Reduction of Dichlorotris(triphenylphosphine)ruthenium(II) in the Presence of Acetonitrile, Pyridine, 2,2'-Bipyridyl, and Styrene †

By **David J. Cole-Hamilton** and **Geoffrey Wilkinson**,* Chemistry Department, Imperial College of Science and Technology, London SW7 2AY

The reduction of dichlorotris(triphenylphosphine)ruthenium(II) in tetrahydrofuran–acetonitrile by sodium or magnesium amalgam produces a compound shown to be a hydrido *ortho*-metallated phosphine ruthenium(II) complex $RuH(C_6H_4PPh_2)(MeCN)(PPh_3)_2$. This compound has all the characteristics of a complex previously reported and alleged to be a ruthenium(0) complex containing a π-bonded acetonitrile ' $Ru(MeCN)(PPh_3)_4{\cdot}MeCN$ '.

Detailed study of the system shows that there are labile intermediates, $Ru(MeCN)_2(PPh_3)_2$ which is paramagnetic, $Ru(MeCN)_3(PPh_3)_2$, and $Ru(MeCN)(PPh_3)_3$. The reduction in pyridine gives two isomers of $RuH(C_6H_4PPh_2)(C_5H_5N)(PPh_3)_2$ while in the presence of 2,2'-bipyridyl the main product is a purple complex $RuH(C_6H_4PPh_2)(bipy)(PPh_3)$. In styrene the known complex $Ru(styrene)_2(PPh_3)_2$ is obtained.

Reactions of the ruthenium(II) species $RuH(C_6H_4PPh_2)(MeCN)(PPh_3)_2$ with propene and water are reported. The various compounds have been characterised by i.r. and ^1H and ^{31}P n.m.r. spectroscopy.

It is concluded that reductions of $RuCl_2(PPh_3)_{3\text{ or }4}$ lead to the abstraction of hydride from the solvent if no strongly co-ordinating ligand is present. In the presence of co-ordinating ligands, species containing *ortho*-metallated triphenylphosphine groups are formed *via* intramolecular oxidative addition of a C–H bond to transient ruthenium(0) intermediates.

PREVIOUS work[1-3] on reactions of hydrido-triphenylphosphine complexes of ruthenium has shown that, with the exception[3,4] of $Ru(PPh_3)_2(styrene)_2$, complexes of ruthenium(0) which do not contain good π-acceptor ligands such as CO, PF_3, and isocyanides, or dienes, are, in general, not easy to isolate. When PPh_3 is the ligand *ortho*-metallation of a phenyl ring is commonly observed.[1,2] When this metallation is accompanied by loss of hydrocarbon, as in reaction (1)[1] we

$$RuH(Me)(PPh_3)_2(thf)_2 \longrightarrow RuH(C_6H_4PPh_2)(PPh_3)(thf)_2 + MeH \quad (1)$$

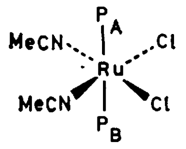
have suggested[1-3] that the loss of alkane involves intraligand hydrogen transfer and no change in oxidation state of the metal in any intermediates. An apparent exception is the electrochemical reduction of $RuCl_2(PPh_3)_4$ in acetonitrile[5] to give a compound formulated as $Ru(PPh_3)_4(\pi\text{-MeCN}){\cdot}MeCN$ in which the co-ordinated acetonitrile is thought to be sideways (π or η^2) bound to the metal.

We have studied the reductions of $RuCl_2(PPh_3)_{3\text{ or }4}$ in the presence of various substrates to test whether true zero-valent ruthenium species can be isolated and whether metallation occurs *via* a direct oxidative addition to such a ruthenium(0) complex.

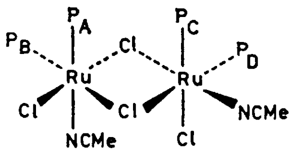
RESULTS AND DISCUSSION

Reductions of $RuCl_2(PPh_3)_{3\text{ or }4}$ *in the Presence of Ligands.*—I.r., ^1H n.m.r., ^{31}P n.m.r., and analytical data are collected in Tables 1—4.

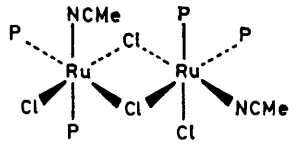
Acetonitrile. $RuCl_2(PPh_3)_4$ is not reduced by magnesium turnings in acetonitrile, although a small amount of a pale yellow solid[6] *cis,cis,cis*-$RuCl_2(MeCN)_2(PPh_3)_2$ is precipitated. The solution affords a yellow complex of stoicheiometry $RuCl_2(MeCN)_2(PPh_3)_2$ but this does not appear to be any of the previously reported[6] isomers. It appears to be the isomer (I) on the basis of the i.r. spectrum which has bands at 2 278 and 2 257 cm^{-1} [ν(C≡N)] and 308 and 259 cm^{-1} [ν(Ru–Cl)] and of the ^{31}P n.m.r. spectrum which has a singlet at 8.0 p.p.m.‡ indicating *trans*-phosphines. The compound can be recrystallised unchanged from MeCN or Et_2O but gives orange $[RuCl_2(MeCN)(PPh_3)_2]_2$ on recrystallisation from



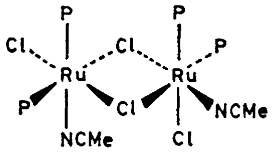
(I)



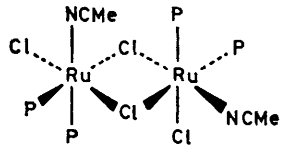
(IIa)



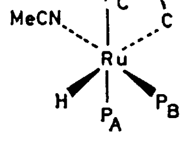
(IIb)



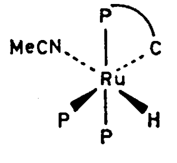
(IIc)



(IId)



(IIIa)



(IIIb)

---

† No reprints available.

‡ ^{31}P chemical shifts are to high frequency of external 85% H_3PO_4.

TABLE 1

Infrared data (cm^{-1}) for ruthenium complexes

Complex	Stereochemistry	ν(Ru–H)	ν(C≡N)	*ortho*-Disubstituted phenyl ring absorption
$RuCl_2(MeCN)_2(PPh_3)_2$	(I)	308,[a] 259[a]	2 278, 2 257	
$[RuCl_2(MeCN)(PPh_3)_2]_2$	(II)	308,[a] 280[a]	2 266	
$RuH(C_6H_4PPh_2)(MeCN)(PPh_3)_2$	(IIIa)	1 910	2 250	1 552, 1 416
$RuH(C_6H_4PPh_2)(MeCN)(PPh_3)_2$	(IIIc)	1 960	2 250	1 552, 1 412
$RuH(C_6H_4PPh_2)(py)(PPh_3)_2$	(VI)	2 013		1 549, 1 410
$RuH(C_6H_4PPh_2)(bipy)(PPh_3)$	(IV)	1 900		1 549, 1 410
$Ru(C_6H_4PPh_2)_2(MeCN)(PPh_3)$	(VII)	1 930, 1 910[b]	2 240	1 550, 1 410

[a] ν(Ru–Cl). [b] See text.

TABLE 2

^1H N.m.r. data for hydrido resonances of ruthenium complexes

Compound	Stereochemistry	Solvent	δ	J_{HPA}[a]	J_{HPB}[a]	J_{HPC}[a]
$RuH(C_6H_4PPh_2)(MeCN)(PPh_3)_2$	(IIIa)	thf–MeCN	−11.8	25	15	23
$RuH(C_6H_4PPh_2)(py)(PPh_3)_2$	(VI)	thf–py	−10.2	28	28	79
$RuH(C_6H_4PPh_2)(py)(PPh_3)_2$	(IIIa)	thf–py	−14.0	25	15	23
$RuH(C_6H_4PPh_2)(bipy)(PPh_3)$	(IV)	C_6D_6	−10.0	20	28	
$RuH_2(py)(PPh_3)_3$[b] H_1	*cis*	py	−9.3	36	36	72
H_2			−17.7	26	26	20
$RuH(C_6H_4PPh_2)(MeCN)(PPh_3)_2$	(VI)	thf–MeCN[c]		16	90	16
$RuH(C_6H_4PPh_2)(MeCN)_2(PPh_3)$	(IV)	thf–MeCN[c]		20	27	

[a] For assignments see diagrams. [b] H_1 *trans* to P_C $J_{HH} = 3$ Hz. [c] At −35 °C from partially decoupled ^{31}P n.m.r. spectra.

TABLE 3

^{31}P N.m.r. data for ruthenium complexes at 28 °C with internal C_6D_6 lock

			Chemical shifts[a]			Coupling constant[a]		
Compound	Stereochemistry	Solvent	P_A	P_B	P_C	P_AP_B	P_BP_C	P_AP_C
$RuCl_2(MeCN)_2(PPh_3)_2$	(I)	MeCN	28.0					
$\{RuCl_2(MeCN)(PPh_3)_2\}_2$	(II)	C_6H_6	52.0	47.4	47.5[b]	38	27[c]	
$RuH(C_6H_4PPh_2)(MeCN)(PPh_3)_2$	(IIIa)	thf–MeCN	63.2	48.1	−35.9	16	25.5	270
$RuH(C_6H_4PPh_2)(MeCN)(PPh_3)_2$	(IIIc)	thf–MeCN[d]	43.7	32.9	−16.7	16.5	16.5	16.5
$RuH(C_6H_4PPh_2)(py)(PPh_3)_2$	(VI)	thf–py	55.1	55.1	−28.3		13	13
$RuH(C_6H_4PPh_2)(py)(PPh_3)_2$	(IIIa)	thf–py	63.5	45.7	−36.2	15.5	26	269
$RuH(C_6H_4PPh_2)(bipy)(PPh_3)$	(IV)	C_6H_6	48.1	−13.5		22.0		
$RuH(C_6H_4PPh_2)(MeCN)_2(PPh_3)$	(IV)	thf–MeCN[d]	50.4	−11.4		19.8		
$Ru(C_6H_4PPh_2)_2(MeCN)(PPh_3)$	(VII)	C_6H_6	37.7	−24.2	−30.0	18.5	17.5	18.5
$Ru(C_6H_4PPh_2)_2(py)(PPh_3)$	(VII)	C_7H_8	36.3	−19.2	−30.8	15.0	16.0	16.0
$Ru(MeCN)(PPh_3)_3$		thf–MeCN[d]	51.5	51.5	51.5			
$Ru(MeCN)_3(PPh_3)_2$	(V)	thf–MeCN[d]	59.5	38.6		56.3		
$RuH_2(py)(PPh_3)_3$		py	60.2	60.2	50.1		13.5	13.5

[a] For assignments see diagrams. [b] $\delta_{PD} = 45$. [c] J_{PCPD}. [d] −35 °C.

TABLE 4

Analytical data for ruthenium complexes

			Found (%)				Required (%)			
Compound	Colour	Decomp. Temp. (°C)	C	H	N	P	C	H	N	P
$RuCl_2(MeCN)_2(PPh_3)_2$	Yellow	160	61.9	5.1	3.4	7.2	61.6	4.6	3.6	8.0
$\{RuCl_2(MeCN)(PPh_3)_2\}_2$[a]	Orange	160—170	62.4	4.4	1.0		61.8	4.4	1.9	
$RuH(C_6H_4PPh_2)(MeCN)(PPh_3)_2$	Yellow	124—130	71.9	5.2	1.5	10.4	72.4	5.2	1.5	10.1
$RuH(C_6H_4PPh_2)(py)(PPh_3)_2$	Yellow	80—120	72.3	5.2	1.1	9.1	73.3	5.2	1.4	9.6
$RuH(C_6H_4PPh_2)(bipy)(PPh_3)$	Purple	155—157[b]	70.0	5.0	4.0	7.9	70.7	4.9	3.6	7.9
$Ru(C_6H_4PPh_2)_2(MeCN)(PPh_3)$	Yellow	90—94	72.0	5.2	2.0	9.7	72.5	5.0	1.5	10.0

[a] Cl: Found, 9.7; requires 9.6. [b] Melts without decomposition.

benzene or toluene. The ^{31}P n.m.r. spectrum of the latter complex (Table 3) unequivocally shows it to be one of the dimers (IIa—d) in which all four phosphorus atoms are non-equivalent.

With sodium or magnesium amalgam, reduction of $RuCl_2(PPh_3)_4$ proceeds smoothly, but since the major product is insoluble in MeCN it is more convenient to carry out the reaction in thf containing MeCN. Thus, stirring $RuCl_2(PPh_3)_{3\text{ or }4}$ in thf containing *ca.* 10% MeCN affords a red solution which pales to orange-yellow over a period of hours. From the final solution may be isolated a yellow crystalline complex which, from analytical and spectroscopic data, is the *ortho*-metallated species $RuH(C_6H_4PPh_2)(MeCN)(PPh_3)_2$. Thus a strong i.r. band at 1 910 cm^{-1} can be assigned as ν(Ru-H) while bands at 1 552 and 1 416 cm^{-1} confirm (see ref. 1) the presence of the *ortho*-metallated phenyl ring on phosphorus; ν(CN) is at 2 250 cm^{-1}. Peaks in the i.r. spectrum at 2 250, 1 910, and 720 cm^{-1} correlate very closely with those reported[5] for ' $Ru(PPh_3)_4$-

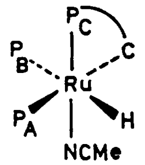
(π-MeCN)·MeCN ', which was obtained by electrochemical reduction of $RuCl_2(PPh_3)_4$ in MeCN. This coincidence of the quoted i.r. peaks, together with the melting points of our complex [124—130° (decomp.); reported for $Ru(PPh_3)_4(\pi$-MeCN)·MeCN: 124—131 °C], their similar solubilities and reactions with propene (see later) suggest that these complexes are identical and that ' $Ru(PPh_3)_4(\pi$-MeCN)·MeCN ' should be reformulated as $RuH(C_6H_4PPh_2)(MeCN)(PPh_3)_2$. The analytical figures for these two formulations differ only slightly and the reported reactions of ' $Ru(PPh_3)_4(\pi$-MeCN)·MeCN ' can easily be accommodated by $RuH(C_6H_4PPh_2)(MeCN)(PPh_3)_2$. Thus, this kind of complex reacts with phenol [2] without loss of H_2 to give $RuH(\eta^6\text{-OPh})(PPh_3)_2\cdot n$PhOH and with chlorinated solvents to give $RuCl_2(PPh_3)_3$ with transfer of hydride to phenyl carbon. Finally, ν(Ru–H) is strong and since this always appears to be the case when MeCN is present in the molecule we assume that it arises from coupling of ν(Ru–H) with the nearby ν(C≡N).

Although the complex is only sparingly soluble in aromatic solvents and tends to decompose on warming (see below) it is sufficiently soluble and stable in tetrahydrofuran (thf) containing MeCN for n.m.r. study. The hydride resonance is a doublet of doublets of doublets at δ −11.8 * suggesting that H is *cis* to all three phosphorus atoms, whilst the ^{31}P n.m.r. spectrum shows that the phosphines are meridionally arranged with the phosphorus atom of the metallated phosphine *trans* to one of the other phosphines as in (IIIa, b),† with (IIIa) which has H *cis* to MeCN being preferred [*cf.* $RuH(C_6H_4PPh_2)(PPh_3)_2(C_2H_4)$, isomer (II) [2]].

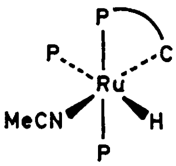
During the reduction of $RuCl_2(PPh_3)_3$, in the presence of acetonitrile, the solution acquires an orange-red colour. This pales to yellow if stirring is stopped and on re-starting the stirrer the red colour re-appears. The decay of the red colour at room temperature has a half-life of *ca.* 1 min but at lower temperatures it can be substantially retarded.

Attempts to isolate the transient red species from the orange-red solution have been unsuccessful, the only isolable product being $RuCl_2(MeCN)_2(PPh_3)_2$ (I) (see above). By carrying out the reaction in an e.p.r. tube, however, and freezing the solution as soon as it is red, a spectrum is obtained which shows, apart from a peak from an unidentified organic radical-anion, two sharp lines of equal intensity which are best interpreted as the two central peaks from an axially symmetric complex with $S = 1$. The outer lines are not visible, suggesting marked anisotropy in the molecule. These peaks are only present when the solution is orange and disappear if the solution is warmed to room temperature, allowed to turn yellow, and re-frozen. They can be regenerated by shaking the solution again with Na–Hg and regenerating the orange colour. (The peak from the organic free radical is present at all times.)

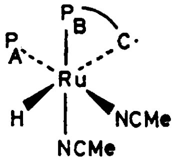
We have unfortunately not been able to isolate this paramagnetic species but, by carrying out the reaction at low temperature under various different conditions, we are able to conclude that it is $Ru(MeCN)_2(PPh_3)_2$.



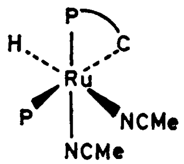
(IIIc)



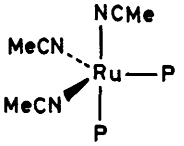
(IIId)



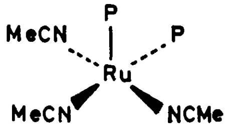
(IVa)



(IVb)



(Va)



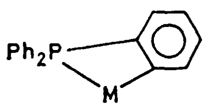
(Vb)

Thus, reaction of $RuCl_2(PPh_3)_3$ with Na–Hg in thf containing 10% acetonitrile at −35 °C leads smoothly to a blood-red solution from which a red diamagnetic solid may be isolated. This solid is unstable in the solid state slowly becoming yellow even at −30 °C. However, a ^{31}P n.m.r. spectrum of the reaction solution shows almost entirely a single peak which does not split when coupling to hydride is introduced. Only traces of free PPh_3 are present so that the compound must contain three equivalent PPh_3 groups [small amounts <10% of two isomers of $RuH(C_6H_4PPh_2)(MeCN)(PPh_3)_2$ are also present]. This and the red colour strongly suggest that the compound is tetrahedral $Ru(MeCN)(PPh_3)_3$. The rapid solid-state decomposition is consistent with this formulation and the i.r. spectrum of the yellow solid so obtained indicates that this is $RuH(C_6H_4PPh_2)(MeCN)(PPh_3)_2$ (IIIa) (see above) together with a species having ν(Ru–H) at 1 960 cm^{-1}. The latter species disappears if either the solid is washed with diethyl ether at room temperature, or is dissolved in thf–MeCN and the solution evaporated to dryness. The ^{1}H n.m.r. spectrum in thf–MeCN, only shows the hydride resonance of $RuH(C_6H_4PPh_2)(MeCN)(PPh_3)_2$. This strongly suggests that the compound with ν(Ru–H) at 1 960 cm^{-1} is another isomer of $RuH(C_6H_4PPh_2)(MeCN)(PPh_3)_2$ but

---

* Solutions in C_6D_6 give a similar resonance together with those of decomposition products (see below).

† In all diagrams and the Scheme, $\overset{\frown}{P\;C}$ represents the *ortho*-metallated phosphine.



and P = PPh_3.

that this isomerises to the isomer with structure (IIIa) very readily. Since the isomer with ν(Ru–H) at 1 960 cm^{-1} is formed in the solid state from Ru(MeCN)(PPh$_3$)$_3$, it is probable that the hydride is *cis* to the co-ordinated C atom of the metallated phenyl ring as in (IIIb, c, d).

As mentioned above, the low-temperature ^{31}P n.m.r. spectrum of the red solution formed from low temperature reduction of RuCl$_2$(PPh$_3$)$_3$ in the presence of acetonitrile shows resonances ascribable to two isomers of RuH(C$_6$H$_4$PPh$_2$)(MeCN)(PPh$_3$)$_2$. One of these is (IIIa) and the other is evidently (IIIc) [*cf.* RuH(C$_6$H$_4$PPh$_2$)(PPh$_3$)$_2$(L), L = Et$_2$O or thf [1]]. We thus suggest that these are the two compounds formed in the solid state decomposition of Ru(MeCN)(PPh$_3$)$_3$.

The e.p.r. spectrum of isolated Ru(MeCN)(PPh$_3$)$_3$ redissolved in thf containing MeCN does show a very weak spectrum for the compound with $S = 1$; this probably arises from equilibrium (2).

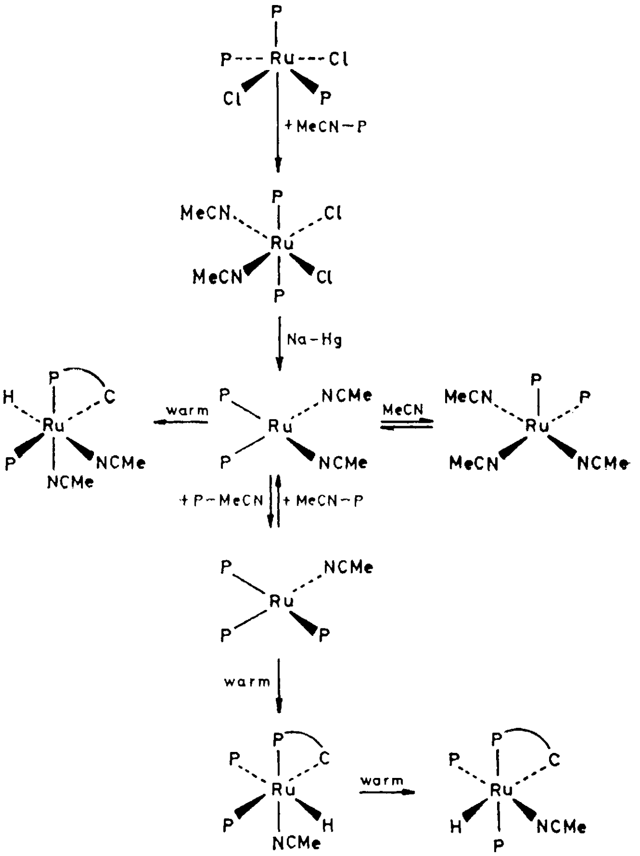
$$\mathrm{Ru(MeCN)(PPh_3)_3 + MeCN \rightleftharpoons Ru(MeCN)_2(PPh_3)_2 + PPh_3} \quad (2)$$

Evidently, if the $S = 1$ system is Ru(MeCN)$_2$(PPh$_3$)$_2$, it is substitutionally labile, even at low temperatures. Accordingly we have attempted to reduce RuCl$_2$(MeCN)$_2$(PPh$_3$)$_2$ at low temperatures. In thf that does not contain added acetonitrile, a red solution is obtained which, according to the ^{31}P n.m.r. spectrum, contains a plethora of complexes. E.p.r. studies do not show the presence of the $S = 1$ species although a very weak resonance, which shifts when the solution is warmed and re-frozen, suggests the possibility of a very small amount of a ruthenium(I) species which metallates to give a ruthenium(III) species. The species, however, are present in such small amounts as to be close to the limit of detection under our conditions. We have not further investigated this reaction.

In the presence of added acetonitrile, however, RuCl$_2$(MeCN)$_2$(PPh$_3$)$_2$ is reduced at −35 °C to give a diamagnetic yellow solution. ^{31}P N.m.r. studies on this solution show that two main products are formed. Both contain two *cis* non-equivalent phosphorus atoms. For one of them, chemical shifts and partial decoupling studies show that the compound has a hydride and an *ortho*-metallated phosphine ligand, with the two phosphorus atoms and the hydride being mutually *cis* as in (IVa) or (IVb). The other compound does not contain a hydride or an *ortho*-metallated phosphorus atom and is thus a complex of Ru^0. It could be Ru(MeCN)$_2$(PPh$_3$)$_2$, with a highly distorted tetrahedral geometry [as for Ru(styrene)$_2$(PPh$_3$)$_2$],[3,4] but since the solution is yellow, it is more likely to be Ru(MeCN)$_3$(PPh$_3$)$_2$ and to have stereochemistry (Va) or (Vb). The comparatively large value of J_{PP} leads us to prefer (Va). Treatment of this yellow reaction solution with PPh$_3$ at low temperature immediately gives the blood-red colour of Ru(MeCN)(PPh$_3$)$_3$ and this is discharged to yellow on warming.

The mechanism of reduction of RuCl$_2$(PPh$_3$)$_3$ is summarised in the Scheme.

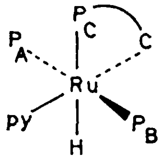
It remains necessary only to account for the different multiplicities of the ground states of Ru(MeCN)(PPh$_3$)$_3$ and Ru(MeCN)$_2$(PPh$_3$)$_2$. The former has C_{3v} point symmetry, the d_{z^2} orbital is probably high in energy and the eight metal electrons may be readily accommodated in the four remaining d orbitals making the complex diamagnetic. Ru(MeCN)$_2$(PPh$_3$)$_2$, on the other hand, has C_{2v} point symmetry and the orbitals should be split in a similar way to those in a tetrahedral complex although small non-degeneracies of the t_2 levels may be present. Thus, it is quite likely that the compound would have two unpaired electrons and a triplet ground state, as is observed for many d^8 tetrahedral complexes of Ni^{II} and Co^{I}.



SCHEME Mechanism of reduction of RuCl$_2$(PPh$_3$)$_3$ by sodium or magnesium amalgam in tetrahydrofuran containing acetonitrile

Pyridine. The reduction of RuCl$_2$(PPh$_3$)$_4$ with sodium or magnesium amalgam in tetrahydrofuran containing pyridine affords an orange solution from which RuH(C$_6$H$_4$PPh$_2$)(C$_5$H$_5$N)(PPh$_3$)$_2$ can be isolated with difficulty. I.r. evidence is consistent with this formulation but ^{1}H and ^{31}P n.m.r. spectra of the reaction solutions indicate that two species are present. The minor product (A) has n.m.r. parameters very similar to those of RuH(C$_6$H$_4$PPh$_2$)(MeCN)(PPh$_3$)$_2$ (IIIa) whilst the hydride of the major product (B) resonates as a doublet of triplets suggesting the structure (VI) analogous to the thermodynamically less stable isomer (I) of RuH-

$(C_6H_4PPh_2)(C_2H_4)(PPh_3)_2$.[2] The ^{31}P n.m.r. spectrum is in full agreement with this formulation. The product isolated from this reaction mixture is mainly (B) but n.m.r. data suggest that it is usually contaminated with up to 10% of (A). These compounds do not appear to interconvert in solution in thf–pyridine and both decompose on warming.



(VI)

2,2′-Bipyridyl. Reduction of $RuCl_2(PPh_3)_4$ with Na–Hg in thf containing 2,2′-bipyridyl (bipy) produces a dark red-purple solution from which $RuH(C_6H_4PPh_2)$(bipy)(PPh_3) may be isolated in high yield. N.m.r. studies on the reaction show that *ca.* 20% of RuH_2(bipy)$(PPh_3)_2$[7] is also produced. N.m.r. spectra of $RuH(C_6H_4PPh_2)$(bipy)(PPh_3) show that the hydride and the two phosphorus atoms are facially orientated [*cf.* (IVa)]. Unlike $RuH(C_6H_4PPh_2)(PPh_3)_2L$ (L = MeCN or py) the complex is stable in benzene.

Styrene. Reduction of $RuCl_2(PPh_3)_3$ with Na–Hg in styrene gives a purple solution from which the previously reported[3,4] Ru^0 complex, $Ru(PPh_3)_2(C_8H_8)_2$, may be isolated in high yield.

Reduction of $RuCl_2(PPh_3)_3$ *in Tetrahydrofuran or Benzene.*—Prolonged interaction of $RuCl_2(PPh_3)_{3\ \mathrm{or}\ 4}$ with Na–Hg or Mg–Hg in tetrahydrofuran at room temperature leads to a red solution from which $RuH_2(PPh_3)_3$(thf)[8] may be isolated in high yield. The source of the hydrido-ligands is presumably the solvent, although the product from the same reaction carried out in C_4D_8O again shows two Ru–H stretching frequencies. This may be because the deuterium abstracted from the solvent takes part in a ready exchange of hydride with *ortho*-hydrogen atoms on the PPh_3 ligand. If the solvent is the source of hydride we feel that it is unlikely that oxidative addition of a C–H bond of thf to an Ru^0 species followed by β-hydride transfer to give the hydride and dihydrofuran occurs. Such a mechanism has been suggested[9] for the formation of PtH_2(diphos) (diphos = $Ph_2PCH_2CH_2PPh_2$) from reduction of $PtCl_2$(diphos) with Na–Hg in thf, but in our system short reaction times lead to $RuHCl(PPh_3)_3$ only, suggesting that the removal of halide ion is step-wise. We feel that the most likely mechanism is similar to that in which $Ph_2P(CH_2)_4OH$ is formed[10] from reactions of Ph_2PCl with Mg in thf.

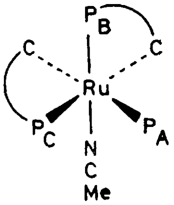
Similarly, mixtures of $RuHCl(PPh_3)_3$ and $RuH_2(PPh_3)_4$ are obtained from reduction of $RuCl_2(PPh_3)_3$ with Na–Hg in benzene.

Magnesium metal does not reduce $RuCl_2(PPh_3)_{3\ \mathrm{or}\ 4}$ in thf.

Reactions of $RuH(C_6H_4PPh_2)(PPh_3)_2L$ (L = MeCN *or* py).—*With propene.* As reported[11] for the 'π-acetonitrile complex', $RuH(C_6H_4PPh_2)(MeCN)(PPh_3)_2$ reacts with propene to give $RuH(C_3H_5)(MeCN)(PPh_3)_2$ in high yield, although we find that in thf–MeCN the reaction proceeds smoothly at 50 °C and one atmosphere. As reported, the complex is not very soluble in cold common organic solvents but it dissolves in hot C_7D_8 sufficiently for detailed ^1H n.m.r. studies. Thus, we have been able to confirm that the hydride is *cis* to both phosphines and that the allyl group is symmetrically co-ordinated. Somewhat surprisingly, the spectrum remains unchanged to +80 °C, so that exchange of hydride with allyl protons as has been demonstrated in other cases by Osborn[12] and Bönnemann,[13] or of allyl protons with *ortho*-protons of the phosphine phenyl rings, which has been suggested[2] by us, does not occur here on the n.m.r. time-scale. At higher temperatures substantial decomposition of the complex occurs.

With water. Although $RuH(C_6H_4PPh_2)(MeCN)(PPh_3)_2$ can be recrystallised unchanged from thf containing MeCN and H_2O, in the absence of MeCN the hydridohydroxy-complex $RuH(OH)(PPh_3)_2$(thf)[8] is formed essentially quantitatively.

Thermal decomposition. $RuH(C_6H_4PPh_2)(PPh_3)_2L$ (L = MeCN or py) are both only sparingly soluble in aromatic solvents but dissolve with decomposition on warming. ^{31}P N.m.r. studies suggest that for L = MeCN, $RuH_2(MeCN)(PPh_3)_3$ and another product which contains no hydride but three phosphines are formed. The phosphorus atoms are all mutually *cis* and non-equivalent and their chemical shifts[2] suggest that two are metallated and one is not. We thus suggest that this compound, which we have isolated by fractional crystallisation in low yield, is the bis *ortho*-metallated complex $Ru(C_6H_4PPh_2)_2(MeCN)(PPh_3)$ with structure (VII). ^{31}P and ^1H n.m.r. studies clearly show that no Ru–H is present yet there are two bands in the i.r. spectrum at 1 930 and 1 910 cm^{-1}. It is not clear to what these can be ascribed; if they are Ru–H stretches it is possible that in the solid state (not in solution) an Ru–H bond is formed by *ortho*-metallation of the third phosphine to give a Ru^{IV} species. Presumably the two products are formed by intermolecular transfer of two hydrogen atoms. Similarly ^{31}P n.m.r. studies suggest the formation of $Ru(C_6H_4PPh_2)_2(py)(PPh_3)$ and $RuH_2(PPh_3)_4$ on thermal decomposition of $RuH(C_6H_4PPh_2)(py)(PPh_3)_2$, although we have not isolated the products. Attempts to prepare $RuH_2(py)(PPh_3)_3$ by recrystallisation of $RuH_2(PPh_3)_4$ from pyridine, have failed. Although $RuH_2(py)(PPh_3)_3$ is apparently the only ruthenium complex in solution (n.m.r. evidence), $RuH_2(PPh_3)_4$ crystallises unchanged.



(VII)

EXPERIMENTAL

Analyses are by Butterworth Microanalytical Consultancy Limited and Imperial College laboratories. I.r. spectra were recorded in Nujol mulls between caesium iodide plates on Perkin-Elmer PE 457 and 597 spectrometers. ^1H N.m.r. spectra were recorded on Perkin-Elmer R12 (60 MHz) and R32 (90 MHz) spectrometers and ^{31}P n.m.r. spectra on a Varian Associates XL-100-12 operating in the Fourier transform mode with noise proton decoupling. Melting points were recorded on an Electrothermal melting-point apparatus and are uncorrected. All solvents were carefully dried over sodium benzophenone ketyl (diethyl ether, tetrahydrofuran, benzene, petroleum, b.p. 40—60 °C), calcium hydride (acetonitrile) or molecular sieves (pyridine) and degassed before use. $RuCl_2(PPh_3)_3$ [14] and amalgams were prepared by standard procedures.

cis,cis,trans-*Bisacetonitriledichlorobis(triphenylphosphine)ruthenium*(II).—$RuCl_2(PPh_3)_3$ (2.0 g) was stirred in thf (100 ml) containing acetonitrile (10 ml) at room temperature. The yellow precipitate was collected, washed with thf (2 × 20 ml) and diethyl ether (20 ml), and dried *in vacuo*; yield 92%.

Recrystallisation from benzene gave: *di-μ-chloro-bis-[(acetonitrile)chlorobis(triphenylphosphine)ruthenium*(II)] which reverted to *cis,cis,trans*-$RuCl_2(MeCN)_2(PPh_3)_2$ on recrystallisation from acetonitrile–diethyl ether.

Acetonitrile(P,2-*η-diphenylphosphinophenyl*)*hydridobis(triphenylphosphine)ruthenium*(II).—(*a*) $RuCl_2(PPh_3)_3$ (2 g) was stirred with Na–Hg (0.5%, 2 ml) in thf (100 ml) containing MeCN (10 ml) for 16 h. The resulting orange-yellow suspension was separated from the amalgam, centrifuged, decanted, and evaporated to *ca.* 10 ml. On addition of acetonitrile (10 ml), the complex separated as yellow needles on standing. These were collected, washed with MeCN–thf (1 : 1) (2 × 5 ml), and dried *in vacuo*; yield *ca.* 70%.

(*b*) The reaction was conducted as above but using Mg–Hg (1%; 5 ml). The product co-crystallised with some $MgCl_2$ but this being a lighter precipitate could mostly be removed by swirling and decanting; yield *ca.* 70%.

(*c*) The same product was obtained if the above reactions were carried out using $RuCl_2(PPh_3)_4$.

(P,2-*η-Diphenylphosphinophenyl*)*hydridopyridinebis(triphenylphosphine)ruthenium*(II).—This compound was prepared similarly using pyridine in place of acetonitrile, except that after centrifugation the deep orange solution was evaporated to *ca.* 5 ml and allowed to crystallise (the crystallisation took several days). The crystals were collected, washed quickly with pyridine (2 ml), and dried *in vacuo*; yield *ca.* 50%.

Acetonitriletris(triphenylphosphine)ruthenium(0).— $RuCl_2(PPh_3)_3$ (2 g) was dissolved in thf (100 ml) containing acetonitrile (10 ml) and the resulting orange solution cooled to −70 °C. Na–Hg (2 ml; 0.5%) was added and the temperature raised to −35 °C, whereupon the amalgam melted. The solution was stirred at −35 °C for 1 h and allowed to settle at −70 °C. The resulting red solution was filtered at −70 °C, evaporated to 10 ml at −40 °C and treated with MeCN (10 ml) at −40° C. The temperature at this stage was fairly critical since at a lower temperature the MeCN froze and at a higher one the complex dissolved. The red microcrystalline solid was collected, washed with MeCN (5 ml), and dried *in vacuo*. The complex slowly became yellow with time even at low temperatures and this process seemed to be accelerated if it was washed with pre-cooled diethyl ether and dried.

Reaction of $RuCl_2(MeCN)_2(PPh_3)_2$ *with* Na–Hg *in the Presence of* MeCN *at Low Temperature*.—The reaction was carried out as in the preceding experiment but using a suspension of $RuCl_2(MeCN)_2(PPh_3)_2$ (I) (1.36 g). The yellow solution was evaporated at low temperature and used for ^{31}P n.m.r. studies. A substantial amount of insoluble *cis,cis,cis*-$RuCl_2(MeCN)_2(PPh_3)_2$ was also formed (i.r. evidence).

Reaction of $RuCl_2(MeCN)_2(PPh_3)_2$ *with* Na–Hg *in thf*.—This reaction was carried out as above but without the addition of MeCN. The red solution was evaporated at low temperature and used for ^{31}P n.m.r. studies.

2,2′-*Bipyridyl*(P,2-*η-diphenylphosphinophenyl*)*hydrido(triphenylphosphine)ruthenium*(II).—$RuCl_2(PPh_3)_3$ (2 g) and 2,2′-bipyridyl (0.8 g) were stirred in thf (50 ml). The immediately produced purple solution precipitated an orange solid which redissolved overnight to give a red-purple solution. This was centrifuged, decanted, and evaporated to 7 ml. Diethyl ether (20 ml) was added to the mixture and after a few minutes the complex separated as dark red crystals which were collected, washed with diethyl ether–thf (2 : 1; 2 × 5 ml), and dried *in vacuo*; yield *ca.* 70%. The green-purple dichroic supernatant liquid was shown to contain $RuH_2(bipy)(PPh_3)_2$ by its ^1H n.m.r. spectrum.

Acetonitrilebis(P,2-*η-diphenylphosphinophenyl*)(*triphenylphosphine*)*ruthenium*(II).— $RuH(C_6H_4PPh_2)(MeCN)(PPh_3)_2$ was warmed in benzene (3 ml) to 70 °C with stirring for 3 h. The resulting orange-red solution was treated with MeCN (10 ml) and cooled to −20 °C to give a pale yellow precipitate of $RuH_2(MeCN)(PPh_3)_3$ (i.r. evidence). The orange supernatant was removed and after evaporation to 2 ml and treatment with MeCN (5 ml), cooled to −20 °C to give an orange-brown tar. When set aside at room temperature, the tar redissolved and a pale yellow solid $RuH_2(MeCN)(PPh_3)_3$ separated. The mother liquors were treated with MeCN (4 ml), cooled to −20 °C for 2 h, and allowed to crystallise at room temperature for several days. The yellow crystals of the complex were collected and dried *in vacuo*; yield *ca.* 10%. Attempts to separate the products by chromatography on alumina merely resulted in extensive decomposition. The ^{31}P N.m.r. spectra of a pre-heated solution of $RuH(C_6H_4PPh_2)(py)(PPh_3)_2$ suggested that a similar reaction had occurred (see text).

Reduction of $RuCl_2(PPh_3)_4$ *with* Mg–Hg *in thf*.—$RuCl_2(PPh_3)_3$ (0.5 g) and PPh_3 (0.135 g) were stirred with Mg–Hg (0.5%, 2 ml) in thf (50 ml) for 16 h. After settling, the resulting red solution was filtered, evaporated to 7 ml, treated with diethyl ether (10 ml), filtered, and cooled to −20 °C to give yellow crystals of $RuH_2(PPh_3)_3(thf)$ (i.r. evidence). At room temperature more $RuH_2(PPh_3)_3(thf)$ crystallised from the mother liquors together with some purple crystals of $RuHCl(PPh_3)_3$ (i.r. evidence).

$RuCl_2(PPh_3)_3$ (0.1 g) and PPh_3 (0.03 g) were stirred in thf (5 ml) with Mg–Hg (0.25%, 2 ml) for 0.5 h. The resulting purple solution was filtered, evaporated to 1 ml, and treated with petroleum (5 ml) to give a copious purple precipitate identified as a mixture of $RuHCl(PPh_3)_3$ and $MgCl_2$.

Reduction of $RuCl_2(PPh_3)_3$ *with* Na–Hg *in Benzene*.—$RuCl_2(PPh_3)_3$ (0.62 g) was stirred with Na–Hg (0.5%, 2 ml) in benzene (40 ml) for 16 h. The red solution was filtered, evaporated to 5 ml, and treated with petroleum (4 ml).

With time, purple crystals of $RuHCl(PPh_3)_3$ were deposited in high yield together with a small amount of yellow $RuH_2(PPh_3)_4$ (i.r. and ^1H n.m.r. evidence).

Reaction of $RuH(C_6H_4PPh_2)(MeCN)(PPh_3)_2$ *with Propene.*—Propene was passed through a solution of $RuH(C_6H_4PPh_2)(MeCN)(PPh_3)_2$ in thf (15 ml) for 1 h at 50 °C. On cooling, $RuH(C_3H_5)(MeCN)(PPh_3)_2$ separated as yellow crystals which were collected and dried *in vacuo*. Further crops were obtained on cooling the mother liquors to -20 °C; total yield *ca.* 75%.

Reaction of $RuH(C_6H_4PPh_2)(MeCN)(PPh_3)_2$ *with* H_2O.—$RuH(C_6H_4PPh_2)(MeCN)(PPh_3)_2$ (0.2 g) was stirred in thf (30 ml) containing H_2O (0.5 ml) for 0.5 h. The resulting orange solution was evaporated to 2 ml and treated with diethyl ether (4 ml). The red crystals that formed were collected, washed with diethyl ether (4 ml), dried *in vacuo*, and identified as $RuH(OH)(PPh_3)_2(thf)$ from their ^1H n.m.r. spectrum.

A similar reaction in the presence of acetonitrile (3 ml) produced only unchanged $RuH(C_6H_4PPh_2)(MeCN)(PPh_3)_2$.

Reduction of $RuCl_2(PPh_3)_3$ *with* Na–Hg *in Styrene.*—$RuCl_2(PPh_3)_3$ (0.5 g) was stirred overnight with Na–Hg (2.5 ml, 1%) in styrene (6 ml). The resulting purple solution was treated with petroleum, filtered, and cooled to -20 °C. The purple crystals that separated were collected and identified as $Ru(styrene)_2(PPh_3)_2$.

We thank Dr. J. F. Gibson for e.p.r. studies, Johnson Matthey Limited for loans of ruthenium and Albright and Wilson Limited for gifts of triphenylphosphine.

[8/1606 *Received, 7th September, 1978*]

REFERENCES

[1] D. J. Cole-Hamilton and G. Wilkinson, *J.C.S. Dalton*, 1977, 797.

[2] D. J. Cole-Hamilton and G. Wilkinson, *Nouveau J. Chim.*, 1977, **1**, 141.

[3] B. N. Chaudret, D. J. Cole-Hamilton, and G. Wilkinson, *J.C.S. Dalton*, 1978, 1739.

[4] M. A. A. F. de C. T. Carrondo, B. N. Chaudret, D. J. Cole-Hamilton, A. C. Skapski, and G. Wilkinson, *J.C.S. Chem. Comm.*, 1978, 463.

[5] E. O. Sherman and P. R. Schreiner, *J.C.S. Chem. Comm.*, 1976, 3.

[6] J. D. Gilbert and G. Wilkinson, *J. Chem. Soc.* (*A*), 1969, 1749.

[7] R. Obeso Rosete, D. J. Cole-Hamilton, and G. Wilkinson, unpublished results.

[8] B. N. Chaudret, D. J. Cole-Hamilton, and G. Wilkinson, *J.C.S. Dalton*, 1977, 1546 and references therein.

[9] T. Yoshida, T. Yamagata, T. Tulip, and J. A. Ibers, *J. Amer. Chem. Soc.*, 1978, **100**, 2063.

[10] A. Y. Garner and A. A. Tedeschi, *J. Amer. Chem. Soc.*, 1964, **84**, 4734.

[11] E. O. Sherman and P. R. Schreiner, *J.C.S. Chem. Comm.*, 1978, 223.

[12] J. W. Byrne, H. V. Blaser, and J. A. Osborn, *J. Amer. Chem. Soc.*, 1975, **97**, 3871.

[13] H. Bönnemann, *Angew. Chem. Internat. Edn.*, 1970, **9**, 736.

[14] P. S. Hallman, T. A. Stephenson, and G. Wilkinson, *Inorg. Synth.*, 1970, **12**, 237.