Reactions of Ruthenium Triphenylphosphine Complexes with Diazadienes. Part 1. Reactions of $[RuCl_2(PPh_3)_3]$ and $[RuH(Cl)(PPh_3)_3]$ † and Disproportionation of a Hydridochloro-complex

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The reactions between $[RuCl_2(PPh_3)_3]$ and half or one equivalent of a diazadiene (dad) give respectively molecular and ionic binuclear triply chloro-bridged complexes, $[Ru_2Cl_4(PPh_3)_3(dad)]$ and $[Ru_2Cl_3(PPh_3)_2(dad)_2]Cl$ which can also be obtained as its BPh_4 salt. The compound $[RuH(Cl)(PPh_3)_3]$ reacts with diazadienes to produce $[RuH(Cl)(PPh_3)_2(dad)]$, which disproportionates in polar solvents to give a hydrido- and a dichloro-compound and reacts with water to give a chlorodihydroxo-bridged hydrido-species, $[Ru_2H(\mu\text{-}OH)_2(PPh_3)_3(dad)]$.

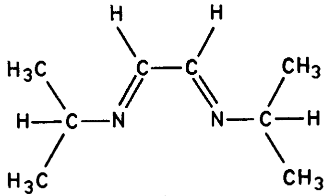
DIAZADIENE (α-DI-IMINE) ligands (dad) have received much attention during the past few years in view of their versatile bonding properties. These ligands are basic but also have a strong π-back-bonding capability,[1] and can thus stabilize low-valent metal complexes such as $[Fe(dad)_2]$ [2] and $[Ni(dad)_2]$.[3] They are also versatile in their modes and sites of co-ordination, *i.e.* they can act as unidentate {*cf.* $[PdCl_2(dad)_2]$},[4] as bidentate {$[Mo(CO)_4(dad)]$},[5] or as bridging ligands ($[\{RhCl(CO)_2\}_2(dad)]$).[4] 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 $[Fe(CO)_3(Bu^tNCHCHNBu^t)]$ [6] both types of co-ordination are present; but for $[Fe(CO)_3(Pr^iNCHCHNPr^i)]$ [6] 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,[7-9] we investigated the reactions of $[RuCl_2(PPh_3)_3]$ with diazadienes. The reaction of $[RuH(Cl)(PPh_3)_3]$ with bipyridyl had been reported to produce a red-brown slightly soluble compound.[10] We investigated the same reaction with diazadienes and obtained a very reactive complex $[RuH(Cl)(PPh_3)_2(dad)]$, 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.*

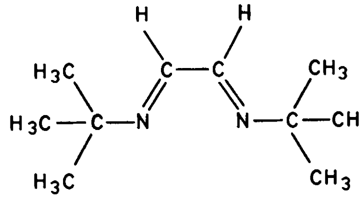
RESULTS AND DISCUSSION

Reactions of $[RuCl_2(PPh_3)_3]$ *with Diazadienes.*—The compound $[RuCl_2(PPh_3)_3]$ does not react with dad-b but does with ⩾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 nonpolar ones. In solution in methanol the products react with $Na[BPh_4]$ to yield yellow or red precipitates.

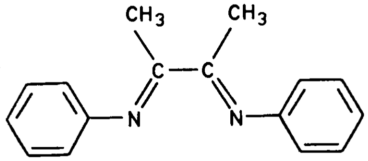
The microanalytical data suggest the formulation $[Ru_2Cl_3(PPh_3)_2(dad)_2]X$ (dad = dad-a or dad-c; X = Cl or BPh_4). All these compounds give solvates after recrystallization from chlorinated solvents although for $[Ru_2Cl_3(PPh_3)_2(dad\text{-}c)_2]X$ the amount of solvent depends on the drying time. Conductivity measurements (54—60 Ω^{-1} cm^2 mol^{-1}) (Table 3) gave values somewhat lower than usually found for 1 : 1 electrolytes (75—95 Ω^{-1} cm^{-2} mol^{-1}) [11] but this seems to be general for such big cations.



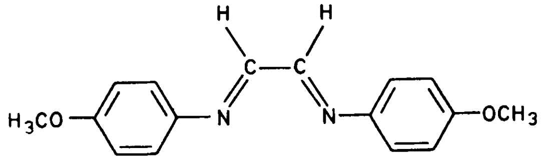
dad – a



dad – b



dad – c



dad – d

The i.r. spectra of $[Ru_2Cl_3(PPh_3)_2(dad\text{-}a)_2]X$ (X = Cl or BPh_4) only show a weak absorption at 300 cm^{-1}

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

attributed to the bridging chloride groups. Similarly, $[Ru_2Cl_3(PPh_3)_2(dad\text{-}c)_2]X$ show a band of medium intensity at 290 cm^{-1} together with another at 1 580 cm^{-1} due to the monosubstituted phenyl ring of the diazadiene ligand.

TABLE 1

Proton n.m.r. spectra of ruthenium complexes

Compound	Solvent	N.m.r. (τ) [a]		
		Hydride	Imino-groups	Other resonances
$[Ru_2Cl_4(PPh_3)_3(C_6H_5NCCH_3CCH_3NC_6H_5)]$	CD_2Cl_2		7.98, 8.04	5.5,[b] 8.5,[c] 9.3 [c]
$[Ru_2Cl_3(PPh_3)_2(C_3H_7NCHCHNC_3H_7)_2]Cl$	CD_2Cl_2		1.3, 1.5; 1.38	5.5,[b] 8.5,[c] 9.3 [c]
$[Ru_2Cl_3(PPh_3)_2(C_3H_7NCHCHNC_3H_7)_2]Cl$	$CDCl_3$		1.3, 1.5; 1.38	5.5,[b] 8.5,[c] 9.3 [c]
$[Ru_2Cl_3(PPh_3)_2(C_3H_7NCHCHNC_3H_7)_2][BPh_4]$	$CDCl_3$		1.3, 1.5	
$[Ru_2Cl_3(PPh_3)_2(C_6H_5NCCH_3CCH_3NC_6H_5)_2]Cl$	$CDCl_3$		7.85, 7.9; 7.70	
$[Ru_2Cl_3(PPh_3)_2(C_6H_5NCCH_3CCH_3NC_6H_5)_2][BPh_4]$	$CDCl_3$		7.85, 7.9	
$[RuH(Cl)(PPh_3)_2(C_3H_7NCHCHNC_3H_7)]$	CD_2Cl_2	19.5 (t) (25)		5.5,[b] 8.5,[c] 9.3 [c]
$[Ru_2Cl_3(PPh_3)_2(C_3H_7NCHCHNC_3H_7)_2]X$	CD_2Cl_2		1.48, 1.43	5.5,[b] 8.5,[c] 9.3 [c]
$[Ru_2H(\mu\text{-}Cl)(\mu\text{-}OH)_2(PPh_3)_3(C_3H_7NCHCHNC_3H_7)]$	C_6D_6	29.1 (dd) (28.6, 34.9)		5.5,[b] 8.5,[c] 9.2,[c] 11.3 (d) [d] (2.2) 12.0 (t) [d] (2.9)

[a] Values of J(PH)/Hz are given in parentheses. [b] Unique proton of isopropyl group of dad–a. [c] Methyl groups of dad–a. [d] Hydroxo-groups.

TABLE 2

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

Compound	Solvent	Chemical shift * (δ)
$[Ru_2Cl_4(PPh_3)_3(C_6H_5NCCH_3CCH_3NC_6H_5)]$	CD_2Cl_2	45.8, 40.1
$[Ru_2Cl_3(PPh_3)_2(C_3H_7NCHCHNC_3H_7)_2]Cl$	$CDCl_3$	37.6
$[Ru_2Cl_3(PPh_3)_2(C_3H_7NCHCHNC_3H_7)_2]Cl$	CD_2Cl_2	37.4
$[Ru_2Cl_3(PPh_3)_2(C_3H_7NCHCHNC_3H_7)_2][BPh_4]$	$CDCl_3$	36.9
$[Ru_2Cl_3(PPh_3)_2(C_6H_5NCCH_3CCH_3NC_6H_5)_2][BPh_4]$	$CDCl_3$	38.5
$[RuH(Cl)(PPh_3)_2(C_3H_7NCHCHNC_3H_7)]$	$(CD_3)_2CO$	24.8
$[Ru_2Cl_3(PPh_3)_2(C_3H_7NCHCHNC_3H_7)_2]X$	$CDCl_3$	37.3
$[Ru_2H(\mu\text{-}Cl)(\mu\text{-}OH)_2(PPh_3)_3(C_3H_7NCHCHNC_3H_7)]$	C_6D_6	34.9, 71.1 (d); 77.2 (d) [J(PP) = 29 Hz]

* To high frequency of external H_3PO_4.

TABLE 3

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

Compound	Λ ohm^{-1} cm^2 mol^{-1}
$[Ru_2Cl_3(PPh_3)_2(C_3H_7NCHCHNC_3H_7)_2]Cl$	56.6
$[Ru_2Cl_3(PPh_3)_2(C_3H_7NCHCHNC_3H_7)_2][BPh_4]$	59.8
$[Ru_2Cl_3(PPh_3)_2(C_6H_5NCCH_3CCH_3NC_6H_5)_2]Cl$	53.9
$[Ru_2Cl_3(PPh_3)_2(C_6H_5NCCH_3CCH_3NC_6H_5)_2][BPh_4]$	54.6

The ^1H n.m.r. spectrum of $[Ru_2Cl_3(PPh_3)_2(dad\text{-}a)_2][BPh_4]$ in $CDCl_3$ or CD_2Cl_2 (Table 1) shows, in addition to resonances of the phenyl groups of triphenylphosphine (also present in all the compounds hereafter described) between τ 2.43 and 3.6, two second-order multiplets at τ 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 τ 5.3 and 5.8 which arise from the unique isopropyl protons. Finally, two singlets are seen at τ 1.5 and 1.7 attributed to the imino-protons of the diazadiene ligands. This 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 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 $[Ru_2Cl_3(PPh_3)_2(dad\text{-}a)_2]Cl$ is very similar to that of the BPh_4 salt (methyl : phenyl ratio, 12 : 15) but between the two imino-resonances a third one of weaker intensity is present at τ 1.38 in $CDCl_3$ and CD_2Cl_2. This peak increases slowly with time in CH_2Cl_2.

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

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 a 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 $[RuH_2(PPh_3)_4]$ with diazadienes.[12] 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

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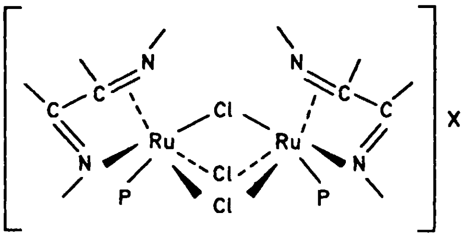
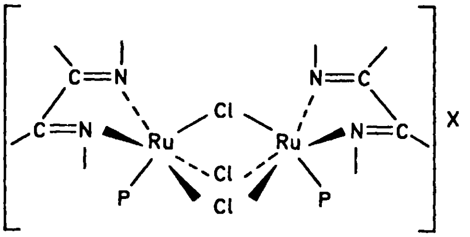
* Chemical shifts are to high frequency of external H_3PO_4.

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 $[RuCl_3(PPh_3)_2(dad\text{-}a)_2]X$ have the structure (3) and since a single peak appears at τ 1.38 in the ^1H n.m.r. spectra of $[RuCl_3(PPh_3)_2(dad\text{-}a)_2]Cl$ it is possible that it isomerizes to the structure (2). A peak of weak intensity at δ 29.1 which could correspond to this isomer is visible in the ^{31}P n.m.r. spectrum. Similarly, the ^1H n.m.r. spectrum of $[Ru_2Cl_3(PPh_3)_2(dad\text{-}c)_2][BPh_4]$ shows two peaks at τ 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 $[Ru_2Cl_3(PPh_3)_2(dad\text{-}c)_2]Cl$ in $CDCl_3$ shows in addition a peak at τ 7.7 which can be attributed to the same kind of rearrangement as before. Finally the ^{31}P n.m.r. spectrum of $[Ru_2Cl_3(PPh_3)_2(dad\text{-}c)_2][BPh_4]$ only shows a single peak at δ 38.5. We thus also attribute to these compounds the structure (3).



(1)



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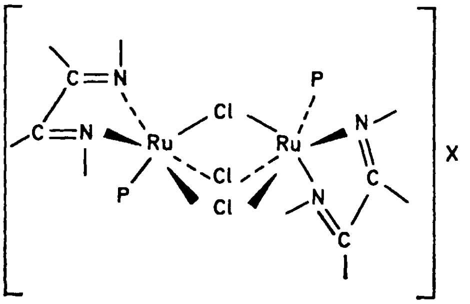
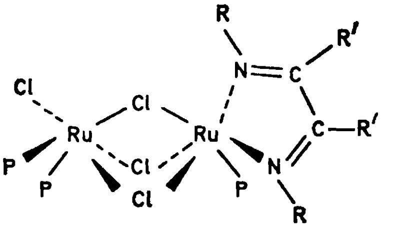


(3)

The compound $[RuCl_2(PPh_3)_3]$ 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 $[Ru_2Cl_4(PPh_3)_3(dad)]$. The product is nonconducting 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 1 590 cm^{-1} is attributed to deformation of the monosubstituted phenyl ring of the diazadiene ligand and two bands at 315 and 280 cm^{-1} indicate the presence of chlorine groups.

The ^1H n.m.r. spectrum shows the resonances of the phenyl rings of the ligands between τ 2.3 and 3.5 (again as all the other complexes described), and the methyl groups of the diazadiene as two peaks at τ 7.98 and 8.04. The ^{31}P n.m.r. spectrum of this complex shows two sharp peaks in the ratio *ca.* 2 : 1 at δ 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 $[Ru_2Cl_4(PEtPh_2)_5]$ [two ν(Ru–Cl) at 315 and 260 cm^{-1}] [7] suggests a similar structure (4) with one terminal and three bridging chlorine atoms. The ^1H 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 ^1H 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.

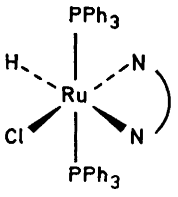


(4)

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

Reactions of $[RuH(Cl)(PPh_3)_3]$ *with Diazadienes.*—(*a*) *Preparation and characterization of* $[RuH(Cl)(PPh_3)_2(dad)]$. The compound $[RuH(Cl)(PPh_3)_3]$ reacts at room temperature with ⩾1 equivalent of dad-a in diethyl ether to give a brown powder, which can be recrystallized from dichloromethane–diethyl ether and analyses for $[RuH(Cl)(PPh_3)_2(dad)]$. The i.r. spectrum of this complex shows ν(Ru–H) at 1 950 cm^{-1} but no ν(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}H n.m.r. spectrum in CD_2Cl_2 shows, together with methyl protons and the unique protons of the isopropyl groups, a high-field hydride resonance at τ 19.5 [triplet, J(PH) = 25 Hz] which decreases in intensity as a doublet corresponding to a monophosphine species appears at τ 22.6 [J(PH) = 26 Hz]. It is obvious that the initial complex containing two equivalent phosphines loses one phosphine ligand. The ^{31}P n.m.r. spectrum indicates that in solution in $(CD_3)_2CO$ there is a complex containing two *trans* equivalent phosphines [δ 24.8 (s)]. This complex is then the *cis*-hydridochloride [RuH(Cl)(PPh$_3$)$_2$(dad-a)]. The imino-protons are not seen. It is therefore not possible to assign a mode of co-ordination to the diazadiene [denoted N–N in structure (5)].



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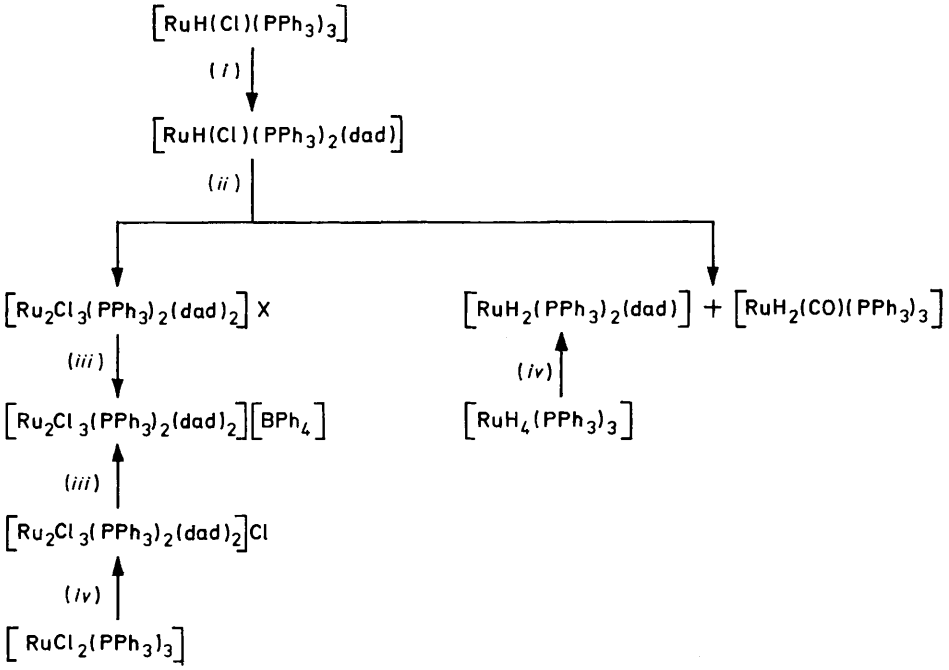


SCHEME Disproportionation of [RuH(Cl)(PPh$_3$)$_2$(dad)] in methanol. (*i*) dad–OEt$_2$; (*ii*) MeOH; (*iii*) Na[BPh$_4$]–MeOH; (*iv*) dad–toluene

(*b*) *Disproportionation of* [RuH(Cl)(PPh$_3$)$_2$(dad-a)] *in methanol.* When [RuH(Cl)(PPh$_3$)$_2$(dad-a)] is stirred in methanol at 50 °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. spectroscopy as a mixture of [RuH$_2$(PPh$_3$)$_2$(dad-a)] {which can be obtained directly from the reaction of [RuH$_2$(PPh$_3$)$_4$] or [RuH$_4$(PPh$_3$)$_3$] with dad-a in toluene [12]} and [RuH$_2$(CO)(PPh$_3$)$_3$].[10]

The brown solution contains an ionic product. The cation can be precipitated by BPh_4^- and is identified as [Ru$_2$Cl$_3$(PPh$_3$)$_2$(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 [RuH(Cl)(PPh$_3$)$_2$(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 X$^-$ anion in the compound [Ru$_2$Cl$_3$(PPh$_3$)$_2$(dad-a)$_2$]X obtained by disproportionation of [RuH(Cl)(PPh$_3$)$_2$(dad-a)]; and the mechanism of this disproportionation. It has not been possible to isolate the X$^-$ anion by precipitation by $AsPh_4^+$ or PPh_4^+, even after precipitation of [Ru$_2$Cl$_3$(PPh$_3$)$_2$(dad-a)$_2$][BPh$_4$]. Thus this anion may be organic rather than inorganic.

The i.r. spectra of the ionic species [Ru$_2$Cl$_3$(PPh$_3$)$_2$(dad-a)$_2$]X show strong absorptions at 3 200—3 300 cm^{-1} attributable to O–H or N–H stretches. They are not visible in the spectrum of the BPh$_4$ salt. The ^{1}H n.m.r. spectrum shows that the diazadiene is bound unsymmetrically. Thus two peaks are observed, arising from imino-protons at τ 1.48 and 1.53 as well as three doublets of respective intensities 1, 1, and 2 at τ 8.48, 8.56, and 9.19 due to methyl groups of the ligands. The ^{31}P n.m.r. in $CDCl_3$ only shows a single peak at δ 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 $[RuH(Cl)(PPh_3)_2(dad\text{-}a)]$ to liberate Cl^- and so transfer a chlorine anion, it is much more difficult to imagine the liberation of 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 $[RuCl_2(PPh_3)(dad)]$, which readily dimerizes to the binuclear cation, and ' $RuH_2(PPh_3)_3$ ' as well as a molecule of diazadiene. Separate studies have shown that: (*i*) $[RuH_2(PPh_3)_4]$ and $[RuH_2(PPh_3)_2(dad)]$ are in equilibrium in toluene [equation (1)]; (*ii*) low-valent ruthenium complexes

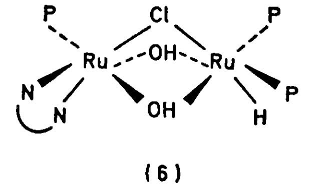
$$[RuH_2(PPh_3)_4] + dad \rightleftharpoons [RuH_2(PPh_3)_2(dad)] + 2PPh_3 \quad (1)$$

react with alcohols in basic media to give carbonyl complexes [13] and $[RuH_2(PPh_3)_4]$ reacts with acetone to give $[RuH_2(CO)(PPh_3)_3]$.[14] The same reaction probably takes place between $[RuH_2(PPh_3)_4]$ and MeOH.[15]

The driving force for this reaction may be the great stability of the binuclear trichloro-bridged cation and the production of $[RuH_2(CO)(PPh_3)_3]$ which is inert.

(*c*) *Reaction of* $[RuH(Cl)(PPh_3)_2(dad\text{-}a)]$ *with water.* In order to determine the influence of water on the preceding reaction, we studied the reaction of $[RuH(Cl)(PPh_3)_2(dad\text{-}a)]$ 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 $[Ru_2H(Cl)(OH)_2(PPh_3)_3(dad\text{-}a)]$ were obtained. The solid-state i.r. spectrum of this compound is somewhat surprising since together with ν(Ru–H) at 1 995 cm^{-1} there are three O–H bands at 3 590m, 3 580w, and 3 565w cm^{-1}. However, in solution in CH_2Cl_2 only two bands are visible at 3 593 and 3 583 cm^{-1} as expected. The second band is probably split by a solid-state effect.

The ^{31}P n.m.r. spectrum of this species shows a singlet at δ 34.9 and two broad doublets at δ 77.2 and 71.1 [$J(PP) = 29$ 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 ^1H n.m.r. spectrum which shows a diazadiene, the two ends of which are non-equivalent (1 dad : $3PPh_3$), a hydride at τ 29.1 [doublet of doublets, $J(P^1H) = 28.6$, $J(P^2H) = 34.9$ Hz] which is coupled to the two non-equivalent phosphines, and hydroxo-groups at τ 11.3 and 12.0 which are probably bridging.[15] Integration shows that there is one hydride to the two non-equivalent hydroxo-groups. The two hydroxo-groups give a doublet [$J(PH) = 2.2$ Hz] and a triplet [$J(PH) = 2.9$ 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 ν(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.



(6)

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}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 $[RuCl_2(PPh_3)_3]$ [16] and $[RuH(Cl)(PPh_3)_4]$ [17] were prepared by published procedures. Analytical data for the new complexes are given in Table 4.

Preparations.—(1) *Tetrachloro*[η-2,3-*di*(*phenylimino*)-*butane*]*tetrakis*(*triphenylphosphine*)*diruthenium*(II). The compound $[RuCl_2(PPh_3)_3]$ (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-μ-chloro-bis*[1,2-*di*(*isopropylimino*)*ethane*]*bis*(*triphenylphosphine*)*diruthenium*(II) *chloride.* (*a*) The compound $[RuCl_2(PPh_3)_3]$ (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 $[Ru_2Cl_3(PPh_3)_2(C_3H_7NCHCHNC_3H_7)_2]Cl$ (0.5 g, 0.44 mmol) was dissolved in methanol (20 cm^3) and $Na[BPh_4]$ (0.15 g, 0.44 mmol) was added. A yellow-brown powder precipitated, was collected, and recrystallized from dichloromethane–diethyl ether affording yellow crystals of the compound. Yield *ca.* 80%.

TABLE 4

Analytical data for new ruthenium complexes

			Analysis (%)									
			Found					Calc.				
Compound	Colour	M.p. (θ_c/°C)	C	H	N	Cl	P	C	H	N	Cl	P
$[Ru_2Cl_4(PPh_3)_3(C_3H_7NCHCHNC_3H_7)]$	Deep red	180	61.4	4.8	2.0	10.4	6.4	61.5	4.5	2.0	10.4	6.8
$[Ru_2Cl_3(PPh_3)_2(C_3H_7NCHCHNC_3H_7)_2]Cl$	Golden yellow	325 (decomp.)	54.5	5.8	5.2	12.2	5.1	54.4	5.4	4.9	12.4	5.4
$[Ru_2Cl_3(PPh_3)_2(C_3H_7NCHCHNC_3H_7)_2]Cl\cdot CH_2Cl_2$	Golden yellow		51.6	5.3	4.6	16.7	5.0	51.6	5.2	4.5	17.3	5.9
$[Ru_2Cl_3(PPh_3)_2(C_3H_7NCHCHNC_3H_7)_2]Cl\cdot 3CHCl_3$	Golden yellow		44.0	4.4		31.7	4.2	43.8	4.3		30.7	4.1
$[Ru_2Cl_3(PPh_3)_2(C_3H_7NCHCHNC_3H_7)_2][BPh_4]$	Golden yellow	218	63.5	5.7	3.7	7.5	4.3	63.7	5.7	3.9	7.4	4.3
$[Ru_2Cl_3(PPh_3)_2(C_6H_5NCCH_3CCH_3NC_6H_5)_2]Cl\cdot CH_2Cl_2$	Red	177 (decomp.)	58.2	4.6	4.0		4.4	58.1	4.5	3.9		4.4
$[Ru_2Cl_3(PPh_3)_2(C_6H_5NCCH_3CCH_3NC_6H_5)_2]Cl\cdot 0.2CH_2Cl_2$	Red		60.3	5.0	4.1	11.5		59.4	4.6	4.1	11.2	
$[Ru_2Cl_3(PPh_3)_2(C_6H_5NCCH_3CCH_3NC_6H_5)_2][BPh_4]\cdot 0.25CH_2Cl_2$	Red	180 (decomp.)	67.0	5.3	2.8	7.8	3.6	67.3	5.0	3.4	7.55	3.8
$[RuH(Cl)(PPh_3)_2(C_3H_7NCHCHNC_3H_7)]\cdot 0.1CH_2Cl_2$	Brown		64.6	5.8	3.3	5.3	7.7	65.3	5.8	3.5	5.3	7.7
$[Ru_2H(\mu\text{-}Cl)(\mu\text{-}OH)_2(PPh_3)_3(C_3H_7NCHCHNC_3H_7)]$	Red-brown		62.0	5.5	2.3	3.6	7.8	62.1	5.3	2.3	3.0	7.8

(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 $[Ru_2Cl_3(PPh_3)_2(C_6H_5NCCH_3CCH_3NC_6H_5)_2]Cl$ (0.58 g, 0.44 mmol). Yield after recrystallization *ca.* 75%.

(6) *Chloro*[1,2-*di*(*isopropylimino*)*ethane*]*hydridobis*(*triphenylphosphine*)*ruthenium*(II). The compound $[RuH(Cl)(PPh_3)_3]$ (1 g, 1.08 mmol) was added to a solution of dad-a (0.31 g, 2.2 mmol) in diethyl ether (100 cm^3) 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* $[RuH(Cl)(PPh_3)_2$(dad-a)] *in methanol.* Half an equivalent of $[RuH(Cl)(PPh_3)_2$(dad-a)] was stirred in methanol (100 cm^3) at 50 °C overnight. After concentration to *ca.* 10 cm^3, a brown solution was separated from a red powder. The red powder was recrystallized from toluene–light petroleum affording successively red crystals of $[RuH_2(PPh_3)_2$(dad-a)] (yield *ca.* 15%) and orange microcrystals of $[RuH_2(CO)(PPh_3)_3]$ (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, $[Ru_2Cl_3(PPh_3)_2(\text{dad-a})_2]^+$. Yield *ca.* 45%. This complex reacted with $Na[BPh_4]$ in methanol to give $[Ru_2Cl_3(PPh_3)_2(\text{dad-a})_2][BPh_4]$. Yield of overall reaction *ca.* 95%.

(8) *μ-Chloro-*[1,2-*di*(*isopropylimino*)*ethane*]*hydrido-μ-hydroxo-tris*(*triphenylphosphine*)*diruthenium*(II). The compound $[RuH(Cl)(PPh_3)_2$(dad-a)] (0.5 g) was added to a mixture containing toluene (60 cm^3) and distilled water (4 cm^3). The mixture was stirred overnight at 50 °C during which the colour of the toluene solution became red-brown. The mixture was then evaporated to dryness, dissolved in diethyl ether (50 cm^3), and cooled at −20 °C affording red-brown crystals. Yield *ca.* 60%.

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