Journal of Organometallic Chemistry, 204 (1981) 115—122
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

REACTIONS OF RUTHENIUM TRIPHENYLPHOSPHINE COMPLEXES WITH DIAZADIENES

II *. REACTIONS OF $RuH_2(PPh_3)_4$ AND $RuH_4(PPh_3)_3$

B. CHAUDRET and R. POILBLANC

Laboratoire de Chimie de Coordination du CNRS associé à l'Université P. Sabatier, 205, route de Narbonne, 31400 Toulouse (France)

(Received June 17th, 1980)

Summary

The reactions between $RuH_2(PPh_3)_4$ or $RuH_4(PPh_3)_3$ and 1,2-di(isopropylimino)ethane (DAD-A), 2,3-di(phenylimino)butane (DAD-C) and 1,2-di-(*p*-methoxyphenylimino)ethane (DAD-D) in toluene produce symmetrical *trans* dihydrido complexes. However the product obtained from DAD-C is difficult to isolate, and attempts to prepare it in alkanes led to the isolation of hexacoordinate *cis*-dihydrido and pentacoordinate *cis*-dihydrido complexes in which the diazadiene is coordinated only through one end. A scheme showing the proposed reaction sequence is presented.

Introduction

Following our study of the reactions between ruthenium triphenylphosphine complexes and diazadiene ligands [1], we have investigated the reactivity of $RuH_2(PPh_3)_4$ and $RuH_4(PPh_3)_3$ towards diazadienes. The versability in the mode of coordination of these ligands [2—4] as well as the fact that they can stabilize metals in a low oxidation state, as for example in $Fe(DAD)_2$ [5], seemed particularly interesting.

It has been shown that the reactions of $RuH_2(PPh_3)_4$ with dienes produce ruthenium(0) diene complexes such as $Ru(C_4H_6)(PPh_3)_3$ [6], whereas with neutral bidentate donor ligands only dihydro complexes are obtained [7]. For example, the reaction of $RuH_2(PPh_3)_4$ with 2,2'-bipyridyl(bipy) yielded $RuH_2(PPh_3)_2(bipy)$ [7].

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* For part I see ref. 1.

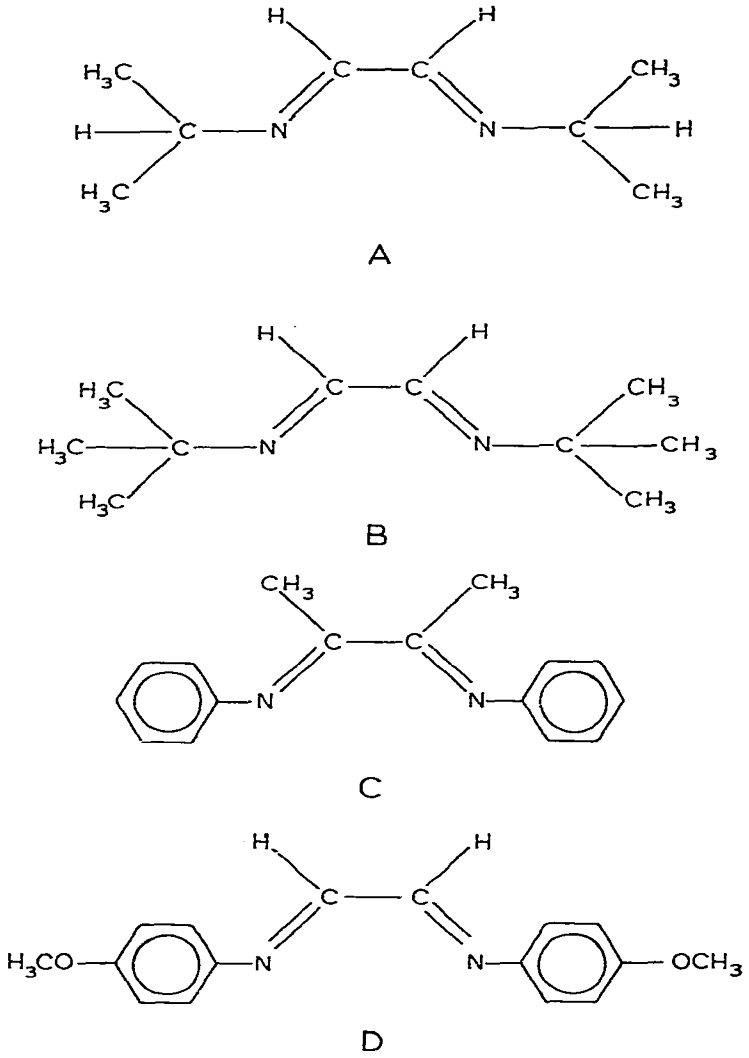

Fig. 1. Structures of the diazadienes employed.

The diazadienes we used are shown in Figure 1, and are subsequently referred to as DAD-A, DAD-B, etc.

Results and discussion

1) Reactions of $RuH_2(PPh_3)_4$ and $RuH_4(PPh_3)_3$ with DAD-D in toluene

The ruthenium hydride complexes do not react with DAD-B even after a few days in boiling toluene. However with one equivalent of DAD-D in hot toluene, a purple solution is quickly obtained from which purple crystals analysing for $RuH_2(PPh_3)_2$(DAD-D) can be isolated. The infrared spectrum of the complex

TABLE 1

SPECTROSCOPIC DATA FOR NEW RUTHENIUM COMPLEXES

Compound	Infrared ν(Ru—H) (cm^{-1})	Solvent	^1H NMR			^{31}P NMR [d] δ (ppm)
			Hydride $\tau(J(PH))$	Imino groups $\tau(J(PH))$	Others	
$RuH_2(PPh_3)_2(C_3H_7NCHCHNC_3H_7)$	1940	C_6D_6	20.5t(32)	2.12t(3)	5.5 [a], 9.14 [b]	
$RuH_2(PPh_3)_2(CH_3OC_6H_4NCHCHNC_6H_4OCH_3)$	1940	C_6D_6	19.4t(31)	2.05t(2)	6.65 [c]	65.95
$RuH_2(PPh_3)_2(CH_3OC_6H_4NCHCHNC_6H_4OCH_3)$-$(CH_3OC_6H_4NCHCHNC_6H_4OCH_3)$	1940	C_6D_6	19.4t(31)	2.05, 1.5	6.65 [c], 6.71 [c]	65.95
$RuH_2(PPh_3)_2(\eta^4$-$C_6H_5NCCH_3CCH_3NC_6H_5)$	1950—1895	C_6D_6	19.9t(27)	8.1t(3.7)		64.3
$RuH_2(PPh_3)_2(\eta^2$-$C_6H_5NCCH_3CCH_3NC_6H_5)$	1910	C_6D_6	20.4t(31.1)	8.1t(3.7), 7.9		24.3

[a] Unique proton of isopropyl groups. [b] Methyl groups of DAD-A. [c] Methyl groups of DAD-D. [d] At low field of external H_3PO_4.

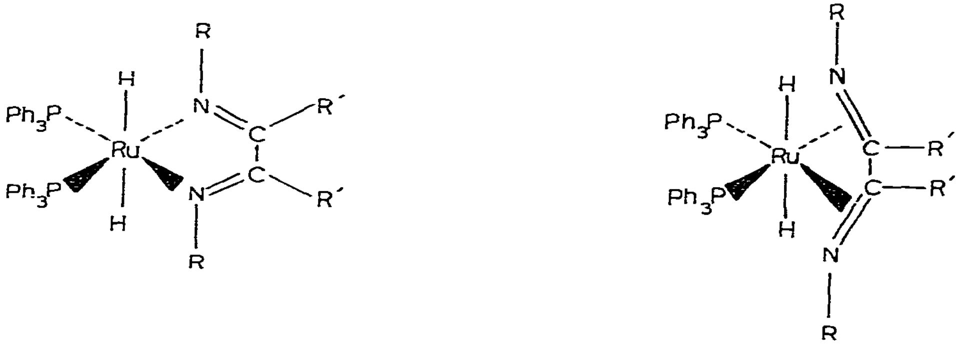

Fig. 2. Two possible structures for *trans* $RuH_2(PPh_3)_2(DAD)$.

(Table 1) shows a strong single ν(Ru—H) absorption at 1940 cm^{-1}, which suggests the presence of two *trans* hydrides as well as two other bands at 1600 and 1580 cm^{-1} due to the *para*-disubstituted rings of the diazadiene ligand.

In addition to broad peaks near τ 3 due to the phenyl protons of the ligands, the ^1H NMR spectrum shows the methoxy groups of the diazadiene at τ 6.65 as well as two triplets at τ 19.40 (J(PH) 31 Hz) and τ 2.05 (J(PH) 2 Hz). The high field resonance is attributed to two hydrides coupled with two equivalent phosphines. The low field signal, which is a real triplet as shown by spectra recorded at 60 and 90 MHz, is attributed to the coupling of the imino protons of the ligand with the phosphines.

The ^{31}P NMR spectrum of the compound shows a single line at δ 65.95 ppm, in a region associated with triphenylphosphine groups *trans* to low *trans* effect ligands [8]. This indicates that the phosphines are *cis* to one another and *trans* to the diazadiene.

These results confirm that we are dealing with a symmetrical *trans*-dihydrido complex $RuH_2(PPh_3)_2$(DAD-D).

The mode of coordination of the diazadiene ligand still has to be decided. There are two possibilities (see Figure 2, structures I and II; $R = C_6H_4OCH_3$; $R' = H$). Structure I seems to be the most acceptable, and this mode of coordination of the ligand is usual in related compounds [1,5]. Nevertheless we cannot entirely rule out the second possibility, especially since a coupling is observed between the imino protons and the phosphines.

In the presence of two equivalent of diazadienes the same reaction occurs but there is cocrystallization of one mole of free DAD per mole of complex, as indicated by ^{31}P and ^1H NMR spectroscopy as well as by elemental analysis.

2) Reactions of $RuH_2(PPh_3)_4$ and $RuH_4(PPh_3)_3$ with DAD-A and DAD-C in toluene.

$RuH_2(PPh_3)_4$ and $RuH_4(PPh_3)_3$ both react at room temperature with one or more equivalents of DAD-A or DAD-C to give red-brown and purple solutions, respectively. From these solutions only $RuH_2(PPh_3)_4$ can be recovered by crystallization because of the existence of an equilibrium. However, we were able to obtain crystals of the product analysing for $RuH_2(PPh_3)_2$(DAD-A) by the double-layer technique of crystallization *. The compound $RuH_2(PPh_3)_2$(DAD-C) was always obtained mixed with $RuH_2(PPh_3)_4$ as shown by its infrared spectra in which the ν(Ru—H) of the complex and of $RuH_2(PPh_3)_4$ are observed at 1950 and 2080 cm^{-1}.

The infrared spectrum of $RuH_2(PPh_3)_2$(DAD-A) is similar to that of $RuH_2(PPh_3)_2$(DAD-D), with a strong ν(Ru—H) band at 1940 cm^{-1}. Its ^1H NMR spectrum, like that of $RuH_2(PPh_3)_2$(DAD-D), shows a triplet at τ 20.50 (J(PH) 32 Hz) due to the hydrides and a triplet at τ 2.12 (J(PH) 3 Hz) due to the imino protons. It also shows a doublet at τ 9.14 (J(HH) 7.35 Hz) due to the methyl groups of the symmetrically bound diazadiene and a multiplet at τ 5.50 due to the unique protons of the isopropyl groups.

These results confirm that we are dealing with a compound $RuH_2(PPh_3)_2$(DAD-A), similar to $RuH_2(PPh_3)_2$(DAD-D); we favour again structure I (see Figure 2) for the complex.

3) *Reactions of $RuH_2(PPh_3)_4$ with DAD-C in alkanes*

Since it was difficult to isolate a product from the reaction between $RuH_2(PPh_3)_4$ and DAD-C in toluene, we carried out the reaction in alkanes.

When $RuH_2(PPh_3)_4$ is stirred in boiling heptane containing 2 or more equivalent of DAD-C, a violet powder analysing for $RuH_2(PPh_3)_2$(DAD-C) (VI) is obtained. If the reaction is carried out under milder conditions, viz. in refluxing hexane for 4 or 8 days different other products, the red-brown III and the red purple IV, respectively, are obtained as precipitates. When III and IV are left in solution in toluene, the colour changes finally only VI is present (see Scheme 1).

The infrared spectrum of III shows a ν(Ru—H) band at 2080 cm^{-1} (as does $RuH_2(PPh_3)_4$). It has not been possible to recrystallize it nor to study its NMR spectra, due to its ready reaction in solution.

The infrared spectrum of IV shows two strong ν(Ru—H) absorptions at 1950 and 1895 cm^{-1}. This compound can be recrystallized quickly from warm toluene, and analyses for $RuH_2(PPh_3)_2$(DAD-C), but, when left in solution, like III it is converted into other products. Thus a ^{31}P NMR spectrum of a solution IV in an aromatic solvent only shows a single peak at δ 64.30 ppm (cf. δ 65.95 for *trans* $RuH_2(PPh_3)_2$(DAD-D). Furthermore, its ^1H NMR spectrum shows a high field triplet at τ 19.90 (J(PH) 27 Hz), as well as another one at τ 8.12 (J(PH) 3 Hz) attributed to the imino methyl groups of the ligand.

These results clearly indicate that in solution a *trans* dihydride is present, which is evidence for an isomerisation in solution from a *cis* dihydride (IV) to a *trans* dihydride (V). Again from this solution only VI could be recrystallized.

The infrared spectrum of VI shows a broad band at 1910 cm^{-1} attributed to ν(Ru—H). Its ^{31}P NMR spectrum shows a single peak at δ 24.30 ppm; a region where *trans* triphenylphosphine groups are usually found.

In the ^1H NMR spectrum a triplet at τ 20.40 (J(PH) 31.1 Hz) is observed as well as a triplet at τ 8.12 (J(PH) 3.7 Hz) and a singlet at τ 7.90 (Integration of these two signals towards phenyl groups: 3/3/40). This indicates the presence

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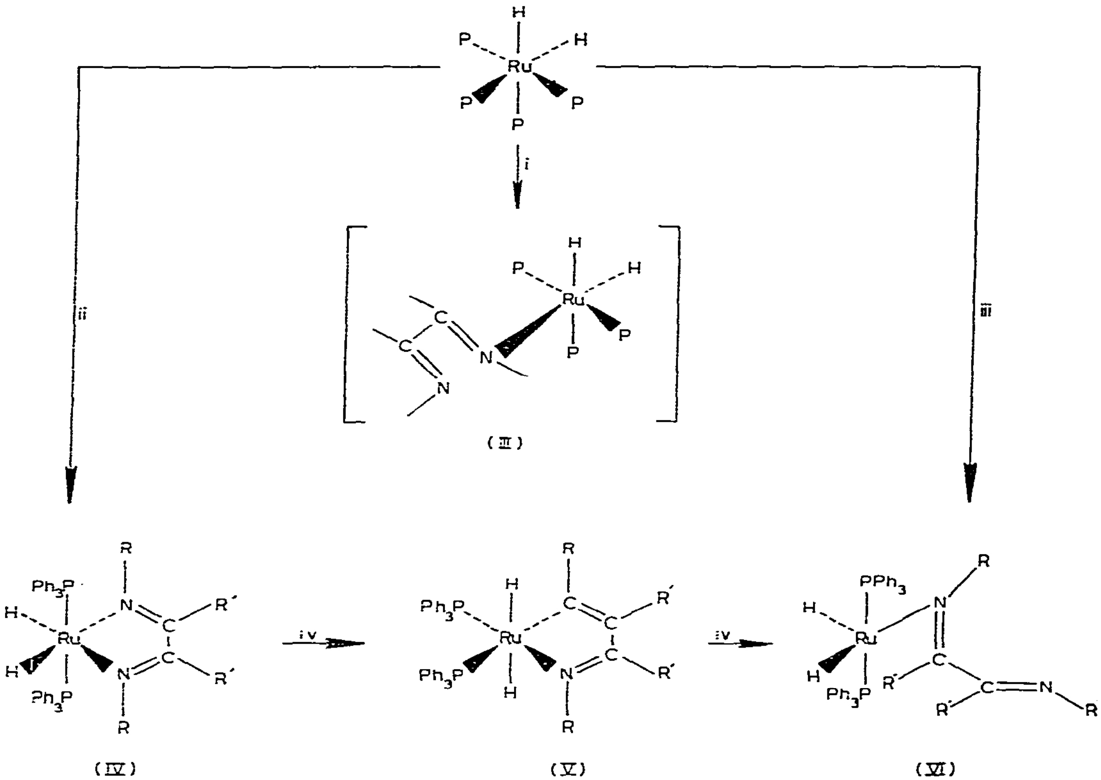
* This compound can also be obtained by disproportionation of $RuHCl(PPh_3)_2$(DAD-D) in methanol [1].



SCHEME 1
REACTIONS BETWEEN $RuH_2(PPh_3)_4$ AND DAD-C IN ALKANES
i boiling hexane, 4 days; ii boiling hexane, 8 days; iii boiling hexane, 3 days; iv in solution in toluene.

of two equivalent hydrides coupled to two equivalent phosphines and of one diazadiene unsymmetrically bound: one end is coupled to the phosphines (as in V) the other resonates at the same place as the free ligand.

We thus propose for this compound a pentacoordinate *cis* dihydride structure with a diazadiene bound only through one end.

These reactions can be summarized as follows; (see Scheme 1).

(a) Formation of a *cis* dihydride (III) possibly $RuH_2(PPh)_3$(DAD-C), by substitution of one phosphine group of PPh_3.

(b) Conversion of this to *cis* $RuH_2(PPh_3)_2$(DAD-C) (IV) with loss of another phosphine.

(c) Ready isomerization of IV in solution to the *trans* dihydride V, similar to $RuH_2(PPh_3)_2$(DAD) (DAD = DAD-A or DAD-C).

(d) Finally formation of VI, into which all the compounds are converted, by opening of one of the Ru—N bonds.

It is somewhat surprising that VI should be the final product of the above reactions but the steric effect of the imino methyl groups may favour the opening of the organometallic cycle created by bidentate coordination of the diazadiene, thus producing a five coordinate species.

TABLE 2

ANALYTICAL DATA FOR NEW RUTHENIUM COMPLEXES

Compounds	Colour	M.p. (°C)	Analysis Found(Calcd.)(%)			
			C	H	N	P
$RuH_2(PPh_3)_2(C_3H_7NCHCHNC_3H_7)$	red	181d	68.9 (68.8)	6.3 (6.3)	3.6 (3.6)	8.1 (8.1)
$RuH_2(PPh_3)_2(CH_3OC_6H_4NCHCHNC_6H_4OCH_3)$	purple	176d	69.2 (69.7)	5.4 (5.4)	3.0 (3.1)	7.1 (7.7)
$RuH_2(PPh_3)_2(CH_3OC_6H_4NCHCHNC_6H_4OCH_3)$-$(CH_3OC_6H_4NCHCHNC_6H_4OCH_3)$	purple	119	70.2 (69.9)	5.5 (5.5)	4.6 (4.8)	5.7 (5.4)
$RuH_2(PPh_3)_2(\eta^4\text{-}C_6H_5NCCH_3CCH_3NC_6H_5)$(III)	red-purple		71.0 (72.3)	5.5 (5.6)	3.8 (3.2)	6.8 (7.2)
$RuH_2(PPh_3)_2(\eta^4\text{-}C_6H_5NCCH_3CCH_3NC_6H_5)$(VI)	purple	95d	71.4 (72.3)	5.7 (5.6)	2.6 (3.2)	6.7 (7.2)

Experimental

Microanalyses were by Centre de Microanalyse du CNRS. Infrared spectra were obtained using Perkin Elmer PE 577 or PE 225 grating diffractometers, NMR spectra using Perkin Elmer R12 (60 MHz) and Bruker WH 90 (90 MHz) spectrometers, the latter in the Fourier transform mode, with proton noise decoupling when recording ^{31}P NMR spectra. Melting points were determined in air on a Leitz Weizlar heating plate.

All solvents were thoroughly degassed before use and all operations were carried out under argon using standard vacuum line techniques.

The diazadienes were prepared according to published methods by adding two equivalents of amine to glyoxal (40% in water solution) or diacetyl at 0° C. The compounds $RuH_2(PPh_3)_4$ [9] and $RuH_4(PPh_3)_3$ [10] were prepared according to published methods. Analytical data for the new complexes are given in Table 2.

1) Dihydridobis(triphenylphosphine) (1,2-di(isopropylimino)ethane) ruthenium(II)

The compound $RuH_4(PPh_3)_3$ (0.84 g; 0.94 mmol) was stirred in a solution of DAD-A (0.30 g; 2.14 mmole) in toluene (40 ml) for two days. The solution turned red-brown. Its volume was reduced to about 5 ml. The solution was filtered and 30 ml of hexane were added dropwise so that two layers were obtained. Red crystals of the complex grew at room temperature; they were collected and washed with light petroleum and dried in vacuo. Yield ca. 35%.

2) Dihydridobis(triphenylphosphine)(1,2-di(p-methoxyphenylimino)ethane) ruthenium(II)

The compound $RuH_2(PPh_3)_4$ (0.50 g, 0.43 mmol) was stirred in a solution of DAD-D (0.12 g, 0.44 mmol) in toluene (40 ml) for 24 hours during which the solution turned deep purple. After volume reduction, addition of light petroleum and cooling at —15° C, deep purple crystals of the complex were obtained.

They were collected, washed with light petroleum and dried in vacuo. Yield ca. 85%.

3) Dihydridobis(triphenylphosphine)(1,2-di(p-methoxyphenylimino)ethane) ruthenium(II)(1,2-di(p-methoxyphenylimino)ethane)

Preparation as in 2) but using 0.23 g (0.87 mmol) DAD-D and a reaction time of one hour. Yield ca. 80%.

4) Reactions between $RuH_2(PPh_3)_4$ and 2,3-di(phenylimino)butane in hexane

a) 0.50 g (0.43 mmol) $RuH_2(PPh_3)_4$ were added to a solution of 0.20 g (0.85 mmol) DAD-C in hexane (50 ml). The resulting suspension was stirred in refluxing hexane for 4 days during which it became purple brown. After decantation, the powder was collected, washed with hexane and dried in vacuo. Its IR spectrum shows a ν(Ru—H) band at 2080 cm^{-1} as well as bands of the diazadiene. In toluene solution the colour changed and another product was obtained after a few days, namely dihydridobis(triphenylphosphine)[η^2-2-3 di(phenylimino)butane]ruthenium II (see § 5). Yield. ca. 20%.

b) As for 4a but the suspension was refluxed for 8 days. A red purple powder precipitated; it was filtered, washed with hexane and dried in vacuo (Yield ca. 85%). It could be recrystallised from warm toluene giving within one hour at room temperature red-purple crystals of *cis*-dihydridobis(triphenylphosphine)[η^4-2,3-di(phenylimino)butane] ruthenium II. They were washed with hexane and dried in vacuo. Yield ca. 25%.

Light petroleum was added to the filtrate and the solution was cooled at —15° C affording after 3 days violet microcrystals of dihydridobis(triphenylphosphine)(η^2-2,3-di(phenylimino)butane ruthenium II. Yield ca. 20%. This operation can be repeated.

5) Dihydridobis(triphenylphosphine)(η^2-2,3-di(phenylimino)butane)ruthenium II.

The preparation was as for 4 but the reaction was carried out in boiling heptane (50 ml) for 3 days. A violet powder precipitated. It was collected, washed with hexane and dried in vacuo (Yield ca. 85%).

This compound could be recrystallized from hot toluene, giving after cooling purple crystals of the complex. They were collected, washed with hexane, and dried in vacuo. Yield ca. 40%.

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