (see Table 4). The ^1H (t-butyl) n.m.r. spectrum consists of two sharp doublets separated by 0·6 Hz with a rather broad resonance in the

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[22] D. F. Gill, R. Mason, B. L. Shaw, and K. M. Thomas, *J. Organometallic Chem.*, 1972, **40**, C67.

[23] O. S. Mills and J. P. Nice, *J. Organometallic Chem.*, 1967, **9**, 339.

[24] R. Belford, M. I. Bruce, M. A. Cairns, M. Green, H. P. Taylor, and P. Woodward, *Chem. Comm.*, 1970, 1159.

[25] R. Mason and A. L. M. Rae, *J. Chem. Soc.* (*A*), 1968, 778.

[26] E. O. Fischer and A. Vogler, *Z. Naturforsch.*, 1962, **17b**, 421

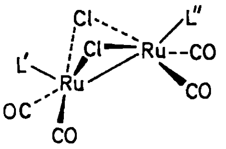
[27] R. J. Irving and P. G. Laye, *J. Chem. Soc.* (*A*), 1966, 161.

centre as might be expected for two overlapping virtually coupled triplets, with an intermediate value for ^3J(P–M–M–P). The spectrum should be of the type $ABX_{18}Y_{18}$, neglecting the further complication of coupling between the two phosphorus nuclei and the phenyl and *p*-tolyl groups. The ^{31}P n.m.r. spectrum in dichloromethane solution with all ^1H nuclei decoupled consists of a very strongly coupled AB-pattern with the chemical shifts relative to 85% H_3PO_4 of −70·5 and −69·9 and ^3J(P–P) = 82 ± 3 Hz. The rare phenomenon of transmittance of phosphorus–phosphorus coupling through a metal–metal bond has been observed previously; for the complex $[H_4Ru_4(CO)_8\{P(OMe)_3\}_4]$.[28]

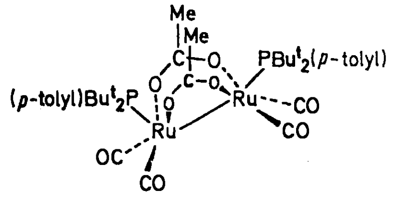
Metathesis of the complexes $[RuCl(CO)_2L]_2$ [L = PBu^t_2Ph, PBu^t_2(*p*-tolyl)] with lithium bromide or sodium iodide in boiling 2-methoxyethanol gives the complexes $[RuX(CO)_2L]_2$ [X = Br; L = PBu^t_2(*p*-tolyl): X = I; L = PBu^t_2Ph or PBu^t_2(*p*-tolyl)]. These complexes have similar i.r. spectra with three carbonyl stretching frequencies *ca.* 2000 cm^{-1} (see Table 4). The complex $[RuBr(CO)_2\{PBu^t_2(p\text{-tolyl})\}]_2$ shows two ruthenium–bromine stretching vibrations at 196 and 187 cm^{-1}. The iodide complexes $[RuI(CO)_2L]_2$ [L = PBu^t_2Ph or PBu^t_2(*p*-tolyl)] show two bands assigned to ν(Ru–I) at *ca.* 160 and *ca.* 150 cm^{-1}. The ^1H n.m.r. spectra of the compounds $[RuX(CO)_2L]_2$ (Table 4) each exhibit an intermediate coupling pattern for the t-butyl groups. The bromo- and iodo-complexes are assigned the same stereochemistry as the corresponding chloro-complexes.

Treatment of the complex $[RuCl(CO)_2\{PBu^t_2(p\text{-tolyl})\}]_2$ with silver acetate in benzene yields the complex $[Ru(OAc)(CO)_2\{PBu^t_2(p\text{-tolyl})\}]_2$. The i.r. spectrum of this complex (Table 4) again shows three strong bands due to ν(C≡O) and two strong bands at 1572 and 1434 cm^{-1} assigned to the carbonyl stretching vibrations of bridging acetate groups. The ^1H n.m.r. spectrum (Table 4) shows a triplet, with a broadened central peak, for the t-butyl groups at τ 8·53 $\{|^3J(P\text{–}H) + {}^6J(P\text{–}H)|$ 12·7 Hz$\}$, a singlet at τ 8·13 assigned to the acetate-methyl groups, and a singlet at τ 7·62 assigned to the tolyl-methyl groups. The observation that the t-butyl groups appear as a triplet with a sharp central peak rather than an intermediate pattern, as in the corresponding halogeno-complexes, would indicate that there is stronger phosphorus–phosphorus coupling through the metal–metal bond. The stronger coupling may arise from a release of strain in the bridge upon replacing halogen by acetate and thus allowing the P–Ru–Ru–P bonds to approach closer to linearity. From these data we have assigned configuration (VI) to the complex. Lewis *et al.*[29] have prepared very similar compounds of the type $[Ru(OAc)(CO)_2Q]_2$ (Q = PPh_3, PBu^n_3, $AsPh_3$, pyridine, *etc.*) by treating $[Ru_3(CO)_{12}]$ with acetic acid, followed by the addition of a neutral ligand, Q. The i.r. data of these complexes closely parallel that which we have reported for $[Ru(OAc)(CO)_2\{PBu^t_2(p\text{-tolyl})\}]_2$, and they have postulated a similar structure to ours.

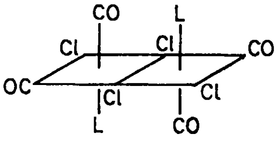
We have attempted to cleave the metal–metal bond in the complexes $[RuCl(CO)_2L]_2$ [L = PBu^t_2Ph, PBu^t_2(*p*-tolyl)] with nitric oxide, but were unable to isolate any well defined products. However, chlorine readily cleaves the metal–metal bond to produce the complexes $[Ru_2Cl_4(CO)_4L_2]$ [L = PBu^t_2Ph or PBu^t_2(*p*-tolyl)]. These complexes are pale yellow insoluble solids which show two bands in the i.r. due to ν(C≡O), one due to terminal ν(Ru–Cl) (at 318 cm^{-1}), and two associated with a bridging $RuCl_2Ru$ system (at 242 and 271 cm^{-1}). The high value of the terminal ν(Ru–Cl) suggests that the chlorine is not *trans* to phosphorus but these data do not distinguish between the two configurations (VII) or (VIII).



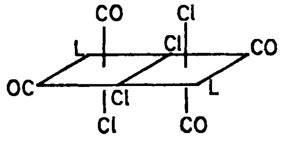
(V)



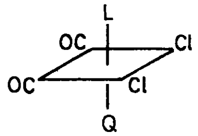
(VI)



(VII)



(VIII)



(IX)

In an attempt to prepare *cis*-$[RuCl_2(CO)_2(PBu^t_2Ph)_2]$ by cleavage of the chlorine bridge in $[Ru_2Cl_4(CO)_4(PBu^t_2Ph)_2]$ with di-t-butylphenylphosphine in 2-methoxyethanol, it was found that rapid conversion back to $[RuCl(CO)_2\{PBu^t_2Ph\}]_2$ occurs (refluxing for 1 min). This reversal could also be accomplished by refluxing in 2-methoxyethanol alone but it takes longer (30 min) and the yield of $[RuCl(CO)_2\{PBu^t_2Ph\}]_2$ is less.

Bridge-splitting Reactions of the Complexes $[Ru_2Cl_4(CO)_4L_2]$ [L′ = PBu^t_2Ph; L″ = PBu^t_2(*p*-tolyl)].—When a suspension of $[Ru_2Cl_4(CO)_4(PBu^t_2Ph)_2]$ in pyridine is heated at 90° for 3 min a clear solution is obtained from which $[RuCl_2(CO)_2py(PBu^t_2Ph)]$, configuration (IX; L = PBu^t_2Ph; Q = pyridine), is isolated. This complex shows two carbonyl stretching frequencies at 2058 and 1985 cm^{-1} in its i.r. spectrum (Table 4), and the far-i.r. spectrum contains two metal–chlorine stretching vibrations at 305 and 284 cm^{-1} which are consistent with the assigned structure. The ^1H n.m.r. spectrum (Table 4) shows a doublet for the t-butyl groups at τ 8·32, ^3J(P–H) 14·0 Hz. The complex $[Ru_2Cl_4(CO)_4\{PBu^t_2(p\text{-tolyl})\}_2]$ reacts similarly with pyridine to yield

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[28] S. A. R. Knox and H. D. Kaesz, *J. Amer. Chem. Soc.*, 1971, **93**, 4594.

[29] G. R. Crooks, B. F. G. Johnson, J. Lewis, I. G. Williams, and G. Gamlen, *J. Chem. Soc.* (*A*), 1969, 2761.

[RuCl$_2$(CO)$_2$(py){PBu$^t_2$(*p*-tolyl)}], configuration (IX; L = PBu$^t_2$(*p*-tolyl); Q = pyridine).

Addition of dimethylphenylphosphine to a suspension of [Ru$_2$Cl$_4$(CO)$_4$(PBu$^t_2$Ph)$_2$] in dichloromethane gives a clear colourless solution from which [RuCl$_2$(CO)$_2$(PMe$_2$Ph)(PBu$^t_2$Ph)], configuration (IX; L = PBu$^t_2$Ph; Q = PMe$_2$Ph), is obtained. The near- and far-i.r. spectra (Table 4) of the complex show two carbonyl stretching frequencies at 2045 and 1977 cm^{-1} and two metal–chlorine stretching frequencies at 303 and 273 cm^{-1}. The ^{1}H n.m.r. spectrum (Table 4) shows a doublet for the t-butyl groups at τ 8·39, ^3J(P–H) 12·9 Hz; and a double doublet for the methyl groups of the dimethylphenylphosphine ligand at τ 7·84 due to coupling with the adjacent ^{31}P nucleus [^2J(P–H) 11·1 Hz] and the ^{31}P nucleus of the di-t-butylphenylphosphine ligand in the *trans*-position [^4J(P–H) 2·0 Hz]. These data confirm the assignment of the stereochemistry to this complex.

EXPERIMENTAL

Melting points were determined on a Kofler hot-stage apparatus and are corrected. All operations involving free tertiary phosphines were carried out under argon. Analytical, m.p., and molecular weight data are given in Tables 1 and 4.

cis-*Dichloro(dicarbonyl)bis(di-n-propyl-t-butylphosphine)ruthenium*(II).—Carbon monoxide was passed through a boiling solution of ruthenium trichloride trihydrate (4·55 g, 18·27 mmol) in 2-methoxyethanol (100 ml) for 16 h. Di-n-propyl-t-butylphosphine (6·86 g, 39·46 mmol) was then added and the mixture heated under reflux for 5 min. The solvent was removed under reduced pressure and the residue recrystallized from dichloromethane–methanol as *prisms* (8·91 g).

The following complexes were prepared in a similar manner: cis-*Dichloro(dicarbonyl)bis(dimethyl-t-butylphosphine)ruthenium*(II), cis-*Dichloro(dicarbonyl)bis(diethyl-t-butylphosphine)ruthenium*(II), cis-*Dichloro(dicarbonyl)bis(di-n-butyl-t-butylphosphine)ruthenium*(II), cis-*Dichloro(dicarbonyl)bis(diphenyl-t-butylphosphine)ruthenium*(II), cis-*Dichloro(dicarbonyl)bis(di-*p*-tolyl-t-butylphosphine)ruthenium*(II), cis-*Dichloro(dicarbonyl)bis(methyldi-t-butylphosphine)ruthenium*(II), cis-*Dichloro(dicarbonyl)bis(n-propyldi-t-butylphosphine)ruthenium*(II), cis-*Dichloro(dicarbonyl)bis(methyldiphenylphosphine)ruthenium*(II), and cis-*Dichloro(dicarbonyl)bis(ethyldiphenylphosphine)ruthenium*(II).

trans-*Dichloro(dicarbonyl)bis(di-n-propyl-t-butylphosphine)ruthenium*(II).—Carbon monoxide was passed through a boiling solution of ruthenium trichloride trihydrate (1·85 g, 7·21 mmol) in 2-methoxyethanol (30 ml) for 2·5 h. Di-n-propyl-t-butylphosphine (3·14 g, 18·02 mmol) was added to the cooled solution and a yellow solid was slowly deposited, which was found to be a mixture of *cis*- and *trans*-isomers. The mixture was separated by chromatography on a column of Keiselgel G with benzene as eluent. The *trans*-isomer, which was eluted first, was recrystallized from dichloromethane–methanol as *prisms* (1·4 g).

The following complexes were prepared and purified in a similar manner: trans-*Dichloro(dicarbonyl)bis(di-n-butyl-t-butylphosphine)ruthenium*(II), and trans-*Dichloro(dicarbonyl)bis(diethyl-t-butylphosphine)ruthenium*(II).

Hydridochloro(dicarbonyl)bis(di-n-propyl-t-butylphosphine)ruthenium(II).—Aqueous potassium hydroxide (1·79 ml; 4·32 M; 7·64 mmol) was added to a solution of cis-dichloro(dicarbonyl)bis(di-n-propyl-t-butylphosphine) ruthenium(II) (4·00 g, 6·95 mmol) in hot 2-methoxyethanol (90 ml) and the mixture heated under reflux for 2¼ h. Isolation gave the *product* (2·65 g) from dichloromethane–methanol.

Action of Hydrogen Chloride on Hydridochloro(dicarbonyl)bis(di-n-propyl-t-butylphosphine)ruthenium(II).—A solution of hydrogen chloride (0·12 mmol) in diethyl ether (1·5 ml) was added to a solution of hydridochloro(dicarbonyl)bis(di-n-propyl-t-butylphosphine)ruthenium(II) (66·1 mg, 0·12 mmol) in benzene (2 ml), and the mixture set aside for 35 min. Isolation gave *cis*-dichloro(dicarbonyl)bis(di-n-propyl-t-butylphosphine)ruthenium(II) (63·2 mg), shown to be identical with an authentic sample by its i.r. spectrum.

Chloro(phenyldi-imide)(dicarbonyl)bis(di-n-propyl-t-butylphosphine)ruthenium(II) *Tetrafluoroborate*.—A mixture of benzenediazonium tetrafluoroborate (0·88 g, 4·57 mmol) and hydridochloro(dicarbonyl)bis(di-n-propyl-t-butylphosphine)ruthenium(II) (0·49 g, 0·91 mmol) suspended in acetone (15 ml) was stirred in the dark for 4 h to yield a deep red solution. The solution was evaporated under reduced pressure and the residue extracted with dichloromethane (2 × 10 ml). After filtration and evaporation the resulting red oil was recrystallized from acetone–diethyl ether to give the *product* (0·44 g) as prisms. (Molar conductivity in *ca.* 2 × 10^{-3} M nitrobenzene solution at 23°: 27·8 Ω^{-1} cm^2 mol^{-1}.)

Di-μ-chloro-tetracarbonylbis(di-t-butylphenylphosphine)diruthenium(I).—Carbon monoxide was passed through a boiling solution of ruthenium trichloride trihydrate (3·36 g, 13·48 mmol) in 2-methoxyethanol (50 ml) for 4 h. Di-t-butylphenylphosphine (6·28 g, 28·3 mmol) was added to the cooled yellow solution, and the mixture refluxed for 5 min. Isolation gave the *product* (4·03 g) as prisms from dichloromethane–methanol.

*Di-μ-chloro-tetracarbonylbis(di-t-butyl-*p*-tolylphosphine)diruthenium*(I).—This was prepared and purified in a similar manner.

*Di-μ-chloro-tetracarbonyl(di-t-butylphenylphosphine)(di-t-butyl-*p*-tolylphosphine)diruthenium*(I).—A mixture of di-μ-chloro-tetracarbonylbis(di-t-butylphenylphosphine)diruthenium(I) (0·26 g, 0·31 mmol) and di-μ-chloro-tetracarbonylbis(di-t-butyl-*p*-tolylphosphine)diruthenium(I) (0·27 g, 0·31 mmol) were refluxed in toluene (15 ml) for 7·5 h. Isolation gave the *product* (0·4 g) as prisms from dichloromethane–methanol.

*Di-μ-iodo-tetracarbonylbis(di-t-butyl-*p*-tolylphosphine)diruthenium*(I).—A mixture of di-μ-chloro-tetracarbonylbis(di-t-butyl-*p*-tolylphosphine)diruthenium(I) (0·27 g, 0·32 mmol) and sodium iodide (1 g, 6·67 mmol) was heated under reflux in 2-methoxyethanol (20 ml) for 1·5 h. Isolation gave the *product* (0·26 g) as prisms from dichloromethane–methanol.

The following two compounds were similarly prepared by metathesis from the corresponding dichloro-complexes by treatment with an excess of lithium bromide or sodium iodide. They were both obtained from dichloromethane–methanol as prisms. *Di-μ-bromo-tetracarbonylbis(di-t-butyl-*p*-tolylphosphine)diruthenium*(I); *Di-μ-iodo-tetracarbonylbis(di-t-butylphenylphosphine)diruthenium*(I).

*Di-μ-acetato-tetracarbonylbis(di-t-butyl-*p*-tolylphosphine)diruthenium*(I).—Silver acetate (0·18 g, 1·09 mmol) was added to a solution of di-μ-chloro-tetracarbonylbis(di-t-butyl-*p*-tolylphosphine)diruthenium(I) (0·42 g, 0·49 mmol) in benzene (40 ml) and the mixture was shaken in the dark for 16·5 h. The solution was filtered and evaporated under reduced pressure to give the *product* (0·31 g) as microneedles from dichloromethane-methanol.

Di-μ-chloro-(dichloro)tetracarbonylbis(di-t-butylphenylphosphine)diruthenium(II).—A solution of chlorine (1·58 mmol) in carbon tetrachloride (1·5 ml) was added to a solution of di-μ-chloro-tetracarbonylbis(di-t-butylphenylphosphine)diruthenium(I) (0·59 g, 0·71 mmol) in chloroform (10 ml). The mixture was set aside for 5 min and then evaporated to dryness to give the *product* (0·62 g) as microprisms.

*Di-μ-chloro-(dichloro)tetracarbonylbis(di-t-butyl-*p*-tolylphosphine)diruthenium*(II).—This was prepared in a similar manner.

Action of Di-t-butylphenylphosphine on Di-μ-chloro-(dichloro)tetracarbonylbis(di-t-butylphenylphosphine)diruthenium(II).—Di-t-butylphenylphosphine (95 μl, 0·42 mmol) was added to a suspension of di-μ-chloro-(dichloro)tetracarbonylbis(di-t-butylphenylphosphine)diruthenium(II) (0·15 g, 0·17 mmol) in 2-methoxyethanol (5 ml) and the mixture was heated under reflux for 1 min to give a clear orange solution, which on cooling deposited di-μ-chloro-tetracarbonylbis(di-t-butylphenylphosphine)diruthenium(I) (0·09 g, 67%), identified by its i.r. spectrum.

Action of Boiling 2-Methoxyethanol on Di-μ-chloro-(dichloro)tetracarbonylbis(di-t-butylphenylphosphine)diruthenium(II).—A suspension of di-μ-chloro-(dichloro)tetracarbonylbis(di-t-butylphenylphosphine)diruthenium(II) (0·08 g) in 2-methoxyethanol (5 ml) was heated under reflux for 30 min to give a clear orange solution. Isolation gave di-μ-chloro-tetracarbonylbis(di-t-butylphenylphosphine)diruthenium(I) (0·03 g, 42%), identified by its i.r. spectrum.

Dichloro(dicarbonyl)pyridine(di-t-butylphenylphosphine)ruthenium(II).— Di-μ-chloro-(dichloro)tetracarbonylbis(di-t-butylphenylphosphine)diruthenium(II) (0·29 g) was suspended in pyridine (5 ml) and the mixture heated at 90° for 3 min to give a clear solution. Isolation gave the *product* (0·29 g) as prisms from dichloromethane-methanol.

*Dichloro(dicarbonyl)pyridine(di-t-butyl-*p*-tolylphosphine)-ruthenium*(II).—This was prepared in a similar manner as *prisms* from ethanol.

Dichloro(dicarbonyl)dimethylphenylphosphine(di-t-butylphenylphosphine)ruthenium(II).— Dimethylphenylphosphine (0·09 ml, 0·6 mmol) was added to a suspension of di-μ-chloro-(dichloro)tetracarbonylbis(di-t-butylphenylphosphine)diruthenium(II) (0·25 g, 0·27 mmol) in dichloromethane (10 ml) and the mixture was set aside for 16·5 h to give a clear solution. Isolation gave the *product* (0·16 g) as prisms from dichloromethane–light petroleum (b.p. 60—80°).

N.M.R. Spectra.—^{1}H N.m.r. spectra were recorded at *ca.* 34° and 60 MHz on Perkin-Elmer R10 or R12A spectrometers. ^{31}P and ^{13}C N.m.r. spectra were recorded on a Bruker Spectrospin HFX spectrometer at ambient temperatures and 36·43 MHz or 22·62 MHz respectively, with C_6F_6 as the field–frequency lock and all ^{1}H nuclei were decoupled.

I.r. Spectra.—These were recorded on a Perkin-Elmer 457 spectrometer (4000—250 cm^{-1}) and a Grubb-Parsons D.B.3/D.N.2 spectrometer (500—200 cm^{-1}).

We thank the S.R.C. for a maintenance award (to D. F. G.) and Johnson-Matthey Ltd. for the generous loan of ruthenium trichloride.

[2/1965 *Received*, 17*th August*, 1972]