

## Reactions of Ruthenium Triphenylphosphine Complexes with Diazadienes. Part 1. Reactions of $[\text{RuCl}_2(\text{PPh}_3)_3]$ and $[\text{RuH}(\text{Cl})(\text{PPh}_3)_3]$ † and Disproportionation of a Hydridochloro-complex

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The reactions between  $[\text{RuCl}_2(\text{PPh}_3)_3]$  and half or one equivalent of a diazadiene (dad) give respectively molecular and ionic binuclear triply chloro-bridged complexes,  $[\text{Ru}_2\text{Cl}_4(\text{PPh}_3)_3(\text{dad})]$  and  $[\text{Ru}_2\text{Cl}_3(\text{PPh}_3)_2(\text{dad})_2]\text{Cl}$  which can also be obtained as its  $\text{BPh}_4$  salt. The compound  $[\text{RuH}(\text{Cl})(\text{PPh}_3)_3]$  reacts with diazadienes to produce  $[\text{RuH}(\text{Cl})(\text{PPh}_3)_2(\text{dad})]$ , which disproportionates in polar solvents to give a hydrido- and a dichloro-compound and reacts with water to give a chlorodihydroxo-bridged hydrido-species,  $[\text{Ru}_2\text{H}(\mu\text{-OH})_2(\text{PPh}_3)_3(\text{dad})]$ .

DIAZADIENE ( $\alpha$ -DI-IMINE) ligands (dad) have received much attention during the past few years in view of their versatile bonding properties. These ligands are basic but also have a strong  $\pi$ -back-bonding capability,<sup>1</sup> and can thus stabilize low-valent metal complexes such as  $[\text{Fe}(\text{dad})_2]$ <sup>2</sup> and  $[\text{Ni}(\text{dad})_2]$ .<sup>3</sup> They are also versatile in their modes and sites of co-ordination, *i.e.* they can act as unidentate [*cf.*  $[\text{PdCl}_2(\text{dad})_2]$ ],<sup>4</sup> as bidentate  $\{[\text{Mo}(\text{CO})_4(\text{dad})]\}$ ,<sup>5</sup> or as bridging ligands  $\{[\text{RhCl}(\text{CO})_2]_2(\text{dad})\}$ .<sup>4</sup> Finally, it has been suggested that they can co-ordinate either through the lone pair of nitrogen or through the C=N double bond: in  $[\text{Fe}(\text{CO})_3(\text{Bu}^t\text{NCHCHN}^t\text{Bu})]$ <sup>6</sup> both types of co-ordination are present; but for  $[\text{Fe}(\text{CO})_3(\text{Pr}^i\text{NCHCHN}^i\text{Pr})]$ <sup>6</sup> only co-ordination through the nitrogen lone pair is observed.

With the exception of numerous bipyridyl complexes, no diazadiene ruthenium complexes were known before this work, and since the preparation and the rearrangement reactions of dichloro-complexes of ruthenium are the subject of numerous interesting studies,<sup>7-9</sup> we investigated the reactions of  $[\text{RuCl}_2(\text{PPh}_3)_3]$  with diazadienes. The reaction of  $[\text{RuH}(\text{Cl})(\text{PPh}_3)_3]$  with bipyridyl had been reported to produce a red-brown slightly soluble compound.<sup>10</sup> We investigated the same reaction with diazadienes and obtained a very reactive complex  $[\text{RuH}(\text{Cl})(\text{PPh}_3)_2(\text{dad})]$ , and have examined its reactions in polar solvents and with water. The diazadienes employed in this work are shown below and are hereafter referred to as dad-a, dad-b, *etc.*

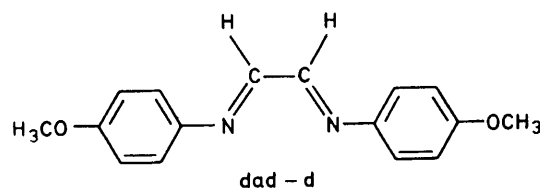
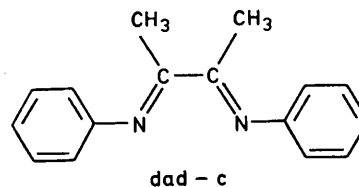
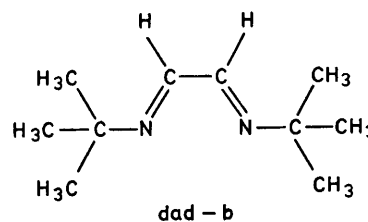
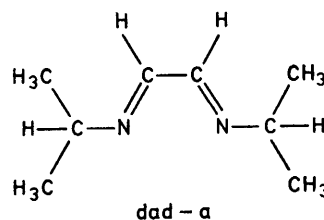
### RESULTS AND DISCUSSION

**Reactions of  $[\text{RuCl}_2(\text{PPh}_3)_3]$  with Diazadienes.**—The compound  $[\text{RuCl}_2(\text{PPh}_3)_3]$  does not react with dad-b but does with  $\geq 1$  equivalent of dad-a or dad-c in toluene or dichloromethane at room temperature. This gives yellow or red products respectively (see Experimental section) which are soluble in polar solvents (alcohols, acetone, chlorinated solvents, *etc.*) and insoluble in non-polar ones. In solution in methanol the products react with  $\text{Na}[\text{BPh}_4]$  to yield yellow or red precipitates.

The microanalytical data suggest the formulation

† Dichlorotris(triphenylphosphine)ruthenium(II) and chlorohydrotis(triphenylphosphine)ruthenium(II) respectively.

$[\text{Ru}_2\text{Cl}_3(\text{PPh}_3)_2(\text{dad})_2]\text{X}$  (dad = dad-a or dad-c; X = Cl or  $\text{BPh}_4$ ). All these compounds give solvates after recrystallization from chlorinated solvents although for  $[\text{Ru}_2\text{Cl}_3(\text{PPh}_3)_2(\text{dad-c})_2]\text{X}$  the amount of solvent depends on the drying time. Conductivity measurements (54—



$60 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ) (Table 3) gave values somewhat lower than usually found for 1 : 1 electrolytes ( $75\text{--}95 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ )<sup>11</sup> but this seems to be general for such big cations.

The i.r. spectra of  $[\text{Ru}_2\text{Cl}_3(\text{PPh}_3)_2(\text{dad-a})_2]\text{X}$  (X = Cl or  $\text{BPh}_4$ ) only show a weak absorption at  $300 \text{ cm}^{-1}$

attributed to the bridging chloride groups. Similarly,  $[\text{Ru}_2\text{Cl}_3(\text{PPh}_3)_2(\text{dad-c})_2]\text{X}$  show a band of medium intensity at  $290\text{ cm}^{-1}$  together with another at  $1580\text{ cm}^{-1}$  due to the monosubstituted phenyl ring of the diazadiene ligand.

The  $^1\text{H}$  n.m.r. spectrum of  $[\text{Ru}_2\text{Cl}_3(\text{PPh}_3)_2(\text{dad-a})_2]\text{Cl}$

that there is inequivalence of the protons rather than coupling to phosphine groups since the chemical shifts remain the same but the shift between the peaks (in Hz) increases.

The spectrum of  $[\text{Ru}_2\text{Cl}_3(\text{PPh}_3)_2(\text{dad-a})_2]\text{Cl}$  is very similar to that of the  $\text{BPh}_4$  salt (methyl : phenyl ratio,

TABLE 1  
Proton n.m.r. spectra of ruthenium complexes

| Compound                                                                                                                       | Solvent                  | N.m.r. ( $\tau$ ) <sup>a</sup> |                 |                                                                                                                     |
|--------------------------------------------------------------------------------------------------------------------------------|--------------------------|--------------------------------|-----------------|---------------------------------------------------------------------------------------------------------------------|
|                                                                                                                                |                          | Hydride                        | Imino-groups    | Other resonances                                                                                                    |
| $[\text{Ru}_2\text{Cl}_4(\text{PPh}_3)_3(\text{C}_6\text{H}_5\text{NCCH}_2\text{CCH}_2\text{NC}_6\text{H}_5)]$                 | $\text{CD}_2\text{Cl}_2$ |                                | 7.98, 8.04      | 5.5, <sup>b</sup> 8.5, <sup>c</sup> 9.3 <sup>c</sup>                                                                |
| $[\text{Ru}_2\text{Cl}_3(\text{PPh}_3)_2(\text{C}_3\text{H}_7\text{NCHCHNC}_3\text{H}_7)_2]\text{Cl}$                          | $\text{CD}_2\text{Cl}_2$ |                                | 1.3, 1.5; 1.38  | 5.5, <sup>b</sup> 8.5, <sup>c</sup> 9.3 <sup>c</sup>                                                                |
| $[\text{Ru}_2\text{Cl}_3(\text{PPh}_3)_2(\text{C}_3\text{H}_7\text{NCHCHNC}_3\text{H}_7)_2]\text{Cl}$                          | $\text{CDCl}_3$          |                                | 1.3, 1.5; 1.38  | 5.5, <sup>b</sup> 8.5, <sup>c</sup> 9.3 <sup>c</sup>                                                                |
| $[\text{Ru}_2\text{Cl}_3(\text{PPh}_3)_2(\text{C}_3\text{H}_7\text{NCHCHNC}_3\text{H}_7)_2][\text{BPh}_4]$                     | $\text{CDCl}_3$          |                                | 1.3, 1.5        |                                                                                                                     |
| $[\text{Ru}_2\text{Cl}_3(\text{PPh}_3)_2(\text{C}_6\text{H}_5\text{NCCH}_2\text{CCH}_2\text{NC}_6\text{H}_5)_2]\text{Cl}$      | $\text{CDCl}_3$          |                                | 7.85, 7.9; 7.70 |                                                                                                                     |
| $[\text{Ru}_2\text{Cl}_3(\text{PPh}_3)_2(\text{C}_6\text{H}_5\text{NCCH}_2\text{CCH}_2\text{NC}_6\text{H}_5)_2][\text{BPh}_4]$ | $\text{CDCl}_3$          |                                | 7.85, 7.9       |                                                                                                                     |
| $[\text{RuH}(\text{Cl})(\text{PPh}_3)_3(\text{C}_3\text{H}_7\text{NCHCHNC}_3\text{H}_7)]$                                      | $\text{CD}_2\text{Cl}_2$ | 19.5 (t) (25)                  |                 | 5.5, <sup>b</sup> 8.5, <sup>c</sup> 9.3 <sup>c</sup>                                                                |
| $[\text{Ru}_2\text{Cl}_3(\text{PPh}_3)_2(\text{C}_3\text{H}_7\text{NCHCHNC}_3\text{H}_7)_2]\text{X}$                           | $\text{CD}_2\text{Cl}_2$ |                                | 1.48, 1.43      | 5.5, <sup>b</sup> 8.5, <sup>c</sup> 9.3 <sup>c</sup>                                                                |
| $[\text{Ru}_2\text{H}(\mu\text{-Cl})(\mu\text{-OH})_2(\text{PPh}_3)_3(\text{C}_3\text{H}_7\text{NCHCHNC}_3\text{H}_7)]$        | $\text{C}_6\text{D}_6$   | 29.1 (dd) (28.6, 34.9)         |                 | 5.5, <sup>b</sup> 8.5, <sup>c</sup> 9.2, <sup>c</sup><br>11.3 (d) <sup>d</sup> (2.2)<br>12.0 (t) <sup>d</sup> (2.9) |

<sup>a</sup> Values of  $J(\text{PH})/\text{Hz}$  are given in parentheses. <sup>b</sup> Unique proton of isopropyl group of dad-a. <sup>c</sup> Methyl groups of dad-a.

<sup>d</sup> Hydroxo-groups.

$[\text{BPh}_4]$  in  $\text{CDCl}_3$  or  $\text{CD}_2\text{Cl}_2$  (Table 1) shows, in addition to resonances of the phenyl groups of triphenylphosphine (also present in all the compounds hereafter described) between  $\tau$  2.43 and 3.6, two second-order multiplets at  $\tau$  8.50 and 9.33 due to the methyl groups of the diazadiene. The methyl : phenyl ratio is *ca.* 24 : 50 as expected. Two complex multiplets are seen at  $\tau$  5.3

12 : 15) but between the two imino-resonances a third one of weaker intensity is present at  $\tau$  1.38 in  $\text{CDCl}_3$  and  $\text{CD}_2\text{Cl}_2$ . This peak increases slowly with time in  $\text{CH}_2\text{Cl}_2$ .

The  $^{31}\text{P}$  n.m.r. spectra of these complexes (Table 2) in different solvents all show a single peak at  $\delta$  *ca.* 37\* which indicates that the two moieties of the binuclear cation are equivalent.

TABLE 2  
Phosphorus-31 n.m.r. spectra of ruthenium complexes

| Compound                                                                                                                       | Solvent                    | Chemical shift * ( $\delta$ )                                    |
|--------------------------------------------------------------------------------------------------------------------------------|----------------------------|------------------------------------------------------------------|
| $[\text{Ru}_2\text{Cl}_4(\text{PPh}_3)_3(\text{C}_6\text{H}_5\text{NCCH}_2\text{CCH}_2\text{NC}_6\text{H}_5)]$                 | $\text{CD}_2\text{Cl}_2$   | 45.8, 40.1                                                       |
| $[\text{Ru}_2\text{Cl}_3(\text{PPh}_3)_2(\text{C}_3\text{H}_7\text{NCHCHNC}_3\text{H}_7)_2]\text{Cl}$                          | $\text{CDCl}_3$            | 37.6                                                             |
| $[\text{Ru}_2\text{Cl}_3(\text{PPh}_3)_2(\text{C}_3\text{H}_7\text{NCHCHNC}_3\text{H}_7)_2]\text{Cl}$                          | $\text{CD}_2\text{Cl}_2$   | 37.4                                                             |
| $[\text{Ru}_2\text{Cl}_3(\text{PPh}_3)_2(\text{C}_3\text{H}_7\text{NCHCHNC}_3\text{H}_7)_2][\text{BPh}_4]$                     | $\text{CDCl}_3$            | 36.9                                                             |
| $[\text{Ru}_2\text{Cl}_3(\text{PPh}_3)_2(\text{C}_6\text{H}_5\text{NCCH}_2\text{CCH}_2\text{NC}_6\text{H}_5)_2][\text{BPh}_4]$ | $\text{CDCl}_3$            | 38.5                                                             |
| $[\text{RuH}(\text{Cl})(\text{PPh}_3)_3(\text{C}_3\text{H}_7\text{NCHCHNC}_3\text{H}_7)]$                                      | $(\text{CD}_3)_2\text{CO}$ | 24.8                                                             |
| $[\text{Ru}_2\text{Cl}_3(\text{PPh}_3)_2(\text{C}_3\text{H}_7\text{NCHCHNC}_3\text{H}_7)_2]\text{X}$                           | $\text{CDCl}_3$            | 37.3                                                             |
| $[\text{Ru}_2\text{H}(\mu\text{-Cl})(\mu\text{-OH})_2(\text{PPh}_3)_3(\text{C}_3\text{H}_7\text{NCHCHNC}_3\text{H}_7)]$        | $\text{C}_6\text{D}_6$     | 34.9, 71.1 (d);<br>77.2 (d)<br>[ $J(\text{PP}) = 29\text{ Hz}$ ] |

\* To high frequency of external  $\text{H}_3\text{PO}_4$ .

and 5.8 which arise from the unique isopropyl protons. Finally, two singlets are seen at  $\tau$  1.5 and 1.7 attributed to the imino-protons of the diazadiene ligands. This

TABLE 3

Molar conductance of ruthenium complexes at  $25^\circ\text{C}$  in degassed nitromethane ( $10^{-3}\text{ mol dm}^{-3}$  solutions). All complexes are 1 : 1 electrolytes

| Compound                                                                                                                       | $\Lambda$<br>$\text{ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$ |
|--------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------|
| $[\text{Ru}_2\text{Cl}_3(\text{PPh}_3)_2(\text{C}_3\text{H}_7\text{NCHCHNC}_3\text{H}_7)_2]\text{Cl}$                          | 56.6                                                       |
| $[\text{Ru}_2\text{Cl}_3(\text{PPh}_3)_2(\text{C}_3\text{H}_7\text{NCHCHNC}_3\text{H}_7)_2][\text{BPh}_4]$                     | 59.8                                                       |
| $[\text{Ru}_2\text{Cl}_3(\text{PPh}_3)_2(\text{C}_6\text{H}_5\text{NCCH}_2\text{CCH}_2\text{NC}_6\text{H}_5)_2]\text{Cl}$      | 53.9                                                       |
| $[\text{Ru}_2\text{Cl}_3(\text{PPh}_3)_2(\text{C}_6\text{H}_5\text{NCCH}_2\text{CCH}_2\text{NC}_6\text{H}_5)_2][\text{BPh}_4]$ | 54.6                                                       |

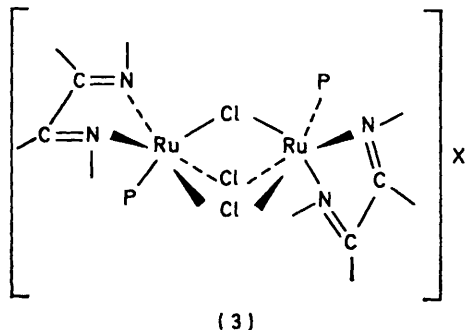
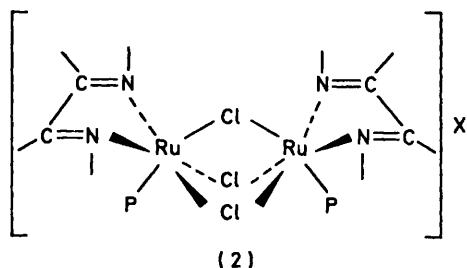
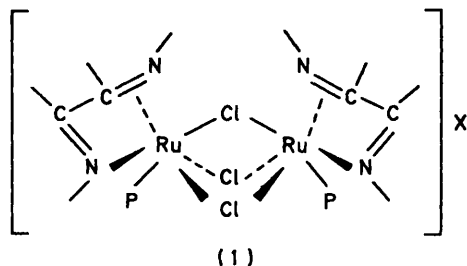
could indicate either that the two moieties of the ligand are inequivalent or that there is coupling between the imino-protons and the phosphine groups. In fact, n.m.r. spectra recorded at 60 and at 90 MHz indicated

The asymmetry of the diazadiene ligand remains to be explained. Two possibilities exist: either the diazadiene molecule is unsymmetrically bound (on one side through the nitrogen lone pair and on the other through the C=N bond) or there is an asymmetry between the two ends of the molecules although each one is bound through the nitrogen lone pair. The first solution [structure (1)] seems less favourable since one should then probably observe a P-H coupling between the phosphines and the imino-protons on the end bound through the C=N bond. Such couplings can be seen in n.m.r. spectra of other complexes obtained by reactions of  $[\text{RuH}_2(\text{PPh}_3)_4]$  with diazadienes.<sup>12</sup> In the second case there are two possible isomers, one in which a plane of symmetry exists [structure (2)] and one in which there is no plane of symmetry [structure (3)]. The diazadiene

\* Chemical shifts are to high frequency of external  $\text{H}_3\text{PO}_4$ .

molecules of this last complex will then have one end *syn* to P and the other *syn* to N. The two ends will thus be inequivalent.

It is probable that the complexes  $[\text{RuCl}_3(\text{PPh}_3)_2(\text{dad-a})_2]\text{X}$  have the structure (3) and since a single peak appears at  $\tau$  1.38 in the  $^1\text{H}$  n.m.r. spectra of  $[\text{RuCl}_3(\text{PPh}_3)_2(\text{dad-a})_2]\text{Cl}$  it is possible that it isomerizes to the structure (2). A peak of weak intensity at  $\delta$  29.1 which



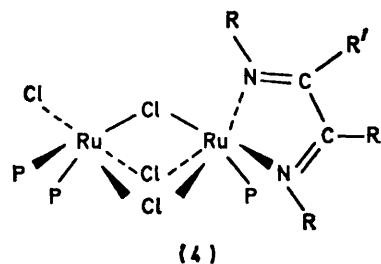
could correspond to this isomer is visible in the  $^{31}\text{P}$  n.m.r. spectrum. Similarly, the  $^1\text{H}$  n.m.r. spectrum of  $[\text{Ru}_2\text{Cl}_3(\text{PPh}_3)_2(\text{dad-c})_2][\text{BPh}_4]$  shows two peaks at  $\tau$  7.85 and 7.9 arising from the methyl groups of the diazadiene ligands as well as the phenyl groups (integration ratio 12 : 70). The spectrum of  $[\text{Ru}_2\text{Cl}_3(\text{PPh}_3)_2(\text{dad-c})_2]\text{Cl}$  in  $\text{CDCl}_3$  shows in addition a peak at  $\tau$  7.7 which can be attributed to the same kind of rearrangement as before. Finally the  $^{31}\text{P}$  n.m.r. spectrum of  $[\text{Ru}_2\text{Cl}_3(\text{PPh}_3)_2(\text{dad-c})_2][\text{BPh}_4]$  only shows a single peak at  $\delta$  38.5. We thus also attribute to these compounds the structure (3).

The compound  $[\text{RuCl}_2(\text{PPh}_3)_3]$  reacts with *half* an equivalent of dad-c in toluene at room temperature to give a red precipitate which can be recrystallized from dichloromethane–diethyl ether to give red crystals analysing for  $[\text{Ru}_2\text{Cl}_4(\text{PPh}_3)_3(\text{dad})]$ . The product is non-conducting and its i.r. spectrum (as well as those of all

the other compounds described here) shows the characteristic band of triphenylphosphine. In addition, a band at  $1590\text{ cm}^{-1}$  is attributed to deformation of the mono-substituted phenyl ring of the diazadiene ligand and two bands at  $315$  and  $280\text{ cm}^{-1}$  indicate the presence of chlorine groups.

The  $^1\text{H}$  n.m.r. spectrum shows the resonances of the phenyl rings of the ligands between  $\tau$  2.3 and 3.5 (again as all the other complexes described), and the methyl groups of the diazadiene as two peaks at  $\tau$  7.98 and 8.04. The  $^{31}\text{P}$  n.m.r. spectrum of this complex shows two sharp peaks in the ratio *ca.* 2 : 1 at  $\delta$  45.8 and 40.1. This and the analytical data indicate that the complex is binuclear, one ruthenium bearing one phosphine group and the other two equivalent phosphines. Two possibilities remain for the stereochemistry of this complex: dichloride- or trichloride-bridging.

The similarity of the far-i.r. spectrum to that of  $[\text{Ru}_2\text{Cl}_4(\text{PEtPh}_2)_5]$  [two  $\nu(\text{Ru}-\text{Cl})$  at  $315$  and  $260\text{ cm}^{-1}$ ] <sup>7</sup> suggests a similar structure (4) with one terminal and



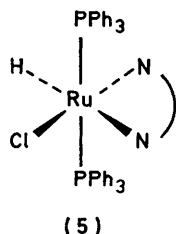
three bridging chlorine atoms. The  $^1\text{H}$  n.m.r. spectrum of the complex in the methyl region again shows two peaks instead of the one expected for symmetrically bound diazadiene. This is due to a chemical-shift difference rather than to a P–H coupling as demonstrated by  $^1\text{H}$  n.m.r. experiments at 60 and 90 MHz. Also, since no P–H coupling is observed, it is probable that both ends of the diazadiene are bound through the nitrogen lone pair. We thus propose the structure (4). This structure is preferred since the two ends of the diazadienes are inequivalent, although the phosphines on the other Ru atom should also be inequivalent. It is possible that the latter have accidentally identical chemical shifts.

This kind of triply bridged complex is quite usual in ruthenium chemistry. Numerous examples of such compounds are known with alkylphosphines,<sup>7</sup> phosphites,<sup>8</sup> or fluorophosphines<sup>9</sup> as ligands; it is nevertheless interesting that the presence of diazadienes can induce the formation of such complexes.

*Reactions of  $[\text{RuH}(\text{Cl})(\text{PPh}_3)_3]$  with Diazadienes.*—*(a) Preparation and characterization of  $[\text{RuH}(\text{Cl})(\text{PPh}_3)_2(\text{dad})]$ .* The compound  $[\text{RuH}(\text{Cl})(\text{PPh}_3)_3]$  reacts at room temperature with  $\geq 1$  equivalent of dad-a in diethyl ether to give a brown powder, which can be recrystallized from dichloromethane–diethyl ether and analyses for  $[\text{RuH}(\text{Cl})(\text{PPh}_3)_2(\text{dad})]$ . The i.r. spectrum of this com-

plex shows  $\nu(\text{Ru-H})$  at  $1\,950\text{ cm}^{-1}$  but no  $\nu(\text{Ru-Cl})$  can be seen.

The n.m.r. spectra of this compound are difficult to obtain in view of its instability. For example, the  $^1\text{H}$  n.m.r. spectrum in  $\text{CD}_2\text{Cl}_2$  shows, together with methyl protons and the unique protons of the isopropyl groups, a high-field hydride resonance at  $\tau\,19.5$  [triplet,  $J(\text{PH}) = 25\text{ Hz}$ ] which decreases in intensity as a doublet corresponding to a monophosphine species appears at  $\tau\,22.6$



[ $J(\text{PH}) = 26\text{ Hz}$ ]. It is obvious that the initial complex containing two equivalent phosphines loses one phosphine ligand. The  $^{31}\text{P}$  n.m.r. spectrum indicates that in solution in  $(\text{CD}_3)_2\text{CO}$  there is a complex containing two *trans* equivalent phosphines [ $\delta\,24.8\text{ (s)}$ ]. This complex is then the *cis*-hydridochloride  $[\text{RuH}(\text{Cl})(\text{PPh}_3)_2(\text{dad-a})]$ . The imino-protons are not seen. It is therefore not

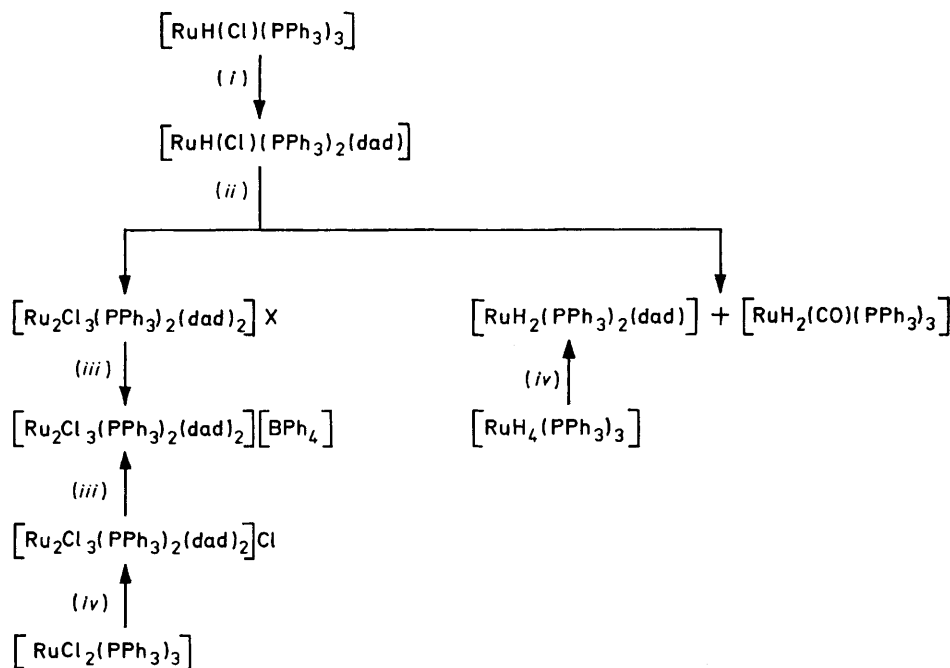
scopy as a mixture of  $[\text{RuH}_2(\text{PPh}_3)_2(\text{dad-a})]$  {which can be obtained directly from the reaction of  $[\text{RuH}_2(\text{PPh}_3)_4]$  or  $[\text{RuH}_4(\text{PPh}_3)_3]$  with dad-a in toluene<sup>12</sup>} and  $[\text{RuH}_2(\text{CO})(\text{PPh}_3)_3]$ .<sup>10</sup>

The brown solution contains an ionic product. The cation can be precipitated by  $\text{BPh}_4^-$  and is identified as  $[\text{Ru}_2\text{Cl}_3(\text{PPh}_3)_2(\text{dad-a})_2]^+$ . Thus disproportionation of a hydridochloro-complex has occurred to give a dihydrido- and a dichloro-complex which then rearranges (see Scheme).

It is noteworthy that the same reaction occurs when  $[\text{RuH}(\text{Cl})(\text{PPh}_3)_2(\text{dad-a})]$  is dissolved in acetone, but in this case we were not able to isolate dihydrido-complexes.

Two problems remain: the nature of the  $\text{X}^-$  anion in the compound  $[\text{Ru}_2\text{Cl}_3(\text{PPh}_3)_2(\text{dad-a})_2]\text{X}$  obtained by disproportionation of  $[\text{RuH}(\text{Cl})(\text{PPh}_3)_2(\text{dad-a})]$ ; and the mechanism of this disproportionation. It has not been possible to isolate the  $\text{X}^-$  anion by precipitation by  $\text{AsPh}_4^+$  or  $\text{PPh}_4^+$ , even after precipitation of  $[\text{Ru}_2\text{Cl}_3(\text{PPh}_3)_2(\text{dad-a})_2][\text{BPh}_4]$ . Thus this anion may be organic rather than inorganic.

The i.r. spectra of the ionic species  $[\text{Ru}_2\text{Cl}_3(\text{PPh}_3)_2(\text{dad-a})_2]\text{X}$  show strong absorptions at  $3\,200\text{--}3\,300\text{ cm}^{-1}$  attributable to O-H or N-H stretches. They are not visible in the spectrum of the  $\text{BPh}_4$  salt. The  $^1\text{H}$  n.m.r.



SCHEME Disproportionation of  $[\text{RuH}(\text{Cl})(\text{PPh}_3)_2(\text{dad})]$  in methanol. (i) dad-OEt<sub>2</sub>; (ii) MeOH; (iii) Na[BPh<sub>4</sub>]-MeOH; (iv) dad-toluene

possible to assign a mode of co-ordination to the diazadiene [denoted N-N in structure (5)].

(b) *Disproportionation of  $[\text{RuH}(\text{Cl})(\text{PPh}_3)_2(\text{dad-a})]$  in methanol.* When  $[\text{RuH}(\text{Cl})(\text{PPh}_3)_2(\text{dad-a})]$  is stirred in methanol at  $50^\circ\text{C}$  a reaction occurs. After reduction in volume of the solution, it is possible to separate a brown solution from a red solid. Fractional crystallization then gave a red solid identified by i.r. and n.m.r. spectro-

spectrum shows that the diazadiene is bound unsymmetrically. Thus two peaks are observed, arising from imino-protons at  $\tau\,1.48$  and  $1.53$  as well as three doublets of respective intensities 1, 1, and 2 at  $\tau\,8.48$ ,  $8.56$ , and  $9.19$  due to methyl groups of the ligands. The  $^{31}\text{P}$  n.m.r. in  $\text{CDCl}_3$  only shows a single peak at  $\delta\,37.3$  where phosphines of triply bridged cations are usually found. Analytical data indicate the presence of one diazadiene

group per phosphine. It does not seem likely then that  $X^-$  is a diazadiene anion or a ruthenium complex but we have not been able to characterize it more fully.

Finally, the nature of the mechanism of this reaction is again not clear. If it is easy to imagine the ionization of  $[\text{RuH}(\text{Cl})(\text{PPh}_3)_2(\text{dad-a})]$  to liberate  $\text{Cl}^-$  and so transfer a chlorine anion, it is much more difficult to imagine the liberation of  $\text{H}^-$ . It is possible that some free diazadiene acts as a base, the solvent then being a source of protons. In any case, it seems that the first step could be an equilibrium producing  $[\text{RuCl}_2(\text{PPh}_3)_2(\text{dad})]$ , which readily dimerizes to the binuclear cation, and ' $\text{RuH}_2(\text{PPh}_3)_3$ ' as well as a molecule of diazadiene. Separate studies have shown that: (i)  $[\text{RuH}_2(\text{PPh}_3)_4]$  and  $[\text{RuH}_2(\text{PPh}_3)_2(\text{dad})]$  are in equilibrium in toluene [equation (1)]; (ii) low-valent ruthenium complexes  $[\text{RuH}_2(\text{PPh}_3)_4] + \text{dad} \rightleftharpoons [\text{RuH}_2(\text{PPh}_3)_2(\text{dad})] + 2\text{PPh}_3$  (1)

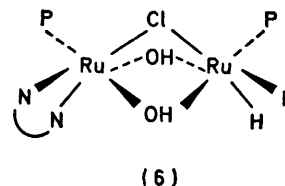
react with alcohols in basic media to give carbonyl complexes<sup>13</sup> and  $[\text{RuH}_2(\text{PPh}_3)_4]$  reacts with acetone to give  $[\text{RuH}_2(\text{CO})(\text{PPh}_3)_3]$ .<sup>14</sup> The same reaction probably takes place between  $[\text{RuH}_2(\text{PPh}_3)_4]$  and  $\text{MeOH}$ .<sup>15</sup>

The driving force for this reaction may be the great stability of the binuclear trichloro-bridged cation and the production of  $[\text{RuH}_2(\text{CO})(\text{PPh}_3)_3]$  which is inert.

(c) *Reaction of  $[\text{RuH}(\text{Cl})(\text{PPh}_3)_2(\text{dad-a})]$  with water.* In order to determine the influence of water on the preceding reaction, we studied the reaction of  $[\text{RuH}(\text{Cl})(\text{PPh}_3)_2(\text{dad-a})]$  with water in a neutral solvent (toluene). After 48 h at room temperature or overnight at 60 °C, a red-brown solution had formed in the toluene phase. After evaporation of the mixture to dryness and recrystallization from diethyl ether, brown crystals of a complex analysing for  $[\text{Ru}_2\text{H}(\text{Cl})(\text{OH})_2(\text{PPh}_3)_3(\text{dad-a})]$  were obtained. The solid-state i.r. spectrum of this compound is somewhat surprising since together with  $\nu(\text{Ru-H})$  at 1995  $\text{cm}^{-1}$  there are three O-H bands at 3590m, 3580w, and 3565w  $\text{cm}^{-1}$ . However, in solution in  $\text{CH}_2\text{Cl}_2$  only two bands are visible at 3593 and 3583  $\text{cm}^{-1}$  as expected. The second band is probably split by a solid-state effect.

The  $^{31}\text{P}$  n.m.r. spectrum of this species shows a singlet at  $\delta$  34.9 and two broad doublets at  $\delta$  77.2 and 71.1 [ $J(\text{PP}) = 29$  Hz]. This is in agreement with an asymmetric binuclear structure, one ruthenium atom accommodating one phosphine and the other two non-equivalent phosphines. This is confirmed by the  $^1\text{H}$  n.m.r. spectrum which shows a diazadiene, the two ends of which are non-equivalent (1 dad : 3 $\text{PPh}_3$ ), a hydride at  $\tau$  29.1 [doublet of doublets,  $J(\text{P}^1\text{H}) = 28.6$ ,  $J(\text{P}^2\text{H}) = 34.9$  Hz] which is coupled to the two non-equivalent phosphines, and hydroxo-groups at  $\tau$  11.3 and 12.0 which are probably bridging.<sup>15</sup> Integration shows that there is one hydride to the two non-equivalent hydroxo-groups. The two hydroxo-groups give a doublet [ $J(\text{PH}) = 2.2$  Hz] and a triplet [ $J(\text{PH}) = 2.9$  Hz] respectively. This can be explained by a *trans* coupling of the first OH with one phosphine group of one ruthenium atom, whereas the

other OH is coupled to one phosphine of each ruthenium [see structure (6)]. No  $\nu(\text{Ru-Cl})$  band was observed, but analysis data (Table 4) clearly demonstrate the presence of chlorine. Again, the mode of co-ordination of diazadiene is unknown but it seems likely that this occurs through the nitrogen lone pair.



In order to explain this reaction we must assume that a diazadiene is liberated and then acts as a base. The surprising effect is that instead of removing only chlorine groups, the base abstracts one hydride of a ruthenium and one chloride of another. Although it is clear from these results that water does not interfere with the disproportionation reaction, it seems likely that a similar mechanism occurs and that free diazadiene acts as a base.

#### EXPERIMENTAL

Microanalyses were by Centre de Microanalyse du CNRS. Infrared spectra were obtained using Perkin-Elmer PE 577 or PE 225 grating diffractometers, n.m.r. spectra using Perkin-Elmer R 12 (60 MHz), Varian A 60 A (60 MHz), and Bruker WH 90 (90 MHz) spectrometers, the latter in the Fourier-transform mode, with proton-noise decoupling when recording  $^{31}\text{P}$  n.m.r. spectra. Melting points were determined in air on a Leitz-Weizlar heating plate. Conductivity measurements were performed on a Beckmann RC 18 A conductivity bridge.

All solvents were thoroughly degassed before use and all operations were carried out in a nitrogen or argon atmosphere using standard Subaseal and catheter techniques.

The diazadiene ligands were prepared according to published methods by adding 2 equivalents of amine to glyoxal (water solution) or diacetyl at 0 °C. The compounds  $[\text{RuCl}_2(\text{PPh}_3)_3]$ <sup>16</sup> and  $[\text{RuH}(\text{Cl})(\text{PPh}_3)_4]$ <sup>17</sup> were prepared by published procedures. Analytical data for the new complexes are given in Table 4.

*Preparations.*—(1) *Tetrachloro[ $\eta$ -2,3-di(phenylimino)-butane]tetrakis(triphenylphosphine)diruthenium(II).* The compound  $[\text{RuCl}_2(\text{PPh}_3)_3]$  (0.5 g, 0.52 mmol) was stirred in a solution of dad-c (0.062 g, 0.26 mmol) in toluene for 15 h during which a red compound precipitated. The solid was collected, washed with diethyl ether, and recrystallized from dichloromethane-diethyl ether, thus affording deep red crystals of the complex. Yield ca. 60%. On addition of diethyl ether to the filtrate, more crystals can be obtained. Total yield 95%.

(2) *Tri- $\mu$ -chloro-bis[1,2-di(isopropylimino)ethane]bis(triphenylphosphine)diruthenium(II) chloride.* (a) The compound  $[\text{RuCl}_2(\text{PPh}_3)_3]$  (0.5 g, 0.52 mmol) was stirred in a solution of dad-a (0.15 g, 1.05 mmol) in toluene for 15 h. The yellow-brown precipitate was collected and washed with diethyl ether, affording the pure complex. Yield 95%. It can be recrystallized from dichloromethane or from chloroform to give golden yellow crystals of the 1/1 and 1/3 solvates respectively. Yield ca. 80%.

(b) As in (a) but performing the reaction in dichloromethane.

(3) *Tri-μ-chloro-bis*[1,2-di(isopropylimino)ethane]bis(triphenylphosphine)diruthenium(II) tetraphenylborate. The compound  $[\text{Ru}_2\text{Cl}_3(\text{PPh}_3)_2(\text{C}_3\text{H}_7\text{NCHCHNC}_3\text{H}_7)_2]\text{Cl}$  (0.5 g, 0.44 mmol) was dissolved in methanol (20 cm<sup>3</sup>) and Na[BPh<sub>4</sub>] (0.15 g, 0.44 mmol) was added. A yellow-brown powder precipitated, was collected, and recrystallized from

methanol to give  $[\text{Ru}_2\text{Cl}_3(\text{PPh}_3)_2(\text{dad-a})_2][\text{BPh}_4]$ . Yield of overall reaction ca. 95%.

(8) *μ-Chloro*-[1,2-di(isopropylimino)ethane]hydrido-μ-hydroxo-tris(triphenylphosphine)diruthenium(II). The compound  $[\text{RuH}(\text{Cl})(\text{PPh}_3)_2(\text{dad-a})]$  (0.5 g) was added to a mixture containing toluene (60 cm<sup>3</sup>) and distilled water (4 cm<sup>3</sup>). The mixture was stirred overnight at 50 °C during which the colour of the toluene solution became red-brown.

TABLE 4  
Analytical data for new ruthenium complexes

| Compound                                                                                                                                                       | Colour        | M.p.<br>(θ <sub>c</sub> /°C) | Analysis (%) |     |     |      |     |       |     |     |      |     |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------|------------------------------|--------------|-----|-----|------|-----|-------|-----|-----|------|-----|
|                                                                                                                                                                |               |                              | Found        |     |     |      |     | Calc. |     |     |      |     |
|                                                                                                                                                                |               |                              | C            | H   | N   | Cl   | P   | C     | H   | N   | Cl   | P   |
| $[\text{Ru}_2\text{Cl}_4(\text{PPh}_3)_3(\text{C}_3\text{H}_7\text{NCHCHNC}_3\text{H}_7)]$                                                                     | Deep red      | 180                          | 61.4         | 4.8 | 2.0 | 10.4 | 6.4 | 61.5  | 4.5 | 2.0 | 10.4 | 6.8 |
| $[\text{Ru}_2\text{Cl}_3(\text{PPh}_3)_2(\text{C}_3\text{H}_7\text{NCHCHNC}_3\text{H}_7)_2]\text{Cl}$                                                          | Golden yellow | 325 (decomp.)                | 54.5         | 5.8 | 5.2 | 12.2 | 5.1 | 54.4  | 5.4 | 4.9 | 12.4 | 5.4 |
| $[\text{Ru}_2\text{Cl}_3(\text{PPh}_3)_2(\text{C}_3\text{H}_7\text{NCHCHNC}_3\text{H}_7)_2]\text{Cl}\cdot\text{CH}_2\text{Cl}_2$                               | Golden yellow |                              | 51.6         | 5.3 | 4.6 | 16.7 | 5.0 | 51.6  | 5.2 | 4.5 | 17.3 | 5.9 |
| $[\text{Ru}_2\text{Cl}_3(\text{PPh}_3)_2(\text{C}_3\text{H}_7\text{NCHCHNC}_3\text{H}_7)_2]\text{Cl}\cdot 3\text{CHCl}_3$                                      | Golden yellow |                              | 44.0         | 4.4 |     | 31.7 | 4.2 | 43.8  | 4.3 |     | 30.7 | 4.1 |
| $[\text{Ru}_2\text{Cl}_3(\text{PPh}_3)_2(\text{C}_3\text{H}_7\text{NCHCHNC}_3\text{H}_7)_2][\text{BPh}_4]$                                                     | Golden yellow | 218                          | 63.5         | 5.7 | 3.7 | 7.5  | 4.3 | 63.7  | 5.7 | 3.9 | 7.4  | 4.3 |
| $[\text{Ru}_2\text{Cl}_3(\text{PPh}_3)_2(\text{C}_6\text{H}_5\text{NCCH}_2\text{CCH}_3\text{NC}_6\text{H}_5)_2]\text{Cl}\cdot\text{CH}_2\text{Cl}_2$           | Red           | 177 (decomp.)                | 58.2         | 4.6 | 4.0 |      | 4.4 | 58.1  | 4.5 | 3.9 |      | 4.4 |
| $[\text{Ru}_2\text{Cl}_3(\text{PPh}_3)_2(\text{C}_6\text{H}_5\text{NCCH}_2\text{CCH}_3\text{NC}_6\text{H}_5)_2]\text{Cl}\cdot 0.2\text{CH}_2\text{Cl}_2$       | Red           |                              | 60.3         | 5.0 | 4.1 | 11.5 |     | 59.4  | 4.6 | 4.1 | 11.2 |     |
| $[\text{Ru}_2\text{Cl}_3(\text{PPh}_3)_2(\text{C}_6\text{H}_5\text{NCCH}_2\text{CCH}_3\text{NC}_6\text{H}_5)_2][\text{BPh}_4]\cdot 0.25\text{CH}_2\text{Cl}_2$ | Red           | 180 (decomp.)                | 67.0         | 5.3 | 2.8 | 7.8  | 3.6 | 67.3  | 5.0 | 3.4 | 7.55 | 3.8 |
| $[\text{RuH}(\text{Cl})(\text{PPh}_3)_2(\text{C}_3\text{H}_7\text{NCHCHNC}_3\text{H}_7)]\cdot 0.1\text{CH}_2\text{Cl}_2$                                       | Brown         |                              | 64.6         | 5.8 | 3.3 | 5.3  | 7.7 | 65.3  | 5.8 | 3.5 | 5.3  | 7.7 |
| $[\text{Ru}_2\text{H}(\mu\text{-Cl})(\mu\text{-OH})_2(\text{PPh}_3)_3(\text{C}_3\text{H}_7\text{NCHCHNC}_3\text{H}_7)]$                                        | Red-brown     |                              | 62.0         | 5.5 | 2.3 | 3.6  | 7.8 | 62.1  | 5.3 | 2.3 | 3.0  | 7.8 |

dichloromethane-diethyl ether affording yellow crystals of the compound. Yield ca. 80%.

(4) *Tri-μ-chloro-bis*[2,3-di(phenylimino)butane]bis(triphenylphosphine)diruthenium(II) chloride was prepared as in (2) (a), using dad-c (0.25 g, 1.05 mmol), yield ca. 95%, or as in (2) (b), using dad-c (0.25 g, 1.05 mmol), yield ca. 80%.

(5) *Tri-μ-chloro-bis*[2,3-di(phenylimino)butane]bis(triphenylphosphine)diruthenium(II) tetraphenylborate was prepared as in (3), using  $[\text{Ru}_2\text{Cl}_3(\text{PPh}_3)_2(\text{C}_6\text{H}_5\text{NCCH}_2\text{CCH}_3\text{NC}_6\text{H}_5)_2]\text{Cl}$  (0.58 g, 0.44 mmol). Yield after recrystallization ca. 75%.

(6) *Chloro*[1,2-di(isopropylimino)ethane]hydridobis(triphenylphosphine)ruthenium(II). The compound  $[\text{RuH}(\text{Cl})(\text{PPh}_3)_2]$  (1 g, 1.08 mmol) was added to a solution of dad-a (0.31 g, 2.2 mmol) in diethyl ether (100 cm<sup>3</sup>) and the resulting suspension was stirred overnight. The brown suspension was filtered off, washed with light petroleum, and dried *in vacuo* thus affording the pure complex (yield ca. 85%). It can be recrystallized from dichloromethane-diethyl ether affording brown crystals. Total yield ca. 60%.

(7) *Reaction of*  $[\text{RuH}(\text{Cl})(\text{PPh}_3)_2(\text{dad-a})]$  *in methanol*. Half an equivalent of  $[\text{RuH}(\text{Cl})(\text{PPh}_3)_2(\text{dad-a})]$  was stirred in methanol (100 cm<sup>3</sup>) at 50 °C overnight. After concentration to ca. 10 cm<sup>3</sup>, a brown solution was separated from a red powder. The red powder was recrystallized from toluene-light petroleum affording successively red crystals of  $[\text{RuH}_2(\text{PPh}_3)_2(\text{dad-a})]$  (yield ca. 15%) and orange microcrystals of  $[\text{RuH}_2(\text{CO})(\text{PPh}_3)_3]$  (yield ca. 15%). The brown solution was evaporated to dryness and the oil obtained was crystallized from dichloromethane-diethyl ether affording brown crystals of an ionic complex of which only the cationic part has been identified,  $[\text{Ru}_2\text{Cl}_3(\text{PPh}_3)_2(\text{dad-a})_2]^+$ . Yield ca. 45%. This complex reacted with Na[BPh<sub>4</sub>] in

The mixture was then evaporated to dryness, dissolved in diethyl ether (50 cm<sup>3</sup>), and cooled at -20 °C affording red-brown crystals. Yield ca. 60%.

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