

## Reaction of Benzyltriphenylphosphonium Bicyclo[2.2.1]hepta-2,5-diene-carbonyltrichlororuthenate(II) with Lewis Bases<sup>1</sup>

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A detailed investigation of the reactions of the salt  $[\text{Ph}_3(\text{PhCH}_2)\text{P}][\text{RuCl}_3(\text{CO})(\text{C}_7\text{H}_8)]$  (I;  $\text{C}_7\text{H}_8 = \text{bicyclo}[2.2.1]\text{-hepta-2,5-diene}$ ) with ligands (L) containing Group VB or VIB donor atoms is presented. Several different types of behaviour are found, depending on both the nature and amount of added L. For  $\text{L} = \text{Me}_2\text{S}$ ,  $\text{Me}_2\text{SO}$ , and  $\text{CH}_2=\text{CH}-\text{CN}$ , the salts  $[\text{Ph}_3(\text{PhCH}_2)\text{P}][\text{RuCl}_3(\text{CO})\text{L}_2]$ , (II), have been isolated in high yield, whereas for  $\text{L} = \text{AsPh}_3$ ,  $\text{SbPh}_3$ , and  $\text{C}_5\text{H}_5\text{N}$ , a mixture of (II) and  $[\text{RuCl}_2(\text{CO})\text{L}(\text{C}_7\text{H}_8)]$ , (III), have been obtained [(I) : L = 1 : 2 molar ratio]. Reaction of complex (I) with excess of  $\text{SbPh}_3$  gives (II), (III), and  $[\text{RuCl}_2(\text{CO})(\text{SbPh}_3)_3]$ , (IV). In contrast, reaction of complex (I) with  $\text{PPh}_3$  (1 : 2 molar ratio) gives  $[\{\text{RuCl}_2(\text{CO})(\text{PPh}_3)_2\}_2]$ , (V), whereas with  $\text{PMe}_2\text{Ph}$ , only  $[\text{RuCl}_2(\text{PMe}_2\text{Ph})_2(\text{C}_7\text{H}_8)]$ , (VI), is isolated. A similar complex of type (VI) is formed with  $\text{PMePh}_2$ , together with some  $[\text{RuCl}_2(\text{CO})(\text{PMePh}_2)_3]$ , (IV), whilst with 2,2'-bipyridyl or 1,10-phenanthroline (L'), the complexes  $[\{\text{RuCl}_2(\text{CO})(\text{L}')\}_n]$ , (VII), and  $[\text{Ph}_3(\text{PhCH}_2)\text{P}][\text{RuCl}_3\text{CO}(\text{L}')]$ , (II), are obtained. Reaction mechanisms consistent with this observed variation in product composition are tentatively proposed.

RECENTLY we reported the synthesis and characterisation of the first anionic diene complexes of ruthenium(II),  $\text{M}[\text{RuX}_3(\text{CO})(\text{C}_7\text{H}_8)]$  {M =  $\text{Ph}_3(\text{PhCH}_2)\text{P}^+$  or  $\text{Cs}^+$ ; X =

<sup>1</sup> Preliminary communication, L. Ruiz-Ramírez, T. A. Stephenson, and E. S. Switkes, *J. Organometallic Chem.*, 1973, **49**, C77.

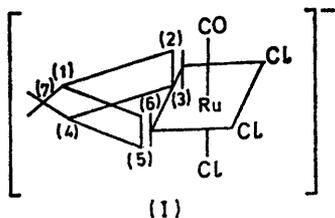
Cl or Br;  $\text{C}_7\text{H}_8 = \eta\text{-bicyclo}[2.2.1]\text{hepta-2,5-diene}$  (norbornadiene)}.<sup>2</sup> Earlier workers, particularly in rhodium chemistry, have shown that olefin compounds are often

<sup>2</sup> T. A. Stephenson and E. S. Switkes, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 805; T. A. Stephenson, E. S. Switkes, and L. Ruiz-Ramírez, *J.C.S. Dalton*, 1973, 2112.

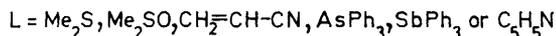
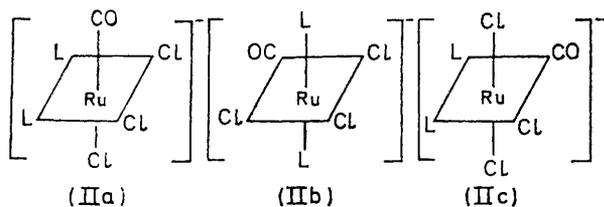
very useful precursors for the synthesis of a range of complexes by substitution of the olefin groups.<sup>3</sup> In view of the small amount of published work on convenient methods of synthesising anionic ruthenium(II) complexes with ligands containing Group VB and VIB donor atoms,<sup>4</sup> we have undertaken a detailed study of the reactions of  $[\text{Ph}_3(\text{PhCH}_2)\text{P}][\text{RuCl}_3(\text{CO})(\text{C}_7\text{H}_8)]$ , (I), with such ligands (L), in an attempt to obtain these complexes. However, several different types of behaviour are found experimentally, depending on the nature and amount of ligand used in these attempted exchange reactions. The different types of product are first described and then reaction mechanisms consistent with this observed variation are tentatively proposed.

## RESULTS

When the complex  $[\text{Ph}_3(\text{PhCH}_2)\text{P}][\text{RuCl}_3(\text{CO})(\text{C}_7\text{H}_8)]$ , (I), was dissolved in dichloromethane and heated under reflux under a nitrogen atmosphere with either  $\text{Me}_2\text{S}$ ,  $\text{Me}_2\text{SO}$ , or  $\text{CH}_2=\text{CH}-\text{CN}$  [(I) : L = 1 : 2 molar ratio] for *ca.* 12 h,



complete displacement of the diene group occurred and yellow or orange crystalline complexes  $[\text{Ph}_3(\text{PhCH}_2)\text{P}][\text{RuCl}_3(\text{CO})\text{L}_2]$ , (II), were isolated from the reaction mixture



in 75–80% yield on addition of diethyl ether. For L =  $\text{Me}_2\text{S}$ , the  $^1\text{H}$  n.m.r. spectrum (methyl region) consisted of a strong singlet at  $\tau$  7.37 together with two very weak doublets (*ca.* 5 Hz separation) centred at  $\tau$  6.58 and 7.37. There are three geometrical isomers possible for (II) and the strong signal at  $\tau$  7.37 could be assigned to isomer (IIa) or (IIb) and the weaker ones to the presence of a small amount of isomer (IIc) (assuming restricted rotation of the methyl groups at 300 K). For L =  $\text{Me}_2\text{SO}$ , the  $^1\text{H}$  n.m.r. spectrum revealed a strong singlet at  $\tau$  6.72 [attributed to isomer (IIa) or (IIb)] and weak signals at  $\tau$  6.60 and 7.36. The highest-field signal corresponds to free  $\text{Me}_2\text{SO}$  and the others to S-bonded  $\text{Me}_2\text{SO}$  {*cf.*

\* This assignment is based on the assumption that the *cis*-influence of CO produces a lower-field shift of the carbon atoms (1), (2), and (6) than that of chloride ion on (3), (4), and (5). This assumption is also made in ref. 2 for the  $^1\text{H}$  n.m.r. spectrum.

<sup>3</sup> For example, see R. R. Schrock and J. A. Osborn, *J. Amer. Chem. Soc.*, 1971, **93**, 2397; L. M. Haines, *Inorg. Chem.*, 1971, **10**, 1685 and references therein.

$[\text{RuX}_2(\text{Me}_2\text{SO})_4]$  (refs. 5 and 6)}. The i.r. spectrum of this complex showed a strong band at 1113  $\text{cm}^{-1}$  assigned to S-bonded  $\text{Me}_2\text{SO}$ , but no bands which can be attributed definitely to O-bonded  $\text{Me}_2\text{SO}$ . The absence of the latter was confirmed by synthesis of the complex  $[\text{Ph}_3(\text{PhCH}_2)\text{P}][\text{RuCl}_3(\text{CO})(\text{C}_7\text{H}_8)(\text{Me}_2\text{SO})_2]$  ( $\nu_{\text{SO}}$  at 1108  $\text{cm}^{-1}$ ).

For L =  $\text{CH}_2=\text{CH}-\text{CN}$ ,  $\nu_{\text{CN}}$  occurred at 2245  $\text{cm}^{-1}$ , suggesting that bonding occurs through the nitrogen atom rather than the double bond {*cf.*  $[\text{RuCl}_3(\text{PPh}_3)_2(\text{CH}_2=\text{CH}-\text{CN})]$ ,  $\nu_{\text{CN}}$  at 2230  $\text{cm}^{-1}$  (ref. 6)}. The far-i.r. spectra of these complexes (see Experimental section) cannot unequivocally distinguish between isomer (IIa) (Cl *trans* to L and CO) and (IIb) (Cl *trans* to CO and Cl), but the similarity in properties between complex (II) and  $[\text{Ph}_3(\text{PhCH}_2)\text{P}][\text{RuCl}_3(\text{CO})(\text{L}')]]$  [L' = 2,2'-bipyridyl or 1,10-phenanthroline (see later)] suggests that (IIa) is the most probable structure. This isomeric form is also consistent with that established for complex (I) by  $^1\text{H}$  (ref. 2) and  $^{13}\text{C}$  n.m.r. studies. The latter shows diene resonances at 77.10, 64.84, 60.92, 50.0, and 48.22 p.p.m., assignable to carbon atoms (2) and (6), (3) and (5), (7), (1), and (4) respectively.\*

In attempts to extend the range of complexes (II), ligands such as  $\text{Et}_2\text{S}$ ,  $\text{Ph}_3\text{S}$ ,  $\text{CS}_2$ ,  $\text{MeCN}$ ,  $\text{PhCH}_2\text{CN}$ , and  $\text{PhCN}$  were reacted under the same conditions with (I), but in all cases (I) was recovered unchanged. However, with L =  $\text{AsPh}_3$ ,  $\text{SbPh}_3$ , or  $\text{C}_5\text{H}_5\text{N}$  [(I) : L = 1 : 2 molar ratio], reaction in  $\text{CH}_2\text{Cl}_2$  for 12 h, followed by addition of diethyl ether, also gave the complexes  $[\text{Ph}_3(\text{PhCH}_2)\text{P}][\text{RuCl}_3(\text{CO})\text{L}_2]$ , (II), but with yields of only 18–25%. In this instance, treatment of the ether filtrate with pentane gave further yellow precipitates (60% yield). These were non-electrolytes containing CO, L, and  $\text{C}_7\text{H}_8$  groups ( $^1\text{H}$  n.m.r. and i.r. evidence) and elemental analyses and molecular-weight determinations indicated the composition  $[\text{RuCl}_2(\text{CO})(\text{L})(\text{C}_7\text{H}_8)]$ , (III). There are three geometrical isomers possible for (III).  $^1\text{H}$  N.m.r. spectra of all these complexes [Figure 1 (L =  $\text{AsPh}_3$ ) and Table 1] consisted of seven diene resonances of relative intensity 1 : 1 : 1 : 1 : 1 : 1 : 2. This clearly eliminates isomer (IIIc), where only five diene resonances should be observed. Homonuclear-decoupling experiments for L =  $\text{AsPh}_3$  indicated that the resonance at  $\tau$  6.34 is coupled to the resonances at  $\tau$  5.60 and 4.52 and that at  $\tau$  5.92 is coupled to the peak at  $\tau$  4.25. The signals at  $\tau$  5.92 and 5.70 are too close for decoupling studies. This information, plus the assumption that the *cis*- and *trans*-influences of L and CO respectively (or *vice versa*) produce lower-field shifts than those of chloride ion, leads to the tentative assignments given in Table 1. Unfortunately, it is not possible to distinguish between isomer (IIIa) and (IIIb) on this evidence, even by careful comparison of  $^1\text{H}$  n.m.r. spectra of complexes with different L groups, because of the lack of information concerning the *relative* magnitudes of such variables as *cis*-influence, *trans*-influence, ring-current effects, *etc.*, of the other ligands on the chemical shifts of the diene protons. However, the similarity in position of the diene resonances for all these complexes, together with the similar position of  $\nu_{\text{CO}}$  in each case (*ca.* 2000  $\text{cm}^{-1}$ ), suggests that the *same* isomer is always produced. On leaving the

<sup>4</sup> For references to earlier work see T. A. Stephenson, E. S. Switkes, and P. W. Armit, *J.C.S. Dalton*, 1974, 1134.

<sup>5</sup> I. P. Evans, A. Spencer, and G. Wilkinson, *J.C.S. Dalton*, 1973, 204.

<sup>6</sup> L. Ruiz-Ramírez, T. A. Stephenson, and E. S. Switkes, *J.C.S. Dalton*, 1973, 1770.

complex  $[\text{RuCl}_2(\text{CO})(\text{AsPh}_3)(\text{C}_7\text{H}_8)]$  in  $\text{CDCl}_3$  for 48 h, additional resonances appeared at  $\tau$  3.25, 6.43, and 8.04 corresponding to free norbornadiene. This indicates that dissociation of the diene group in complexes (III) occurs slowly in solution and that intermolecular exchange

(V). A similar complex  $[\{\text{RuCl}_2(\text{CO})(\text{PEt}_2\text{Ph})_2\}_2]$  has been obtained by reaction of  $[\text{Ru}_2\text{Cl}_4(\text{PEt}_2\text{Ph})_6]$  with butyraldehyde.<sup>9</sup> The i.r. spectrum of complex (V) showed several carbonyl bands (2 029m, 1 993s, 1 960s, br  $\text{cm}^{-1}$ ) indicative of a mixture of isomers. The  $^{31}\text{P}$  n.m.r. spectrum

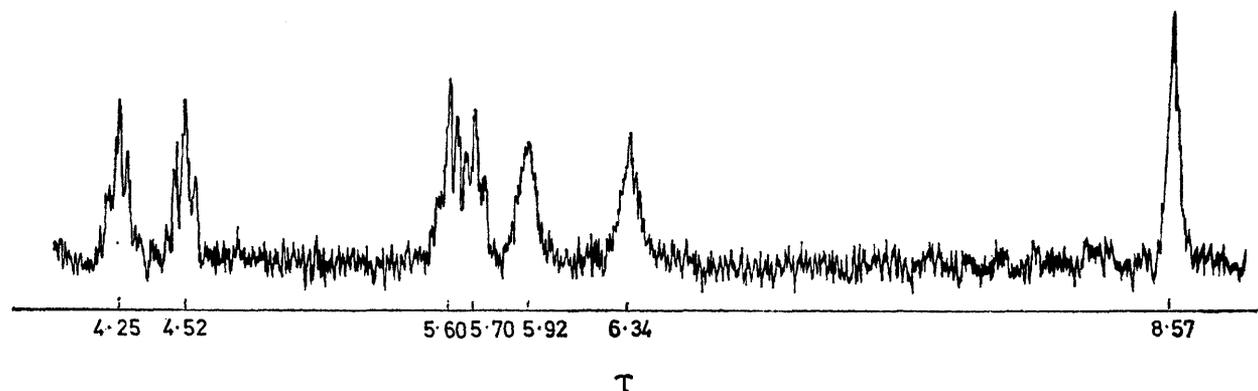
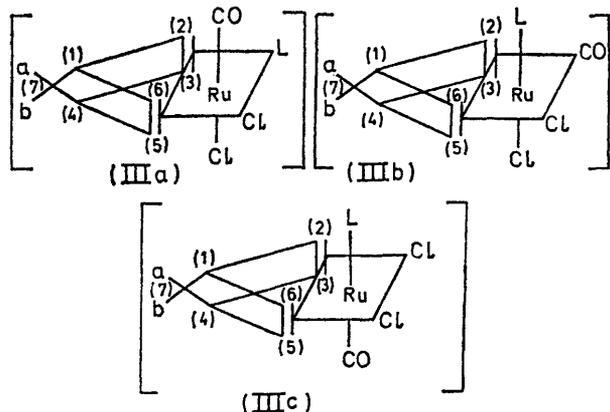


FIGURE 1  $^1\text{H}$  n.m.r. spectrum (diene region) in  $\text{CDCl}_3$  of the complex  $[\text{RuCl}_2(\text{CO})(\text{AsPh}_3)(\text{C}_7\text{H}_8)]$

between free and bound diene is negligible at ambient temperatures.

When complex (I) was refluxed with excess of  $\text{SbPh}_3$  in  $\text{CH}_2\text{Cl}_2$ , the orange-red complex  $[\text{RuCl}_2(\text{CO})(\text{SbPh}_3)_3]$ , (IV) ( $\nu_{\text{CO}}$  at  $1\ 948\ \text{cm}^{-1}$ ), was isolated, together with small

amounts of (II) and (III). An orange-brown isomer of (IV) has been reported earlier ( $\nu_{\text{CO}}$  at  $1\ 961\ \text{cm}^{-1}$ ) and was obtained by direct reaction of  $\text{SbPh}_3$  with an ethanolic 'carbonyl-containing' ruthenium solution.<sup>7</sup> Comparison of far-i.r. spectra indicates  $\nu_{\text{RuCl}}$  at  $320\ \text{cm}^{-1}$  for the orange-brown isomer and  $<300\ \text{cm}^{-1}$  for the orange-red isomer. This evidence, together with similarity of the  $\nu_{\text{CO}}$  positions to those of the two isomers established by  $^1\text{H}$  n.m.r. methods for the complex  $[\text{RuCl}_2(\text{CO})(\text{PMe}_2\text{Ph})_3]$ ,<sup>8</sup> suggests that the orange-red isomer has configuration (IVa) and the other has configuration (IVb).



$\text{L} = \text{AsPh}_3, \text{SbPh}_3$  or  $\text{C}_5\text{H}_5\text{N}$

amounts of (II) and (III). An orange-brown isomer of (IV) has been reported earlier ( $\nu_{\text{CO}}$  at  $1\ 961\ \text{cm}^{-1}$ ) and was obtained by direct reaction of  $\text{SbPh}_3$  with an ethanolic 'carbonyl-containing' ruthenium solution.<sup>7</sup> Comparison of far-i.r. spectra indicates  $\nu_{\text{RuCl}}$  at  $320\ \text{cm}^{-1}$  for the orange-brown isomer and  $<300\ \text{cm}^{-1}$  for the orange-red isomer. This evidence, together with similarity of the  $\nu_{\text{CO}}$  positions to those of the two isomers established by  $^1\text{H}$  n.m.r. methods for the complex  $[\text{RuCl}_2(\text{CO})(\text{PMe}_2\text{Ph})_3]$ ,<sup>8</sup> suggests that the orange-red isomer has configuration (IVa) and the other has configuration (IVb).

For  $\text{L} = \text{PPh}_3$ , reaction with complex (I) in  $\text{CH}_2\text{Cl}_2$  [(I) : L = 1 : 2 molar ratio] gave a non-conducting, dimeric, orange complex analysing closely for  $[\{\text{RuCl}_2(\text{CO})(\text{PPh}_3)_2\}_2]$ .

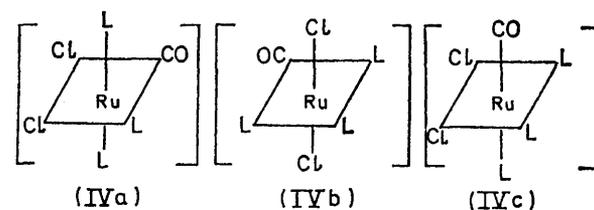
\* Added in proof: However, this complex has now been synthesised by reaction of  $[\text{RuCl}_2\text{CO}(\text{PPh}_3)_2(\text{dmf})]$  and  $[\text{RuCl}_2(\text{PPh}_3)_2]$  (1 : 1 molar ratio) in acetone (dmf = *NN*-dimethylformamide).

TABLE I  
 $^1\text{H}$  N.m.r. spectra ( $\tau$  values, in  $\text{CDCl}_3$ ) and assignments for the complexes  $[\text{RuCl}_2(\text{CO})(\text{L})(\text{C}_7\text{H}_8)]$ , (III)

L = AsPh <sub>3</sub> <sup>a</sup>	L = SbPh <sub>3</sub> <sup>b</sup>	L = C <sub>5</sub> H <sub>5</sub> N <sup>c</sup>	Rel. intensity	Fine structure	Assign- ment <sup>d</sup>
4.25	4.29	4.35	1	Triplet <sup>e</sup>	H <sub>6</sub>
4.52	4.46	4.73	1	Triplet <sup>e</sup>	H <sub>5</sub>
5.60	5.05	5.04	1	Triplet <sup>e</sup>	H <sub>3</sub>
5.70	5.31	5.22	1	Triplet <sup>e</sup>	H <sub>2</sub>
5.92	5.85	5.67	1	Multiplet	H <sub>1</sub>
6.34	6.26	6.18	1	Multiplet	H <sub>4</sub>
8.57	8.59	8.50	2	Singlet <sup>f</sup>	H <sub>a,b</sub>

<sup>a</sup> Also  $\tau$  2.30—2.70 (15), \* phenyl. <sup>b</sup> Also  $\tau$  2.00—2.70 (15), \* phenyl. <sup>c</sup> Also  $\tau$  1.70, 2.30, and 2.72 (5), \* pyridine. <sup>d</sup> Configuration (IIIa) or (IIIb). <sup>e</sup> Shown by double-resonance experiments on  $\text{L} = \text{AsPh}_3$  to be an overlapping doublet of doublets. <sup>f</sup> Broad.

\* Numbers in parentheses indicate normalised integrated intensities.



$\text{L} = \text{PPh}_3, \text{SbPh}_3, \text{PMePh}_2$  or  $\text{Me}_2\text{S}$

$[\{\text{RuCl}_2(\text{CO})(\text{PPh}_3)_2\}_2]$  but with the carbonyl band at  $1\ 960\ \text{cm}^{-1}$  increased in intensity with respect to higher-frequency bands. There is no evidence here for formation of the triple-chloride-bridged dimer  $[(\text{Ph}_3\text{P})_2\text{ClRuCl}_3\text{Ru}(\text{CO})(\text{PPh}_3)_2]$ ,\* in addition to the double-chloride-bridged dimer

<sup>7</sup> T. A. Stephenson and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1966, **28**, 945.

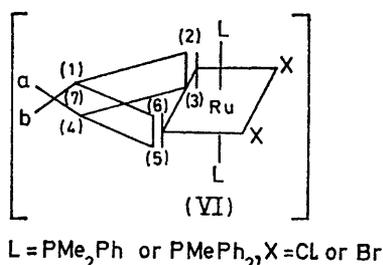
<sup>8</sup> J. M. Jenkins, M. S. Lupin, and B. L. Shaw, *J. Chem. Soc. (A)*, 1966, 1787.

<sup>9</sup> R. H. Prince and K. A. Raspin, *J. Chem. Soc. (A)*, 1969, 612.

$[\{\text{RuCl}_2(\text{CO})(\text{PPh}_3)_2\}_2]$ , (V). This is in contrast to the reaction between the complex  $[\text{RuCl}_2(\text{PPh}_3)_3]$  and  $\text{CS}_2$ , which produces both  $[\{\text{RuCl}_2(\text{CS})(\text{PPh}_3)_2\}_2]$  and  $[(\text{Ph}_3\text{P})_2\text{ClRuCl}_3\text{-Ru}(\text{CS})(\text{PPh}_3)_2]$ .<sup>4</sup>

When complex (V) was reacted with excess of  $\text{Ph}_3\text{P}$  [or when (I) was reacted directly with excess of  $\text{Ph}_3\text{P}$ ], an orange solid was obtained which analysed for  $[\text{RuCl}_2(\text{CO})(\text{PPh}_3)_3]$ , (IV), and whose i.r. spectrum contained carbonyl bands at 2 025m, 1 982m, and 1 945s  $\text{cm}^{-1}$ . One isomer of this complex has been previously reported with  $\nu_{\text{CO}}$  at 1 950  $\text{cm}^{-1}$ .<sup>7,10</sup> By analogy with related work on  $\text{PMe}_2\text{Ph}$  complexes,<sup>8</sup> the band at 1 945  $\text{cm}^{-1}$  is probably due to isomer (IVa) and that at 1 982  $\text{cm}^{-1}$  to isomer (IVb). The band at 2 025  $\text{cm}^{-1}$  may be due to isomer (IVc), which has not been previously observed in complexes of this type. Unfortunately, attempts to separate these products by either fractional recrystallisation or chromatography proved unsuccessful. It is of interest to note that no products of type (II) or (III) were isolated (or observed) with  $\text{L} = \text{PPh}_3$ .

In contrast, reaction of complex (I) with dimethylphenylphosphine in  $\text{CH}_2\text{Cl}_2$  (1:2 molar ratio or excess)



gave a single product, which contained *no* carbonyl group. This complex is monomeric, non-conducting, and analysed

$[\text{Ph}_3(\text{PhCH}_2)\text{P}][\text{RuBr}_3(\text{CO})(\text{C}_7\text{H}_8)]$  and  $\text{PMe}_2\text{Ph}$  gave  $[\text{RuBr}_2(\text{PMe}_2\text{Ph})_2(\text{C}_7\text{H}_8)]$ , which had a very similar  $^1\text{H}$  n.m.r. spectrum. The same complexes were also obtained by reaction of  $[\text{RuX}_3(\text{PMe}_2\text{Ph})_3]$ <sup>12</sup> and excess of  $\text{C}_7\text{H}_8$  in methanol. Related complexes  $[\text{RuX}_2(\text{L})_2(\text{C}_7\text{H}_8)]$  ( $\text{L} = \text{PPh}_3$ ,<sup>6,13</sup> or  $\text{AsPh}_3$ ,<sup>6</sup>  $\text{X} = \text{Cl}$  or  $\text{Br}$ ),  $[\text{RuH}(\text{X})\text{L}_2(\text{diene})]$  ( $\text{L} = \text{PPh}_3$ ,  $\text{P}(\text{OR})_3$ , *etc.*),<sup>14</sup> and  $[\text{Ru}(\text{OH})_2(\text{CO})_2(\text{C}_7\text{H}_8)]$ <sup>15</sup> have been reported elsewhere.

Rather surprisingly, reaction of complex (VI) ( $\text{X} = \text{Cl}$ ) with excess of pyridine, 2,2'-bipyridyl, or triphenylarsine led to recovery of the starting materials. We have no explanation of the kinetic inertness of complexes (VI) towards these nucleophiles, although, of course, chloride ion is known to be a low *trans*-effect ligand. If this is the correct explanation, then we must ascribe the higher reactivity of complex (I) (where the diene group is also *trans* to chloride ions)<sup>2</sup> to its formal negative charge.

When complex (I) was heated under reflux with methyl-diphenylphosphine in  $\text{CH}_2\text{Cl}_2$  (1:2 molar ratio), a pale yellow solid was isolated and shown by  $^1\text{H}$  n.m.r. studies (Figure 2) to be a mixture of  $[\text{RuCl}_2(\text{PMePh}_2)_2(\text{C}_7\text{H}_8)]$  and  $[\text{RuCl}_2(\text{CO})(\text{PMePh}_2)_3]$ , (IV). Although attempts to separate this mixture of complexes by either t.l.c. or fractional recrystallisation were unsuccessful, the formulation of the mixture as 53%  $[\text{RuCl}_2(\text{PMePh}_2)_2(\text{C}_7\text{H}_8)]$  and 47% (IV) (from  $^1\text{H}$  n.m.r. integration) is consistent with the analytical data. The  $^1\text{H}$  n.m.r. spectrum of the diene complex was that expected for configuration (VI). For the complex  $[\text{RuCl}_2(\text{CO})(\text{PMePh}_2)_3]$ , the doublet and triplet pattern of resonances are indicative of either isomer (IVa) or (IVb). The position of  $\nu_{\text{CO}}$  (1 938s  $\text{cm}^{-1}$ ) is consistent with isomer (IVa). The  $^{31}\text{P}$  n.m.r. spectrum consisted of three singlets at 7.53 [(VI)], 8.17, and 14.54 p.p.m. [(IVa)]. When excess of  $\text{PMePh}_2$  is used, the same work-up procedure gave a yellow solid with a very similar i.r. spectrum

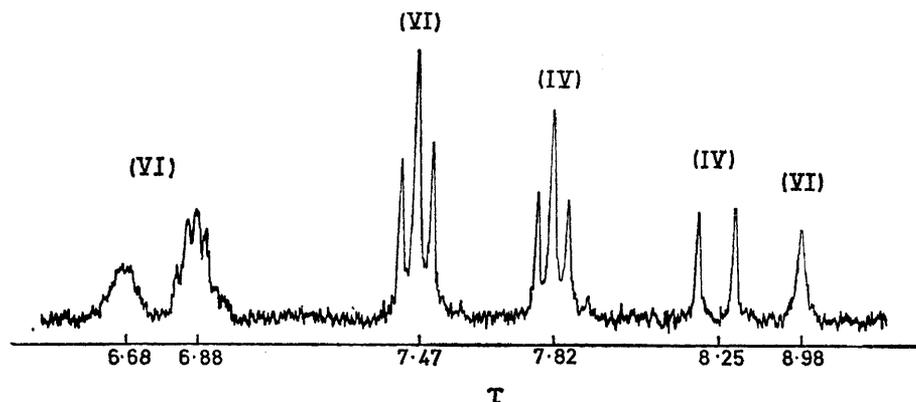


FIGURE 2  $^1\text{H}$  N.m.r. spectrum in  $\text{CDCl}_3$  ( $\tau$  6.0—9.0) of the product mixture from the reaction of complex (I) with  $\text{PMePh}_2$  [(I):  $\text{PMePh}_2 = 1:2$  molar ratio]

for  $[\text{RuCl}_2(\text{PMe}_2\text{Ph})_2(\text{C}_7\text{H}_8)]$ . The  $^1\text{H}$  n.m.r. spectrum unequivocally showed *trans*- $\text{PMe}_2\text{Ph}$  groups (virtually coupled 'triplet')<sup>11</sup> and the three diene resonances expected for configuration (VI). The  $^{31}\text{P}$  n.m.r. spectrum, which consists of a singlet at 6.91 p.p.m., also supports this formulation. Similarly, reaction of the complex

<sup>10</sup> J. Halpern, B. R. James, and A. L. W. Kemp, *J. Amer. Chem. Soc.*, 1966, **85**, 5142.

<sup>11</sup> M. S. Lupin and B. L. Shaw, *J. Chem. Soc. (A)*, 1968, 741.

<sup>12</sup> J. Chatt, G. J. Leigh, D. M. P. Mingos, and R. J. Paske, *J. Chem. Soc. (A)*, 1968, 2636.

to the mixture above but its  $^1\text{H}$  n.m.r. spectrum contained an extra peak at  $\tau$  8.30. Dissolution of the mixture in  $\text{CH}_2\text{Cl}_2$  and reprecipitation with diethyl ether gave a yellow powder and a small amount of orange crystals which could be separated manually. The former consists of complexes (IVa) and (VI) and the orange solid is identical

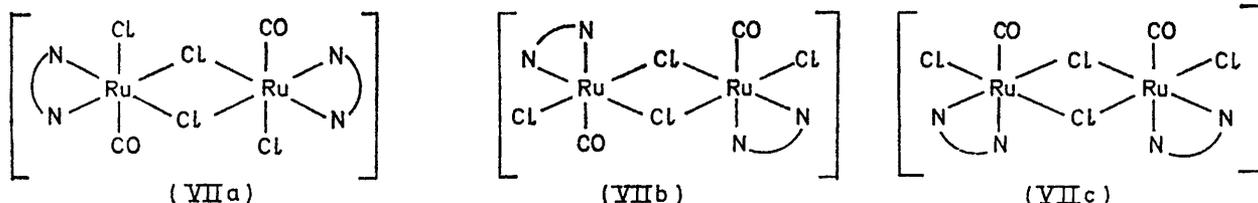
<sup>13</sup> S. D. Robinson and G. Wilkinson, *J. Chem. Soc. (A)*, 1966, 300.

<sup>14</sup> J. J. Hough and E. Singleton, *J.C.S. Chem. Comm.*, 1972, 371.

<sup>15</sup> R. B. King and P. N. Kapoor, *Inorg. Chem.*, 1972, **11**, 336.

(i.r. and  $^1\text{H}$  n.m.r. spectra) to  $[\text{RuCl}_2(\text{PMePh}_2)_4]$ , which we recently prepared in high yield by reaction of  $[\text{RuCl}_2(\text{PPh}_3)_2]$  with  $\text{PMePh}_2$  in hexane.<sup>16</sup> Presumably, the small amount of tetrakisphosphine complex arises from slow reaction of  $[\text{RuCl}_2(\text{PMePh}_2)_2(\text{C}_7\text{H}_8)]$  with excess of  $\text{PMePh}_2$ .

Reaction for 12 h of complex (I) with 2,2'-bipyridyl (bipy) or 1,10-phenanthroline (phen) ( $\text{L}'$ ) [ $(\text{I}) : \text{L}' = 1 : 1$  molar ratio] in  $\text{CH}_2\text{Cl}_2$  gave yellow precipitates which analysed closely for  $[\{\text{RuCl}_2(\text{CO})(\text{L}')\}_n]$ . These precipitates are too insoluble for either molecular-weight or  $^1\text{H}$  n.m.r. measurements, but the observation of only one carbonyl band in their i.r. spectrum (e.g. for  $\text{L}' = \text{bipy}$ ,  $\nu_{\text{CO}}$  is at  $1940\text{ cm}^{-1}$ ) is consistent with a structure such as (VIIa) or (VIIb)



[cf.  $\{\{\text{RuCl}_2(\text{CO})(\text{C}_7\text{H}_8)\}_n\}$ ,  $\nu_{\text{CO}}$  at  $2045\text{ cm}^{-1}$ ].<sup>13</sup> Work-up of the orange filtrates gave, in addition to  $[\text{Ph}_3(\text{PhCH}_2)\text{P}]\text{Cl}$ , small amounts of orange solids which were reasonably close in analysis to  $[\text{Ph}_3(\text{PhCH}_2)\text{P}][\text{RuCl}_3(\text{CO})(\text{L}')] ]$ . In this instance, configuration (IIb) is impossible and therefore, on the basis of earlier results with  $\text{L} = \text{Me}_2\text{S}$ ,  $\text{Me}_2\text{SO}$ , etc. [which indicated either configuration (IIa) or (IIb) but not (IIc)], we tentatively suggest that (IIa) is the most probable structure.

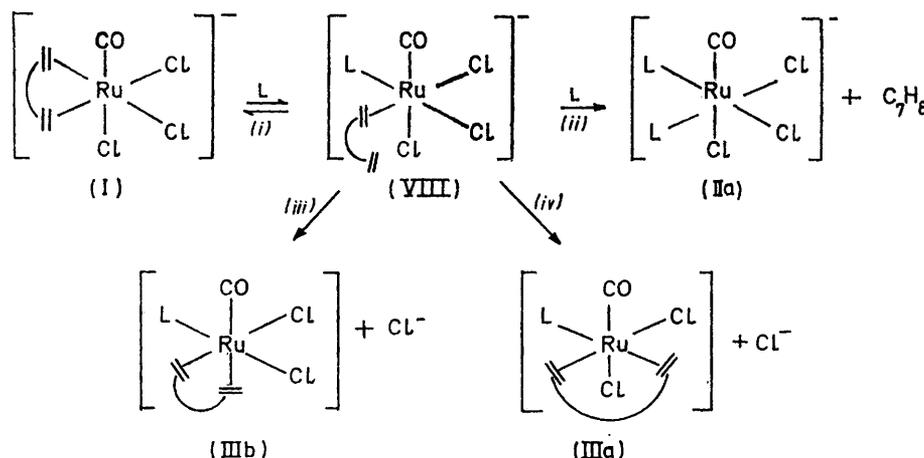
Reaction of complex (I) with excess of bipy gave an orange precipitate which also analysed for  $[\{\text{RuCl}_2(\text{CO})(\text{bipy})\}_n]$  but contained *two* carbonyl bands in its i.r. spectrum at

ation, this might be a sample of  $[\text{RuCl}(\text{CO})(\text{bipy})_2]\text{Cl}$  (cf. purple  $[\text{RuCl}(\text{H}_2\text{O})(\text{bipy})_2]\text{Cl}\cdot\text{H}_2\text{O}$ ).<sup>6,17</sup>

#### DISCUSSION

It remains to devise an overall mechanism of reaction between complex (I) and the various ligands ( $\text{L}$ ) which will explain the rather surprising differences in behaviour as a function of electronic and steric properties of the ligands. In Scheme 1, a mechanism for reaction of complex (I) with all the ligands (1:2 molar ratio) except  $\text{PR}_3$ , bipy, and phen is presented. Thus, we postulate that in all these reactions, the initial step is

cleavage of a ruthenium-olefin bond by  $\text{L}$ , to give an anionic intermediate (VIII) containing the  $\text{C}_7\text{H}_8$  group bound through only *one* olefinic bond. Further reaction can then occur by one of four competing paths: (i) reversion to complex (I) by displacement of  $\text{L}$  from (VIII) by the free double bond (this is very unlikely especially in the presence of free  $\text{L}$  and is not considered further); (ii) cleavage of the second ruthenium-olefin bond by  $\text{L}$  to give (IIa); (iii) displacement of the chloride ion *trans* to  $\text{CO}$  by the free double bond with formation of (IIIb); and (iv) displacement of the chloride ion *trans* to  $\text{L}$  by



SCHEME 1

$1952$  and  $1918\text{ cm}^{-1}$ . Again, the material is too insoluble for further study but it could be formulated either as an isomer such as (VIIc), with *cis*-carbonyl groups, or a mixture of two isomers with *trans*-carbonyl groups. The filtrate from this experiment contained the anionic complex (II) together with a very small amount of a purple complex. Although insufficient of the latter was produced for examin-

the free double bond with formation of (IIIa). If this mechanism is valid, then the percentage yields of complexes (IIa), (IIIa), and (IIIb) will depend on the *relative* magnitudes of the rates of these competing reactions. This assumes, of course, that none of these products undergo further reaction. For example, one

<sup>16</sup> P. W. Armit and T. A. Stephenson, *J. Organometallic Chem.*, 1973, **57**, C80.

<sup>17</sup> F. J. Miller and T. J. Meyer, *J. Amer. Chem. Soc.*, 1971, **93**, 1294; S. A. Adeyeni, F. J. Miller, and T. J. Meyer, *Inorg. Chem.*, 1972, **11**, 994.

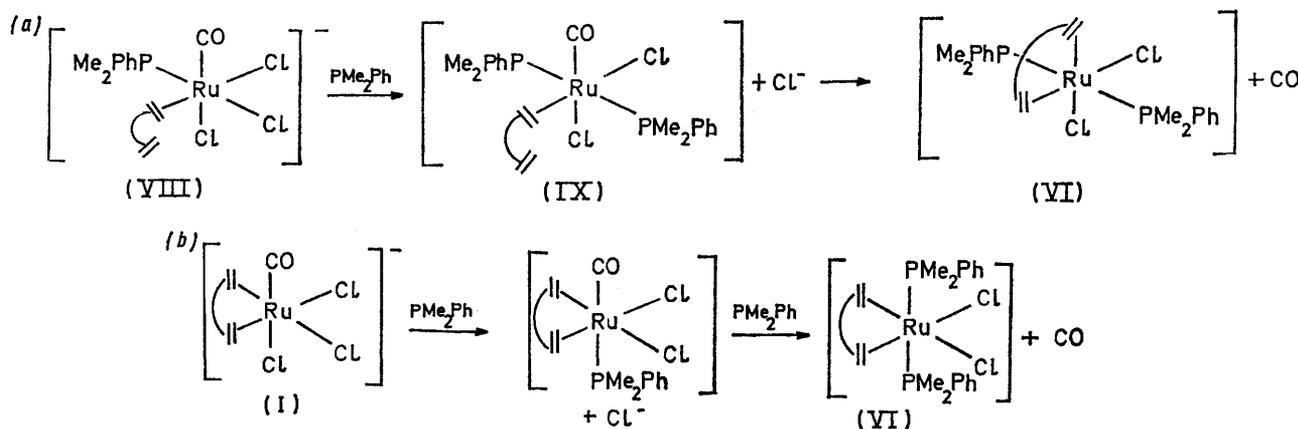
other possible way to form either complex (IIIa) or (IIIb) is by reaction of (IIa) with free diene. However, this path has been eliminated by showing that there is no reaction between the complex  $[\text{Ph}_3(\text{PhCH}_2)\text{P}][\text{RuCl}_2(\text{CO})(\text{AsPh}_3)_2]$  and  $\text{C}_7\text{H}_8$  when these are heated under reflux in  $\text{CH}_2\text{Cl}_2$  for 12 h.

It is now reasonable to ask what properties of ligand L will enhance the rate of sub-step (ii) compared to that of (iii) or (iv). Clearly, if L is a fairly strong, small, nucleophile, this should favour step (ii). Conversely, the bulkier the nucleophile, the slower reaction (ii) should become and the more facile the ring-closure reaction [steps (iii) and (iv)] will become in order to relieve steric repulsions between the bulky L and the bicyclic diene groups. Experimentally, this is exactly what is found since for  $\text{L} = \text{Me}_2\text{S}$ ,  $\text{Me}_2\text{SO}$ , and  $\text{CH}_2=\text{CH}-\text{CN}$  (small bases) only complex (Ia) is formed [*i.e.* (ii)  $\gg$  (iii) or (iv)], whereas for  $\text{L} = \text{AsPh}_3$ ,  $\text{SbPh}_3$ , and  $\text{C}_5\text{H}_5\text{N}$  (larger bases), a mixture of (IIa) and (III)

enhanced in the less-polar solvent. For  $\text{L} = \text{Me}_2\text{SO}$  in benzene, only complex (IIa) is isolated.

This proposed mechanism hinges on facile formation of a long-lived intermediate, (VIII), containing an unco-ordinated double bond. Although we were unable to isolate such an intermediate in a pure state, hydrogenolysis (after 30 min of reaction) of a dichloromethane solution containing (I),  $\text{AsPh}_3$  (1:2 molar ratio), and  $[\text{RhCl}(\text{PPh}_3)_3]$  (a good hydrogenation catalyst)<sup>18</sup> gave a mixture of compounds whose  $^1\text{H}$  n.m.r. spectrum contained additional signals at  $\tau$  8.60, 8.74, and 8.90. These resonances are close to those found in this region for norbornene ( $\tau$  8.43, 8.68, 8.93, and 9.06).<sup>19</sup> Under the same conditions, no hydrogenation occurred using a mixture of either  $[\text{RhCl}(\text{PPh}_3)_3]$  and  $\text{C}_7\text{H}_8$  or  $[\text{RhCl}(\text{PPh}_3)_3]$ ,  $\text{C}_7\text{H}_8$ , and  $\text{AsPh}_3$ . Therefore, this evidence supports formation of an intermediate with one free double bond.

Finally, it is not easy to decide whether isomer (IIIa)



(a or b) is produced [*i.e.* (ii)  $\leq$  (iii) or (iv)]. The failure to observe reactions of complex (I) with bases such as  $\text{Et}_2\text{S}$  and  $\text{PhCN}$  can presumably be attributed to the inability of these weaker nucleophiles to cleave the ruthenium-olefin bonds. Furthermore, if the mechanism shown in Scheme 1 is valid, increasing solvent polarity should favour reaction (ii) rather than (iii) or (iv). In agreement with this, for  $\text{L} = \text{AsPh}_3$ , changing the solvent medium from  $\text{CH}_2\text{Cl}_2$  to  $\text{MeOH}$  increases the yield of complex (IIa) compared to that of (III), whereas in  $\text{C}_6\text{H}_6$  the reverse is true. However, for  $\text{L} = \text{Me}_2\text{S}$ , changing the solvent from  $\text{CH}_2\text{Cl}_2$  to  $\text{C}_6\text{H}_6$  gives a lower yield of complex (IIa) (52%) together with some  $[\text{RuCl}_2(\text{CO})(\text{Me}_2\text{S})_3]$  (20%) [ $\nu_{\text{CO}}$  at  $1\ 943\ \text{cm}^{-1}$ , configuration (IVa)]. The failure to isolate any diene complex here would suggest that even in benzene (ii)  $>$  (iii) or (iv), but that the tendency of the resulting anion to undergo further reaction with  $\text{Me}_2\text{S}$  is considerably

or (IIIb) is preferentially formed. If the main factor determining this is the *trans*-effect of CO compared to L, then, since earlier work<sup>20</sup> has shown that CO has a higher *trans*-effect than either  $\text{AsPh}_3$ ,  $\text{SbPh}_3$ , or  $\text{C}_5\text{H}_5\text{N}$ , isomer (IIIb) is favoured. However, since this *trans*-effect series is based on evidence obtained from substitution reactions in square-planar platinum(II) complexes, it does not necessarily follow that a similar order is valid for such reactions in octahedral ruthenium(II) complexes. Furthermore, isomer (IIIa) is more sterically favoured than (IIIb). Hence at this juncture, we prefer to reserve judgement until more direct evidence is available.

For  $\text{L} = \text{PMe}_2\text{Ph}$ , we have to explain why only complex (VI) is obtained on reaction with (I). As shown in Scheme 2(a), the same intermediate (VIII) is proposed but, in this instance, we suggest that the high *trans*-effect of  $\text{PMe}_2\text{Ph}$ , together with the high affinity of this ligand for ruthenium(II),<sup>21</sup> results in displacement

<sup>18</sup> J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc. (A)*, 1966, 1711.

<sup>19</sup> K. Tori, K. Aono, Y. Hata, R. Muneyuki, T. Tsuji, and H. Tanida, *Tetrahedron Letters*, 1966, 9.

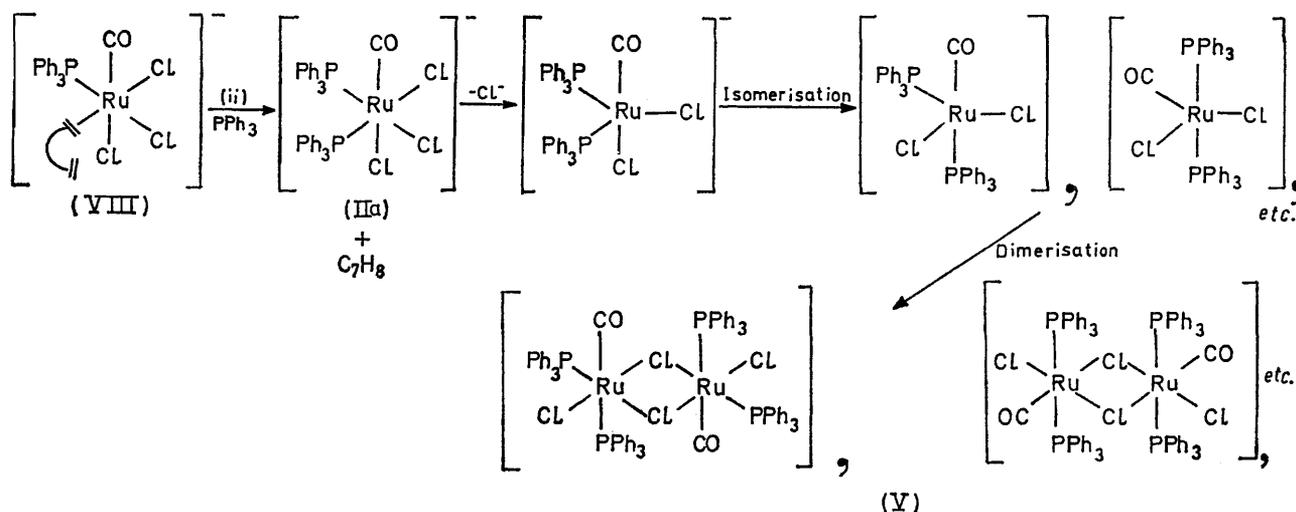
<sup>20</sup> For detailed list see F. R. Hartley, 'The Chemistry of Platinum and Palladium,' Applied Science Publishers Ltd., London, 1973, p. 299.

<sup>21</sup> P. G. Douglas and B. L. Shaw, *J. Chem. Soc. (A)*, 1970, 1556.

from (VIII) of a chloride ion *trans* to the  $\text{PMe}_2\text{Ph}$  group to give (IX) in preference to formation of (IIa) or (III). Ring closure of the free olefin group in complex (IX) with expulsion of carbon monoxide to give  $[\text{RuCl}_2(\text{PMe}_2\text{Ph})_2(\text{C}_7\text{H}_8)]$ , (VI), then appears to be a reasonable final step. The alternative site of attack (*i.e.* the chloride ion *trans* to CO) would give the complex  $[\text{RuCl}(\text{CO})(\text{C}_7\text{H}_8)(\text{PMe}_2\text{Ph})_2]\text{Cl}$  which might be favoured in more polar solvents. In fact, reaction of complex (I) and  $\text{PMe}_2\text{Ph}$  in methanol gives a conducting green solution, but only an unstable green oil could be isolated from the reaction mixture. An alternative mechanism is shown in Scheme 2(b). Again, the affinity of  $\text{PMe}_2\text{Ph}$  for ruthenium(II) and the high *trans*-effect of CO combine to give the complex  $[\text{RuCl}_2(\text{CO})(\text{PMe}_2\text{Ph})(\text{C}_7\text{H}_8)]$ , and this is followed by expulsion of CO by  $\text{PMe}_2\text{Ph}$  to give (VI). Both these mechanisms are consistent with results of earlier studies of ruthenium-phosphine

compared to the  $\text{PMe}_2\text{Ph}$  reaction, thus leading to formation of  $[\text{RuCl}_2(\text{CO})(\text{PMePh}_2)_3]$ , (IVa).

For  $\text{L} = \text{PPh}_3$ , a mechanism to explain formation of an isomeric mixture of  $[\{\text{RuCl}_2(\text{CO})(\text{PPh}_3)_2\}_2]$  is presented in Scheme 3. It seems reasonable to postulate that the same intermediate (VIII) is first formed and then, since  $\text{PPh}_3$  is a stronger nucleophile than  $\text{EPh}_3$  ( $\text{E} = \text{As}$  or  $\text{Sb}$ ), that reaction (*ii*) will be facilitated more than (*iii*) or (*iv*). After formation of complex (IIa), we suggest that the higher *trans*-influence of  $\text{PPh}_3$  compared to the other ligands studied, together with the unfavourable *cis*-arrangement of these bulky groups in (IIa) (since  $\text{PPh}_3$  has a larger ligand cone angle than  $\text{EPh}_3$  on coordination to a metal),<sup>23</sup> could readily lead to expulsion of a chloride ion, in order to relieve steric crowding, with formation of  $[\text{RuCl}_2(\text{CO})(\text{PPh}_3)_2]$ . This five-co-ordinate species might then be expected to undergo facile intramolecular-rearrangement reactions in order to minimise



SCHEME 3

chemistry<sup>7,22</sup> which indicate that *trans*- $\text{R}_3\text{P-Ru-PR}_3$  arrangements are *not* formed *via* isomerisation of *cis*- $\text{Ru}(\text{PR}_3)_2$  arrangements. A possible way of distinguishing between mechanisms 2(a) or 2(b) is by means of hydrogenation experiments. Reaction of complex (I) and  $\text{PMe}_2\text{Ph}$  solutions with  $[\text{RhCl}(\text{PPh}_3)_3]$  and hydrogen gave solutions with additional strong  $^1\text{H}$  n.m.r. signals at  $\tau$  8.29, 8.42, and 9.14. These resonances did not appear on reaction of hydrogen with dichloromethane solutions of  $[\text{RhCl}(\text{PPh}_3)_3]$ ,  $\text{C}_7\text{H}_8$ , and  $\text{PMe}_2\text{Ph}$ . Thus, the mechanism depicted in Scheme 2(a) involving an intermediate with a free olefin group is preferred.

For  $\text{PMePh}_2$  a similar mechanistic path can be invoked to explain formation of the complex  $[\text{RuCl}_2(\text{PMePh}_2)_2(\text{C}_7\text{H}_8)]$ . However, in this instance, the lower affinity of  $\text{PMePh}_2$  for ruthenium(II) might enable competing reaction steps to be more dominant as com-

pared to the  $\text{PMe}_2\text{Ph}$  reaction, thus leading to formation of  $[\text{RuCl}_2(\text{CO})(\text{PMePh}_2)_3]$ , (IVa). Similar rearrangements have been elegantly demonstrated for related complexes  $[\text{IrH}(\text{CO})_2(\text{PR}_3)_2]$  ( $\text{R} = \text{Ph}$ <sup>24,25</sup> or *p*- $\text{MeC}_6\text{H}_4$ <sup>25</sup>).

Finally, it seems reasonable to propose that the various five-co-ordinate isomers might then recombine to produce dimeric species containing energetically favourable six-co-ordinate ruthenium(II) ions. Similar processes readily occur for  $[\text{RuX}_2(\text{PR}_3)_3]$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ;  $\text{R}_3 = \text{Et}_2\text{Ph}$  or  $\text{EtPh}_2$ ) to give the binuclear complexes  $[\text{Ru}_2\text{X}_3(\text{PR}_3)_6]\text{X}$ .<sup>16</sup> Reaction of more  $\text{PPh}_3$  with this isomeric mixture of  $[\{\text{RuCl}_2(\text{CO})(\text{PPh}_3)_2\}_2]$  complexes would then be expected to give an isomeric mixture of  $[\text{RuCl}_2(\text{CO})(\text{PPh}_3)_3]$  complexes. However, a very recent paper<sup>26</sup> reported the preparation of the yellow complex  $[\text{RuCl}_2(\text{CO})(\text{PPh}_3)_2]$  (m.p. 259–263 °C) by recrystallis-

<sup>22</sup> B. F. Prater, *J. Organometallic Chem.*, 1972, **34**, 379.

<sup>23</sup> For a full discussion of ligand cone angles see C. A. Tolman, *J. Amer. Chem. Soc.*, 1970, **92**, 2956.

<sup>24</sup> G. Yagupsky and G. Wilkinson, *J. Chem. Soc. (A)*, 1969, 725.

<sup>25</sup> P. Meakin, E. L. Muetterties, and J. P. Jesson, *J. Amer. Chem. Soc.*, 1972, **94**, 5271.

<sup>26</sup> B. R. James, L. D. Markham, B. C. Hui, and G. L. Rempel, *J.C.S. Dalton*, 1973, 2247.

ation of  $[\text{RuCl}_2(\text{CO})(\text{PPh}_3)_2\text{L}']$  ( $\text{L}' = \text{NN}$ -dimethylformamide or  $\text{NN}$ -dimethylacetamide) from  $\text{CH}_2\text{Cl}_2$ -MeOH. This monomeric complex [ $\nu_{\text{CO}}$  at 1 921 and 1 931 (Nujol), 1 940  $\text{cm}^{-1}$  ( $\text{CH}_2\text{Cl}_2$ )] is reported to isomerise in  $\text{CH}_2\text{Cl}_2$  with the original 1 940  $\text{cm}^{-1}$  carbonyl band being gradually replaced by a rather broad band at 1 970  $\text{cm}^{-1}$ ; however, only the original isomer precipitates from solution on addition of methanol.

In view of the disagreement between the results of this work and that required to support our proposed mechanism, namely facile dimerisation of a monomeric intermediate such as  $[\text{RuCl}_2(\text{CO})(\text{PPh}_3)_2]$ , we re-examined this 'isomerisation' reaction. Our results indicate that the five-co-ordinate monomer is more correctly formulated as the six-co-ordinate complex  $[\text{RuCl}_2(\text{CO})(\text{PPh}_3)_2(\text{MeOH})]$ . This formulation is based on mass-spectral evidence, which indicates methanol, and the presence of an extra i.r. band at 1 020  $\text{cm}^{-1}$  {cf.  $[\text{RuCl}_3(\text{PPh}_3)_2(\text{MeOH})]$ , 1 012  $\text{cm}^{-1}$ ;  $[\text{RuCl}_3(\text{PhSPri})_2(\text{MeOH})]$ , 990  $\text{cm}^{-1}$  (ref. 27)} when compared with the i.r. spectrum of the complex  $[\{\text{RuCl}_2(\text{CO})(\text{PPh}_3)_2\}_2]$ . Elemental analyses quoted in ref. 26 are also consistent with this formulation {Found: C, 60.3; H, 4.3; Cl, 9.1.  $[\text{RuCl}_2(\text{CO})(\text{PPh}_3)_2(\text{MeOH})]$  requires C, 60.5; H, 4.5; Cl, 9.4%}. Furthermore, on gentle heating under reflux of a  $\text{CH}_2\text{Cl}_2$  solution of this yellow complex, an orange solution is formed from which a pale orange solid can be precipitated on addition of pentane. This complex contains no methanol but its i.r. spectrum [ $\nu_{\text{CO}}$  at 1 960br  $\text{cm}^{-1}$  (Nujol)] and m.p. [168–170 °C (decomp.)] are very similar to those reported by us for the most stable isomer of  $[\{\text{RuCl}_2(\text{CO})(\text{PPh}_3)_2\}_2]$ . Finally, addition of methanol to a dichloromethane solution of the complex  $[\{\text{RuCl}_2(\text{CO})(\text{PPh}_3)_2\}_2]$  (prepared either from the diene anion or methanol complex) reprecipitates  $[\text{RuCl}_2(\text{CO})(\text{PPh}_3)_2(\text{MeOH})]$ . This is analogous to recrystallisation of the complex  $[\{\text{RuCl}_2(\text{CO})_3\}_2]$  from ethanol-stabilised  $\text{CHCl}_3$  which is reported to give some  $[\text{RuCl}_2(\text{CO})_3(\text{EtOH})]$ .<sup>28</sup>

Therefore, the information reported, but incorrectly interpreted, in ref. 26 provides good evidence for the feasibility of the mechanism outlined in Scheme 3. For  $\text{L}' = \text{bipy}$  and phen, a similar mechanism involving a five-co-ordinate intermediate  $[\text{RuCl}_2(\text{CO})(\text{L}')]_2$  might also explain formation of  $[\{\text{RuCl}_2(\text{CO})(\text{L}')\}_n]$  but, in this instance, more information is required to substantiate this speculative proposal.

#### EXPERIMENTAL

Microanalyses were by A. Bernhardt, West Germany, and the University of Edinburgh Chemistry Department. Molecular weights were determined on a Perkin-Elmer-Hitachi osmometer (model 115) at 37 °C. I.r. spectra were recorded in the region 4 000–250  $\text{cm}^{-1}$  on Perkin-Elmer 225 and 457 grating spectrometers using Nujol mulls on caesium iodide plates. Solution spectra were run in potassium bromide cells.  $^1\text{H}$  N.m.r. spectra were obtained on a Varian Associates HA-100 spectrometer and  $^{13}\text{C}$  and  $^{31}\text{P}$  n.m.r. spectra on a Varian XL100 spectrometer operating in the pulse and Fourier-transform mode at 25.2 and 40.5

\* Numbers in parentheses indicate normalised integrated intensities.

MHz respectively. Conductivity measurements were made on a model 310 Portland Electronics conductivity bridge. M.p.s were determined with a Köfler hot-stage microscope and are uncorrected. Analytical data for the new ruthenium(II) complexes are given in Table 2.

*Preparations.*—*Benzyltriphenylphosphonium carbonyltrichlorobis(dimethyl sulphide)ruthenate*(II), (II). The complex  $[\text{Ph}_3(\text{PhCH}_2)\text{P}][\text{RuCl}_3(\text{CO})(\text{C}_7\text{H}_8)]$ , (I)<sup>2</sup> (0.20 g), and dimethyl sulphide (0.04  $\text{cm}^3$ ; 1:2 molar ratio) were dissolved in dichloromethane (100  $\text{cm}^3$ ) and the solution gently heated under reflux for 12 h under an atmosphere of nitrogen. The resulting pale orange solution was then reduced in volume and a pale orange solid was precipitated on addition of excess of diethyl ether. This product was washed with warm distilled water and then recrystallised from dichloromethane–diethyl ether (70% yield) ( $\nu_{\text{CO}}$  at 1 953  $\text{cm}^{-1}$ ; i.r. (400–250  $\text{cm}^{-1}$ ) 312s, 309, 295w, 285, 271m, and 249m  $\text{cm}^{-1}$ ). When the reaction was carried out in benzene under the same conditions, a yellow solution was obtained. After filtering off some  $[\text{Ph}_3(\text{PhCH}_2)\text{P}]\text{Cl}$ , addition of excess of diethyl ether gave a pale orange solid (52%) identified as  $[\text{Ph}_3(\text{PhCH}_2)\text{P}][\text{RuCl}_3(\text{CO})(\text{Me}_2\text{S})_2]$ , (II). Concentration of the filtrate followed by pentane addition gave a yellow solid which was identified as *carbonyldichlorotris(dimethyl sulphide)ruthenium*(II), (IV) (20%) ( $\nu_{\text{CO}}$  at 1 943  $\text{cm}^{-1}$ ).  $^1\text{H}$  N.m.r. spectrum ( $\text{CDCl}_3$ ):  $\tau$  7.48 (singlet) (2)\* and 7.65 (singlet) (1)\*. I.r. spectrum (400–250  $\text{cm}^{-1}$ ): 330w; 319w; and 275m  $\text{cm}^{-1}$ .

*Benzyltriphenylphosphonium carbonyltrichlorobis(dimethyl sulphoxide)ruthenate*(II), (II). This complex was prepared from (I) and  $\text{Me}_2\text{SO}$  (1:2 molar ratio) heated under reflux in  $\text{CH}_2\text{Cl}_2$  (12 h). The resulting yellow solution gave a crystalline yellow solid on addition of diethyl ether. The product was recrystallised from  $\text{CH}_2\text{Cl}_2$ - $\text{Et}_2\text{O}$  (78%) ( $\nu_{\text{CO}}$  at 1 980  $\text{cm}^{-1}$ ) [ $\Lambda$  (0.001M) 18.8  $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$  in  $\text{CH}_2\text{Cl}_2$ ]. I.r. spectrum (400–250  $\text{cm}^{-1}$ ): 379s; 330s; 316m; and 283s  $\text{cm}^{-1}$ . When benzene was used as solvent, the same product was formed (70%). *Benzyltriphenylphosphonium carbonyltrichlorobis(perdeuteriodimethyl sulphoxide)ruthenate*(II), (II). This was prepared as above using  $[\text{Ph}_3(\text{PhCH}_2)\text{P}][\text{RuBr}_3(\text{CO})(\text{Me}_2\text{SO})_2]$  and  $\text{Me}_2\text{SO}$  to give a yellow crystalline solid (60%) ( $\nu_{\text{CO}}$  at 1 975,  $\nu_{\text{SO}}$  at 1 080  $\text{cm}^{-1}$ ). I.r. spectrum (400–250  $\text{cm}^{-1}$ ): 323w; 300s; and 280w  $\text{cm}^{-1}$ .

*Benzyltriphenylphosphonium bis(acrylonitrile)carbonyltrichlororuthenate*(II) monohydrate, (II). This was prepared as for the other anionic complexes as a yellow solid and was recrystallised from dichloromethane–pentane (80%) ( $\nu_{\text{CO}}$  at 1 950,  $\nu_{\text{CN}}$  at 2 245  $\text{cm}^{-1}$ ). The same product was formed when an excess of acrylonitrile rather than 1:2 molar ratios were used [ $\Lambda$  (0.001M) 16.5  $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$  in  $\text{CH}_2\text{Cl}_2$ ]. I.r. spectrum (400–250  $\text{cm}^{-1}$ ): 316m; 307m; 281w; and 271w  $\text{cm}^{-1}$ .

*Benzyltriphenylphosphonium carbonyltrichlorobis(triphenylarsine)ruthenate*(II), (II). Complex (I) (0.20 g) and triphenylarsine (0.20 g; 1:2 molar ratio) were heated under

<sup>27</sup> J. Chatt, G. J. Leigh, and A. P. Storace, *J. Chem. Soc. (A)*, 1971, 1380.

<sup>28</sup> E. Benedetti, G. Braca, G. Sbrana, F. Salvetti, and B. Grassi, *J. Organometallic Chem.*, 1972, **37**, 361.

reflux in  $\text{CH}_2\text{Cl}_2$  ( $100 \text{ cm}^3$ ) under a nitrogen atmosphere for 12 h. The resulting yellow solution (shown to be a mixture by t.l.c.) gave an orange precipitate on addition of diethyl ether. This was washed with light petroleum (b.p.  $40-60^\circ\text{C}$ ), then water, and recrystallised from dichloromethane-pentane (20%) ( $\nu_{\text{CO}}$  at  $1928 \text{ cm}^{-1}$ ). I.r. spectrum ( $400-250 \text{ cm}^{-1}$ ): 348; 332s; and  $320 \text{ cm}^{-1}$ . The remaining solution was concentrated and then treated with pentane to

I.r. spectrum ( $400-250 \text{ cm}^{-1}$ ): 355w; 330w; 320w; 270s; and  $250 \text{ cm}^{-1}$ . Treating the residual solution with pentane gave a yellow precipitate of *bicyclo[2.2.1]hepta-2,5-diene*carbonyldichloro(triphenylstibine)ruthenium(II) (III) (60%) which was recrystallised from dichloromethane-pentane. This complex is more insoluble than the corresponding  $\text{Ph}_3\text{As}$  derivative in common organic solvents. Reaction of complex (I) (0.20 g) with excess of  $\text{SbPh}_3$

TABLE 2  
Analytical data for some new ruthenium(II) complexes

Complex	Colour	M.p. ( $t/^\circ\text{C}$ )	Found (%)				M	Calc. (%)				M
			C	H	N	Cl		C	H	N	Cl	
$[\text{Ph}_3(\text{PhCH}_2)\text{P}][\text{RuCl}_3(\text{CO})(\text{Me}_2\text{S})_2]$ (II)	Orange	206 (decomp.)	50.5	4.2		17.3		50.5	4.8		14.9	
$[\text{Ph}_3(\text{PhCH}_2)\text{P}][\text{RuCl}_3(\text{CO})(\text{Me}_2\text{SO})_2]$ (II)	Yellow	184—185 (decomp.)	48.2	4.5				48.4	4.6			
$[\text{Ph}_3(\text{PhCH}_2)\text{P}][\text{RuCl}_3(\text{CO})\{^2\text{H}\}\text{Me}_2\text{SO}_2]$ (II)	Yellow	160—161 (decomp.)	47.9	6.1 <sup>a</sup>		11.1		47.6	6.1 <sup>a</sup>		13.9	
$[\text{Ph}_3(\text{PhCH}_2)\text{P}][\text{RuBr}_3(\text{CO})(\text{Me}_2\text{SO})_2]$ (II)	Yellow	197—198 (decomp.)	43.5	4.3				41.2	3.9			
$[\text{Ph}_3(\text{PhCH}_2)\text{P}][\text{RuCl}_3(\text{CO})-(\text{CH}_2=\text{CH}-\text{CN})_2, \text{H}_2\text{O}]$ (II)	Yellow	157—158 (decomp.)	53.8	3.9	3.8	14.8		53.9	4.1	3.9	14.9	
$[\text{Ph}_3(\text{PhCH}_2)\text{P}][\text{RuCl}_3(\text{CO})(\text{AsPh}_3)_2]$ (II)	Orange	215—217 (decomp.)	60.5	4.2				62.1	4.3			
$[\text{Ph}_3(\text{PhCH}_2)\text{P}][\text{RuBr}_3(\text{CO})(\text{AsPh}_3)_2]$ (II)	Pale brown	136—138 (decomp.)	53.7	3.8				50.0	3.8			
$[\text{Ph}_3(\text{PhCH}_2)\text{P}][\text{RuCl}_3(\text{CO})(\text{SbPh}_3)_2]$ (II)	Pink	128—130 (decomp.)	53.0	3.5		8.6		57.5	4.0		8.2	
$[\text{Ph}_3(\text{PhCH}_2)\text{P}][\text{RuCl}_3(\text{CO})(\text{C}_5\text{H}_5\text{N})_2]$ (II)	Yellow	120—122 (decomp.)	57.1	4.3	3.0			57.9	4.3	3.7		
$[\text{Ph}_3(\text{PhCH}_2)\text{P}][\text{RuCl}_3(\text{CO})(\text{bipy})]$ (II)	Orange	173—175 (decomp.)	51.9	3.7	4.0			58.1	4.0	3.8		
$[\text{Ph}_3(\text{PhCH}_2)\text{P}][\text{RuCl}_3(\text{CO})(\text{phen})]$ (II)	Orange	183—185 (decomp.)	53.2	3.5	4.6			59.3	3.9	3.7		
$[\text{Ph}_3(\text{PhCH}_2)\text{P}][\text{RuBr}_3(\text{CO})(\text{bipy})]$ (II)	Orange-brown	195—196 (decomp.)	47.5	3.4	5.0			49.2	3.4	3.2		
$[\text{RuCl}_2(\text{CO})(\text{AsPh}_3)(\text{C}_7\text{H}_8)]$ (III)	Yellow	215—217 (decomp.)	52.1	3.8		12.4	613 <sup>b</sup>	52.2	3.8		11.9	597
$[\text{RuCl}_2(\text{CO})(\text{SbPh}_3)(\text{C}_7\text{H}_8)]$ (III)	Yellow	231—232 (decomp.)	51.5	3.8				48.4	3.6			
$[\text{RuCl}_2(\text{CO})(\text{C}_5\text{H}_5\text{N})(\text{C}_7\text{H}_8)]$ (III)	Yellow	171—174 (decomp.)	43.2	3.5	3.7		390 <sup>b</sup>	42.1	3.5	3.8		371
$[\{\text{RuCl}_2(\text{CO})(\text{bipy})\}_n]$ (VII)	Yellow	>280	36.6	2.1	7.7	20.5		37.1	2.2	7.9	20.0	
$[\{\text{RuCl}_2(\text{CO})(\text{phen})\}_n]$ (VII)	Yellow	>280	37.9	2.3	6.7			38.2	2.7	6.9		
$[\{\text{RuCl}_2(\text{CO})(\text{PPh}_3)_2\}_2]$ (V)	Orange	168—172 (decomp.)	59.8	4.2			{1 460 <sup>b</sup> 1 386 <sup>d</sup>	61.3	4.2			1 448
$[\text{RuCl}_2(\text{PMe}_2\text{Ph})_2(\text{C}_7\text{H}_8)]$ (VI)	Yellow	247 (decomp.)	51.0	5.5			{580 <sup>b</sup> 600 <sup>d</sup>	51.0	5.5			520
$[\text{RuBr}_2(\text{PMe}_2\text{Ph})_2(\text{C}_7\text{H}_8)]$ (VI)	Yellow	214—215 (decomp.)	45.7	4.8				44.0	4.8			
$[\text{RuCl}_2(\text{CO})(\text{Me}_2\text{S})_3]$ (IV)	Yellow	200—202 (decomp.)	22.3	4.7				21.8	4.6			

<sup>a</sup> (H + D)%. <sup>b</sup> Osmometrically in  $\text{CHCl}_3$  ( $37^\circ\text{C}$ ). <sup>c</sup> Obtained from (I): bipy = 1 : 1 molar ratio. <sup>d</sup> Osmometrically in  $\text{C}_6\text{H}_6$  ( $37^\circ\text{C}$ ).

give a yellow solid which, on recrystallisation from dichloromethane-pentane, gave microcrystals of *bicyclo[2.2.1]hepta-2,5-diene*carbonyldichloro(triphenylarsine)ruthenium(II) (II) (60%) ( $\nu_{\text{CO}}$  at  $2008 \text{ cm}^{-1}$ ). I.r. spectrum ( $400-250 \text{ cm}^{-1}$ ): 354m; 338; 325s; 308w; 280m; and  $250 \text{ cm}^{-1}$ . When the reaction was carried out in the presence of excess of concentrated hydrochloric acid, the same relative amounts of products were found. However, if methanol was used instead of dichloromethane as solvent, under the same conditions, an increase of 35% in the yield of the complex (II) accompanied by a 42% decrease in the yield of (III) was observed.

*Benzyltriphenylphosphonium carbonyltrichlorobis(triphenylstibine)ruthenate*(II), (II). This complex was prepared as for the triphenylarsine derivative, isolated as a pink powder (18%), and recrystallised from  $\text{CH}_2\text{Cl}_2-\text{Et}_2\text{O}$  ( $\nu_{\text{CO}}$  at  $2002 \text{ cm}^{-1}$ ) [ $\Lambda$  (0.001M)  $18.5 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$  in  $\text{CH}_2\text{Cl}_2$ ].

(0.40 g) heated under reflux in  $\text{CH}_2\text{Cl}_2$  for 12 h gave an orange solution. Work-up as above gave samples of complexes (II) and (III) and a residual orange solution. On concentration and pentane addition the orange-red solid *carbonyldichlorotris(triphenylstibine)ruthenium*(II) (IV) ( $\nu_{\text{CO}}$  at  $1948 \text{ cm}^{-1}$ ) was precipitated, m.p.  $215-216^\circ\text{C}$  (Found: C, 53.2; H, 3.6%). Calc. for  $\text{C}_{55}\text{H}_{45}\text{Cl}_2\text{ORuSb}_3$ : C, 52.5; H, 3.6%). Similarly yellow  $[\text{Ph}_3(\text{PhCH}_2)\text{P}][\text{RuCl}_3(\text{CO})(\text{C}_5\text{H}_5\text{N})_2]$  (II) (22%) ( $\nu_{\text{CO}}$  at  $1925 \text{ cm}^{-1}$ ) [ $\Lambda$  (0.001M)  $17.5 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$  in  $\text{CH}_2\text{Cl}_2$ ] and yellow  $[\text{RuCl}_2(\text{CO})(\text{C}_5\text{H}_5\text{N})(\text{C}_7\text{H}_8)]$  (III) (60%) ( $\nu_{\text{CO}}$  at  $2010 \text{ cm}^{-1}$ ) were prepared from complex (I) and  $\text{C}_5\text{H}_5\text{N}$  (1 : 2 molar ratio) in  $\text{CH}_2\text{Cl}_2$ .

*Di- $\mu$ -chloro-bis[carbonylchlorobis(triphenylphosphine)ruthenium*(II)], (V). Complex (I) (0.24 g) and triphenylphosphine (0.20 g; 1 : 2 molar ratio) were dissolved in  $\text{CH}_2\text{Cl}_2$  ( $100 \text{ cm}^3$ ) and the solution heated under reflux

under a nitrogen atmosphere for 12 h. The resulting pale orange solution was reduced in volume and diethyl ether added to give a white precipitate of  $[\text{Ph}_3(\text{PhCH}_2)\text{P}]\text{Cl}$ . The remaining solution was treated with pentane to give the pale orange *solid* (70%) ( $\nu_{\text{CO}}$  at 2 029m, 1 993s, and 1 960s  $\text{cm}^{-1}$ ).  $^{31}\text{P}$  N.m.r. spectrum ( $\text{CDCl}_3$ ): 17.2 (singlet) (s); 25.5 (singlet) (s); 38.5 (multiplet) (w); 42.3 (multiplet) (w); and 52.6 p.p.m. (multiplet) (w). Recrystallisation from hot dichloromethane-pentane gave a deeper orange product (with the carbonyl band at 1 960  $\text{cm}^{-1}$  increased in intensity with respect to higher-frequency bands) but still analysing for (V) [Found: C, 60.5; H, 4.4.  $\{[\text{RuCl}_2(\text{CO})(\text{PPh}_3)_2]_2\}$  requires C, 61.3; H, 4.2%].

When complex (I) (0.24 g) and excess of triphenylphosphine (0.40 g) were heated under reflux in  $\text{CH}_2\text{Cl}_2$  (100  $\text{cm}^3$ ) under a nitrogen atmosphere for 12 h and the resulting orange solution treated exactly as above, orange crystals of *carbonyldichlorotris(triphenylphosphine)ruthenium*-(II) (IV) (72%) were isolated, m.p. 150 °C [lit.,<sup>9</sup> for isomer (IVa) 70–72 °C] (Found: C, 66.3; H, 4.6. Calc. for  $\text{C}_{55}\text{H}_{45}\text{Cl}_2\text{O}_3\text{P}_3\text{Ru}$ : C, 66.9; H, 4.6%) ( $\nu_{\text{CO}}$  at 2 025m, 1 982m, and 1 945s  $\text{cm}^{-1}$ ).<sup>\*</sup> The same mixture of isomers was obtained by reaction of  $\{[\text{RuCl}_2(\text{CO})(\text{PPh}_3)_2]_2\}$  with  $\text{PPh}_3$  under the same conditions.

(*Bicyclo[2.2.1]hepta-2,5-diene*)*dichlorobis(dimethylphenylphosphine)ruthenium*(II), (VI). Complex (I) (0.20 g) was heated under reflux in  $\text{CH}_2\text{Cl}_2$  (100  $\text{cm}^3$ ) under a nitrogen atmosphere with  $\text{PMe}_2\text{Ph}$  (0.10  $\text{cm}^3$ ) for ca. 12 h. Reduction in volume of the yellow solution followed by diethyl ether addition gave a white precipitate of  $[\text{Ph}_3(\text{PhCH}_2)\text{P}]\text{Cl}$ . The remaining solution was then treated with pentane to give the yellow solid which was washed with methanol and recrystallised from dichloromethane-pentane (80%). The same complex was obtained when an excess of  $\text{PMe}_2\text{Ph}$  was used.  $^1\text{H}$  N.m.r. spectrum in  $\text{CDCl}_3$ :  $\tau$  6.70 (protons 1, 4); 7.20 (2, 3, 5, 6); 8.50 (a, b); 2.00–2.60 (phenyl multiplet); and 7.74 (1:2:1 'triplet,'  $\text{PMe}_2\text{Ph}$ ). I.r. spectrum (400–250  $\text{cm}^{-1}$ ): 305w; 277s; and 253s  $\text{cm}^{-1}$ . The complex  $[\text{RuBr}_2(\text{PMe}_2\text{Ph})_2(\text{C}_7\text{H}_8)]$  was prepared in the same way from  $[\text{Ph}_3(\text{PhCH}_2)\text{P}][\text{RuBr}_3(\text{CO})(\text{C}_7\text{H}_8)]$  and  $\text{PMe}_2\text{Ph}$  as a yellow crystalline solid (65%).  $^1\text{H}$  N.m.r. spectrum in  $\text{CDCl}_3$ :  $\tau$  6.67 (protons 1 and 4); 7.12 (2, 3, 5, 6); 8.74 (a, b); 2.00–2.60 (phenyl multiplet); and 7.56 (1:2:1 'triplet,'  $\text{PMe}_2\text{Ph}$ ).

*Reactions.*—Complex (I) and  $\text{PMePh}_2$ . Complex (I) (0.20 g) and  $\text{PMePh}_2$  (0.10  $\text{cm}^3$ ; 1:2 molar ratio) were heated under reflux in  $\text{CH}_2\text{Cl}_2$  (100  $\text{cm}^3$ ) under a nitrogen atmosphere for ca. 12 h. Concentration of the solution followed by diethyl ether addition gave a white precipitate of  $[\text{Ph}_3(\text{PhCH}_2)\text{P}]\text{Cl}$ . Pentane addition to the residual yellow solution gave a pale yellow *solid*, shown by  $^1\text{H}$  n.m.r. studies to be a mixture of complexes  $[\text{RuCl}_2(\text{PMePh}_2)_2(\text{C}_7\text{H}_8)]$ , (VI), and  $[\text{RuCl}_2(\text{CO})(\text{PMePh}_2)_3]$  (IV) ( $\nu_{\text{CO}}$  at 1 938  $\text{cm}^{-1}$ ) (53 and 47% respectively as established by integration). This mixture, which could not be separated by t.l.c. or fractional recrystallisation, analysed closely for the relative percentages of complexes indicated by the  $^1\text{H}$  n.m.r. studies {Found: C, 59.3; H, 4.9.  $[\text{RuCl}_2(\text{PMePh}_2)_2(\text{C}_7\text{H}_8)]$  (53%) and  $[\text{RuCl}_2(\text{CO})(\text{PMePh}_2)_3]$  (47%) requires C, 58.7; H, 4.9%}.  $^1\text{H}$  N.m.r. spectra in  $\text{CDCl}_3$  (Figure 2):  $[\text{RuCl}_2(\text{PMePh}_2)_2(\text{C}_7\text{H}_8)]$  (VI)  $\tau$  6.68 (protons 1, 4), 6.88 (2, 3, 5, 6), 8.98 (a, b), 2.00–2.60 (phenyl multiplet), 7.47 (1:2:1 'triplet,'  $\text{PMePh}_2$ );  $[\text{RuCl}_2(\text{CO})(\text{PMePh}_2)_3]$  (IVa)  $\tau$  7.82 (triplet) (2) and 8.25 (doublet) (1).

When excess of  $\text{PMePh}_2$  was used, the same work-up

procedure gave a yellow solid (Found: C, 60.1; H, 5.3%). This material had a very similar i.r. spectrum to the solid obtained earlier, but contained an extra peak in its  $^1\text{H}$  n.m.r. spectrum at  $\tau$  8.30. When the mixture was dissolved in  $\text{CH}_2\text{Cl}_2$  (green solution) and reprecipitated on addition of diethyl ether, a yellow powder and orange crystals were obtained. The orange crystals are identical (i.r. and  $^1\text{H}$  n.m.r. spectra) to  $[\text{RuCl}_2(\text{PMePh}_2)_4]$ .<sup>18</sup>

*Complex (I) and 2,2'-bipyridyl (bipy)*. Complex (I) (0.20 g) and bipy (0.045 g; 1:1 molar ratio) were heated under reflux in  $\text{CH}_2\text{Cl}_2$  (100  $\text{cm}^3$ ) under a nitrogen atmosphere for 12 h. The resulting yellow *precipitate* of  $\{[\text{RuCl}_2(\text{CO})(\text{bipy})]_n\}$  ( $\nu_{\text{CO}}$  at 1 940  $\text{cm}^{-1}$ ) was filtered, then washed with  $\text{CH}_2\text{Cl}_2$ , methanol, and diethyl ether, and finally dried *in vacuo* at 40 °C (58%). This product was insoluble in all common organic solvents. I.r. spectrum (400–250  $\text{cm}^{-1}$ ): 344m; 322w; and 278w  $\text{cm}^{-1}$ . The remaining orange solution was reduced in volume and diethyl ether added giving a white precipitate of  $[\text{Ph}_3(\text{PhCH}_2)\text{P}]\text{Cl}$ . The residual solution was treated with pentane to give an orange precipitate of *benzyltriphenylphosphonium (2,2'-bipyridyl)carbonyltrichlororuthenate*(II) (20%) ( $\nu_{\text{CO}}$  at 1 926  $\text{cm}^{-1}$ ), recrystallised from dichloromethane-pentane [ $\Lambda$  (0.001M) 15.0  $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$  in  $\text{CH}_2\text{Cl}_2$ ]. When the reaction was stopped after 1 h, the complex  $\{[\text{RuCl}_2(\text{CO})(\text{bipy})]_n\}$  was present but the solution only contained starting materials. When the complex  $\{[\text{RuCl}_2(\text{CO})(\text{bipy})]_n\}$  and  $[\text{Ph}_3(\text{PhCH}_2)\text{P}]\text{Cl}$  were heated under reflux in  $\text{CH}_2\text{Cl}_2$  for 12 h, a very small amount of  $[\text{Ph}_3(\text{PhCH}_2)\text{P}][\text{RuCl}_3(\text{CO})(\text{bipy})]$  was isolated from the solution. Using an excess of bipy, an orange *precipitate* ( $\nu_{\text{CO}}$  at 1 952 and 1 918  $\text{cm}^{-1}$ ) analysing reasonably closely for  $\{[\text{RuCl}_2(\text{CO})(\text{bipy})]_n\}$  was obtained (Found: C, 40.6; H, 2.7; N, 8.7. Required: C, 37.1; H, 2.2; N, 7.9%). I.r. spectrum (400–250  $\text{cm}^{-1}$ ): 336w; 321m; 300w; and 270w  $\text{cm}^{-1}$ . The residual solution contained the complex  $[\text{Ph}_3(\text{PhCH}_2)\text{P}][\text{RuCl}_3(\text{CO})(\text{bipy})]$  (orange) contaminated by a very small amount of purple material (t.l.c. evidence). Similarly, reaction of complex (I) and 1,10-phenanthroline (1:1 molar ratio) in  $\text{CH}_2\text{Cl}_2$  gave an insoluble yellow *precipitate* of  $\{[\text{RuCl}_2(\text{CO})(\text{phen})]_n\}$  (57%) ( $\nu_{\text{CO}}$  at 1 945  $\text{cm}^{-1}$ ) and orange  $[\text{Ph}_3(\text{PhCH}_2)\text{P}][\text{RuCl}_3(\text{CO})(\text{phen})]$  (20%) ( $\nu_{\text{CO}}$  at 1 925  $\text{cm}^{-1}$ ) [ $\Lambda$  (0.001M) 13.2  $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$  in  $\text{CH}_2\text{Cl}_2$ ].

*Hydrogenation Experiments.*—Complex (I) (0.20 g) and triphenylarsine (0.20 g; 1:2 molar ratio) were heated under reflux in dichloromethane under a nitrogen atmosphere for ca. 30 min. Then the complex  $[\text{RhCl}(\text{PPh}_3)_3]$  (0.05 g) was added to the reaction mixture and hydrogen passed through the solution under reflux for a further 2 h. Reduction in volume of a portion of this solution, followed by addition of diethyl ether, gave an orange solid identified as  $[\text{Ph}_3(\text{PhCH}_2)\text{P}][\text{RuCl}_3(\text{CO})(\text{AsPh}_3)_2]$ , (II). Treatment of the filtrate with pentane gave a yellow solid. This was a mixture (t.l.c. evidence), conducting, and its n.m.r. spectrum in  $\text{CDCl}_3$  showed extra peaks at  $\tau$  8.60, 8.74, and 8.90 (*cf.* norbornene:<sup>19</sup>  $\tau$  8.43, 8.68, 8.93, and 9.06). The remainder of the solution was hydrogenated for a further hour. The orange complex (II) and the yellow solid were isolated by the same method as above and analysis of the latter product was consistent with a mixture of  $[\text{RuCl}_2(\text{CO})(\text{AsPh}_3)(\text{C}_7\text{H}_8)]$  and  $[\text{Ph}_3(\text{PhCH}_2)\text{P}][\text{RuCl}_3(\text{CO})(\text{AsPh}_3)(\text{C}_7\text{H}_9)]$  (Found: C, 56.3; H, 4.3%). Similarly, when the reaction was repeated but the  $\text{CH}_2\text{Cl}_2$  solution was simply

<sup>\*</sup> We thank Dr. E. S. Switkes for the preparation of this complex.

reduced in volume and a  $^1\text{H}$  n.m.r. spectrum obtained, additional resonances occurred at  $\tau$  8.26, 8.76, and 9.14 which shows that these peaks do not arise because of the work-up procedure. Under the same conditions, no such evidence for hydrogenation was found using a mixture of either  $[\text{RhCl}(\text{PPh}_3)_3]$  and  $\text{C}_7\text{H}_8$  or  $[\text{RhCl}(\text{PPh}_3)_3]$ ,  $\text{C}_7\text{H}_8$ , and  $\text{AsPh}_3$ . Similarly, hydrogenation of dichloromethane solutions of complex (I),  $\text{PMe}_2\text{Ph}$ , and  $[\text{RhCl}(\text{PPh}_3)_3]$  for 4 h gave a solution with additional  $^1\text{H}$  n.m.r. signals at  $\tau$  8.29, 8.42, and 9.14. No additional resonances were found when

solutions of  $[\text{RhCl}(\text{PPh}_3)_3]$ ,  $\text{C}_7\text{H}_8$ , and  $\text{PMe}_2\text{Ph}$  were treated with hydrogen under the same conditions.

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