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# RUTHENIUM COMPLEXES WITH DIAZADIENES

## VII *. 1,5-CYCLOOCTADIENE-1,4-DIAZA-1,3-DIENE HYDRIDORUTHENIUM COMPLEXES (COD)(DAD)Ru(H)Cl: SYNTHESIS, STRUCTURE AND CATALYTIC PROPERTIES

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## Summary

Displacement of piperidine from Ru(COD)(piperidine)-*trans*-(H)Cl (I) by 1,4-diaza-1,3-dienes (DAD: RN=CR'CR'=NR) gives the complexes *cis*-Ru(COD)(DAD)-(H)Cl (III). With relatively bulky DAD ligands the complexes III are unstable and are converted into compounds IV, which are also formed from III on heating. Complexes III are not accessible from Ru(COD)(DAD)$Cl_2$(V). If the analogous starting material involving a cycloheptatriene Ib in place of the COD ligand is used, a piperidide anion is preserved as ligand instead of a hydride. In the room temperature $^1$H NMR spectra of rigid asymmetric III all twelve hydrogen atoms of the COD ligand can be seen separately. A full assignment has been made by use of 2D-H/H-correlated spectra. The highest field resonance (1.2 ppm) is assigned to an olefinic H atom, shielded by the DAD chelate. Complexes III catalyse the isomerization of terminal alkenes to a *cis/trans* mixture (20/80) of internal alkenes. During the catalytic hydrosilylation of 1-alkenes this isomerization is a competing side reaction. Thermal decomposition of III gives free 1,3-COD; the decomposition under hydrogen gives cyclooctane stoichiometrically. In catalytic experiments III is found to catalyse the isomerization of 1,5-COD to 1,3-COD via 1,4-COD. Under hydrogen pressure (20 bar), III catalyses the hydrogenation of 1-hexene and cyclohexene. Four different ways in which one, two, or three 'vacant sites' can be generated starting from III are discussed.

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* Part VI, ref. 1; Part V, ref. 28; Part IV, ref. 10.

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## Introduction

In homogeneous catalysis phosphorus-containing ligands are of great importance. But much of the apparent superiority of use of $PR_3$ ligands is probably due to the relative neglect of other systems. We were able to show that reduction of iron(II) complexes of the type $(DAD)FeCl_2$ (DAD = RN=CR'CR'=NR) leads to $[(DAD)Fe^0]$ fragments, which have an outstanding catalytic ability in the cyclodimerization of 1,3-dienes. The diazadiene (DAD) control ligands are responsible for the chemo-, regio- and stereoselectivity, including good enantio-selectivity, in such reactions [2,3]. The selectivity is often much more pronounced than with the well-known nickel-phosphine system [4]. Similarly good results in catalytic reaction were obtained with other metals [5–7]. One of the obvious disadvantages of the $[(DAD)Fe^0]$ system is the entry into the catalytic cycle by reductive activation of the stable precursors $(DAD)FeCl_2$ with main group organometallics. The probable intermediates, $(DAD)FeR_2$, are too unstable to be isolated [8] and then used as catalytic precursors. So far, we have been unable to isolate compounds of the type $[(DAD)Fe(\eta^6\text{-arene})]$, although a bipyridyl analogue $[(bipy)Fe(\eta^6\text{-toluene})]$, prepared by metal atom techniques, is known [9]. On the other hand, $[(DAD)Ru(\eta^6\text{-arene})]$ complexes can be easily prepared, and their chemistry is known to some extent [10]. Their thermal stability rules out thermal initiation of catalytic reactions by a $[(DAD)Ru^0]$ fragment analogous to the iron species mentioned.

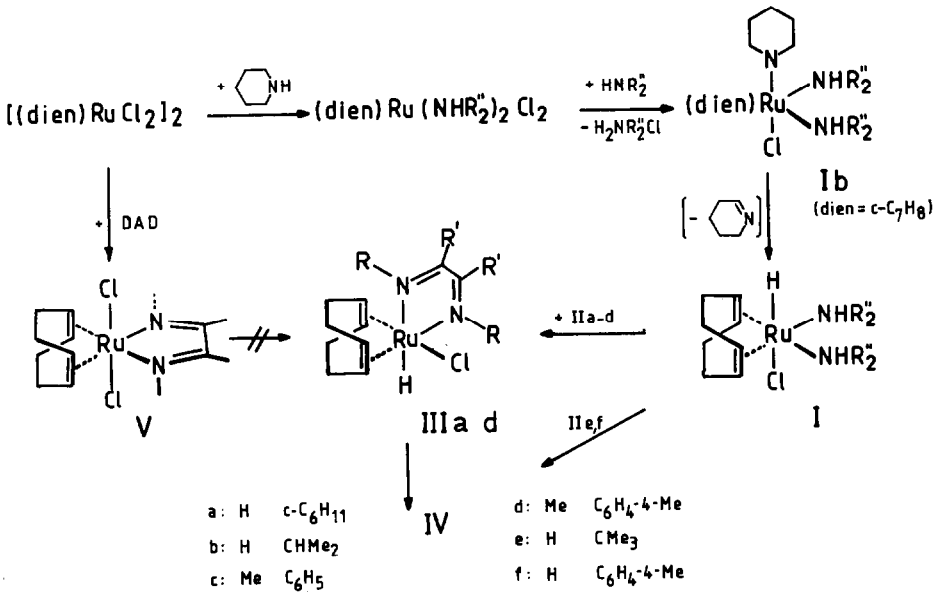
As DAD ligands are known to bind strongly to $Ru^0$ and to $Ru^{II}$ [11], and these two oxidation states probably occur in numerous catalytic reactions with this element, such as hydrogenation [12], hydrosilylation [7], hydroformylation [13], isomerizations [14] etc., we were especially interested in diazadiene hydridoruthenium complexes in which the other ligands are similar to those in potential catalytic substrates. Some [(DAD)Ru(H)] complexes with phosphines are known [15]. An idea of the versatile coordination chemistry of diazadienes in oligonuclear ruthenium complexes may be gained from the excellent structural contributions by Vrieze's and Van Koten's groups [16].

In this paper we report the synthesis and the structural characterization of 1,5-cyclooctadienehydridochloro complexes of ruthenium containing one diazadiene ligand, along with some preliminary data on their catalytic behaviour.

## Results and discussion

### *Synthesis of Ru(COD)(DAD)(H)Cl*

An unsuccessful attempt was made to prepare hydridochloro complexes from $Ru(COD)(DAD)Cl_2$ or $Ru(nor\text{-}C_7H_8)(DAD)Cl_2$ [17] in a way analogous to the reduction of $Ru(PPh_3)_3Cl_2$ with $H_2$, $NaBH_4$ or $Et_3SiH$ [18]. Potvin reported the synthesis of $Ru(piperidine)_2(COD)(H)Cl$ (I) by treatment of the insoluble $[Ru(COD)Cl_2]_x$ with an excess of piperidine and the replacement of the piperidine ligands by other nucleophiles [19]. It is noteworthy that the corresponding cycloheptatriene complex $[Ru(c\text{-}C_7H_8)Cl_2]$ [20] upon similar treatment with excess piperidine yields a very air-sensitive compound of composition $Ru(c\text{-}C_7H_8)(piperidine)_2$-(piperidide)Cl (Ib) which dissolves in benzene, methanol, or acetone to give yellow solutions. The composition of this compound indicates that the hydride in $Ru(COD)(piperidine)_2(H)Cl$ comes from a $\beta$-elimination of a piperidide ligand. The




SCHEME 1

piperidinium chloride (Scheme 1) was isolated in equimolar amounts. The $\Delta^1$-piperideine could not be isolated. Such compounds are known to polymerize or cyclotrimerize rapidly [21].

When a suspension of the hydridochloro complex I, which has *trans* stereochemistry [19], is stirred with an excess of DAD, II, in ether at temperatures below 30°C the new DAD complexes III are formed within 1 to 3 days. The outcome of this reaction depends on the bulk of the DAD substituents R and R'. With the bulky glyoxalbis(t-butylimine) (IIe) or the glyoxal derivative (IIf) which has coplanar aromatic *N*-substituents, another product is subsequently formed, and is similar to products, (IV), formed during the thermal decomposition of III in boiling tetrahydrofuran. Compounds III can be recrystallized from methylene chloride/pentane at temperatures below 25°C.

If thermal decomposition of III is carried out in these non-polar solvents, free 1,3-cyclooctadiene can be detected and some (unidentified) oligomeric compounds are formed. Heating of complexes III under hydrogen gives cyclooctane. These observations prompted us to perform some preliminary catalysis experiments (see below).

*Spectroscopic characterization*

The four hydrido complexes IIIa–d are very similar. They show a characteristic and strong Ru–H stretching absorption around 2040 $cm^{-1}$ and a band near 1500 $cm^{-1}$ (m) typical of DAD chelate complexes. The characteristic colour change to wine-red during the synthesis from I stems from the intense absorption bands in the visible part of the electronic absorption spectrum (Table 1). Although complexes with only one DAD ligand that exhibit two rather intense bands in the visible are known, the intensity of high energy band is never more than 30% of that of the main

TABLE 1

INFRARED DATA (in KBr, $cm^{-1}$) AND ELECTRON ABSORPTION SPECTROSCOPY DATA (in $CH_2Cl_2$; $\lambda$ in nm, $\varepsilon$ in cm $mmol^{-1}$) OF III

| No. | R′ | R | $\nu$(M–H) | $\nu$(C=N) | $\lambda_1$ ($\varepsilon$) | $\lambda_2$ ($\varepsilon$) |
|---|---|---|---|---|---|---|
| IIIa | H | c-$C_6H_{11}$ | 2040 | 1460 | 540 (2250) | 455 (2010) |
| IIIb | H | i-$C_3H_7$ | 2040 | 1465 | 542 (2870) | 450 (2300) |
| IIIc | $CH_3$ | $C_6H_5$ | 2035 | 1485 | 532 (3140) | 474 (2700)sh |
| IIId | $CH_3$ | $C_6H_4$-4-$CH_3$ | 2037 | 1505 | 534 (3080) | 470 (2600)sh |

band [22]. The very unsymmetrical electron distribution in these octahedral complexes with $C_1$ symmetry (that is, with no symmetry elements at all except E) and the presence of a hydride ligand, with its strong *trans* effect [19], may be responsible for this phenomenon. Any two MLCT transitions of similar energy in the one-electron description will mix and gain intensity from each other. No solvatochromy studies have been performed to support the assignment to a CT transition [22].

Detailed information can be obtained from the $^1H$ NMR spectra, which were recorded at 360 MHz. In Table 2 data for the COD part of the spectra are listed in the upper half and other resonances in the lower half. All four spectra for the COD part are very similar, and so only the spectrum of the *N*-isopropyl complex IIIb is discussed in detail. The appearance of twelve different signals for the twelve COD protons and the eight line signal for four anisochronous methyl groups, coupled to a methine proton, clearly show that the complex is asymmetric and rigid. Figure 1 gives the numbering scheme for the complex, Fig. 2 shows the $^1H$ NMR spectrum of IIIb, and Fig. 3 the coupling correlation in a 2D COSY experiment [23].

In contrast to the starting material [19] the complexes III have the hydrido and chloro ligands in a *cis* disposition. There is no direct evidence for the position of the hydride ($\delta$ −4 ppm) relative to the chelating DAD and COD. We propose a position meridional with respect to the DAD; in this way the hydride avoids a position *trans* to an olefinic ligand. Furthermore the intensity pattern for the hydride signal and that for the low field signal of glyoxalic protons R′ are the same. This is consisted with the assumption that the long range coupling for the hydride with the two protons R′ is different in the meridional (DAD/H) configuration shown in Fig. 1.

From the 2D-experiment it is obvious that the signal from one olefinic proton of the COD part shows an abnormal chemical shift. Except for IIIa, for which such a signal is hidden in the 1D spectrum under the $\beta$- and $\gamma$-protons of the cyclohexyl ring, a signal between $\delta$ 1.1–1.4 (in chlorinated solvents) can be assigned to an olefinic proton (H(5)). Inspection of molecular models in which the DAD and the COD ligand occupy *cis* position clearly shows one COD olefinic hydrogen very close (above or below) to the DAD plane. Although some indications of a shielding effect by DAD chelates had been noted earlier [24], this is the strongest high field shift so far observed. If the hydride ligand instead of being in the position shown in Fig. 1, were *trans* to a double bond, this should result in some shift of two olefinic signals. In the corresponding complexes (COD)(DAD)$RuCl_2$(V) which have a *trans* stereochemistry, the olefinic protons for Vc appear at $\delta$ 3.94 and the $CH_2$ protons at $\delta$ 2.44 (eq) and 1.84 (ax). The values for Vd differ only slightly [25]. It is not

clear, why the chemical shift for the isopropyl methine protons is so large ($\delta$ 5.3, 5.0). In [(DAD)Ru($\eta^6$-$C_6H_6$)Cl]$^+$, a less electron-rich cationic complex, these protons appear at $\delta$ 4.7 [10]. In a comparable $\eta^4$-cycloheptatriene complex, ($\eta^4$-CHT)(DAD)RuCl($NR_2$), with an amide instead of a hydride, these signals are at 4.2 and 4.3 ppm. One resonance of the two for *cis*-$(DAD)_2RuCl_2$ appears at a comparable position [27].

One final observation is probably related to the special conformation in these sterically rather crowded *cis* complexes III: The $^1H$ resonances of the aromatic substituents in IIIc and IIId show not only the two expected sets of signals for two different R groups but also reveal that rotation of the phenyl rings around the N–C bond is hindered. One of the *ortho* protons show a rather strong shielding in both complexes. The phenyl group on the nitrogen atom, which is in a *cis/cis* position relative to the two COD double bonds, is in a sterically more demanding environment, and it seems possible that its conformation leads to a "sandwiching" of one *ortho* proton of this ring between the two olefinic planes of the COD ligand. The conformation of the free ligand IId and of IId in sterically undemanding complexes is known [28]. Interligand repulsion stemming from this crowding may be one of the factors making complexes III thermally rather unstable. It also accounts for the fact that the same type of compound was unaccessible with DAD ligands bearing either tertiary *N*-alkyl substituents, *ortho*-substituted aromatic *N*-substituents, or aromatic derivatives of glyoxal with coplanar *N*-substituents.

A $^{13}C$ NMR spectrum of IIIb shows the expected number of 16 signals, in agreement with the $C_1$ symmetry. No attempt was made to relate the signals to the corresponding proton signals via a 2D-H/C correlated spectrum. The average $\delta$ values are similar to those for Ru(COD)(pyridine)$_2$(H)Cl [19].

*Catalytic reactions*

Observations made during the thermal decomposition of solutions of III prompted us to try some preliminary catalytic tests, mostly with IIIb. In the presence of this complex, olefins are slowly hydrosilylated by $HSi(OC_2H_5)_3$. During the room temperature reaction of 1-hexene, isomerization to *trans* and *cis*-2-hexenes and -3-hexenes occurs as a major side reaction (see below). The hydrosilylation of 1,3-dienes is rather regioselective [7,29], and from isoprene 2-methyl-4-triethoxysilyl-2-butene is obtained in more than 80% yield. For the hydrosilylation reaction thermal lability of a precatalyst (to create vacant coordination sites) is not essential since a silane $HSiY_3$ can itself activate metal complexes via reduction or dehalogenation.

As a second experiment (Scheme 2), isomerization of a terminal olefin was attempted. At room temperature, and much faster at 50°C, 1-hexene was transformed to a mixture of 72–80% *trans* internal hexenes and 20–28% *cis* internal hexenes, the exact ratio depending on the temperature and the DAD ligand.

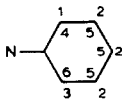
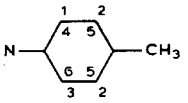
Under hydrogen pressure (20 bar) 1-hexene and cyclohexene are hydrogenated. The $H_2$ addition in dichloroethane is complete within 2 h at 80°C and within 8–10 h at room temperature. A catalyst/substrate ratio of 1/400 was used in most experiments.

We did not investigate the relative rates of the double bond isomerization and the hydrogenation. The results for the cyclohexene and the 1-hexene hydrogenations indicate that isomerization is again competitive, as in the hydrosilylation of 1-hexene.

(*Continued on p. 244*)

TABLE 2

$^1$H CHEMICAL SHIFTS FOR COMPLEXES III (for the numbering scheme of the COD ligand see Fig. 1)

| | IIIa $CDCl_3$ | IIIb $CDCl_3$ | IIIb $C_6D_6$ | IIIc $CDCl_3$ | IIId $CD_2Cl_2$ |
|---|---|---|---|---|---|
| H(1) | 4.01 | 4.03 | 4.56 | 3.81 | 3.60 |
| H(2) | 3.23 | 3.28 | 3.53 | 3.85 | 2.80 |
| H(6) | 3.07 | 3.10 | 2.95 | 2.77 | 2.62 |
| H(5) | n.o. | 1.38 | 1.19 | 1.12 | 1.14 |
| H(3a) | n.o. | 1.76 | 1.76 | 1.40 | 1.37 |
| H(3e) | 2.74 | 2.46 | 2.38 | 2.00 | 2.00 |
| H(4a) | n.o. | 1.94 | 1.91 | 1.79 | 1.72 |
| H(4e) | n.o. | 2.37 | 2.25 | 2.00 | 2.00 |
| H(7a) | n.o. | 1.64 | 1.64 | 1.40 | 1.34 |
| H(7e) | n.o. | 2.35 | 2.25 | 1.97 | 1.97 |
| H(8a) | n.o. | 2.00 | 2.00 | 1.89 | 1.89 |
| H(8e) | 2.93 | 2.55 | 2.57 | 2.45 | 2.31 |
| H(Ru) | −4.07 | −4.12 | −3.71 | −4.21 | −4.35 |
| R′ | 8.34 | 8.41 | 7.59 | 2.33 | 2.28 |
| | 8.12 | 8.17 | 7.34 | 2.09 | 2.04 |
| R | 4.87 $\alpha$ | 5.33 $\alpha$ | 5.18 $\alpha$ | 8.00[1] | 7.75[1] |
| | 4.57 $\alpha'$ | 5.02 $\alpha'$ | 4.73 $\alpha'$ | 7.33[2] | 7.29[2] |
| | 1–2 | 1.69 $\beta_1$ | 1.55 $\beta_1$ | 6.36[3] | 6.30[3] |
| | | 1.60 $\beta_1'$ | 1.54 $\beta_1'$ | 7.85[4] | 7.63[4] |
| | | 1.59 $\beta_2$ | 1.24 $\beta_2$ | 7.48[5] | 7.32[5] |
| | | 1.28 $\beta_2'$ | 0.91 $\beta_2'$ | 7.18[6] | 7.06[6] |

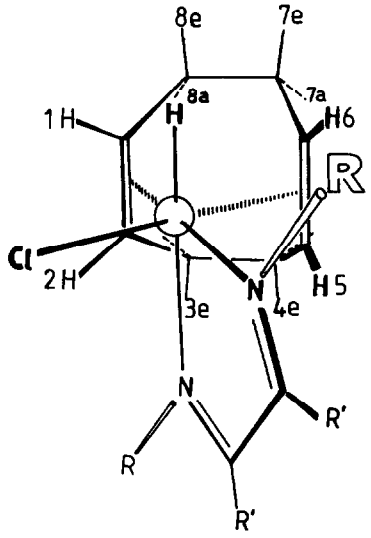



Fig. 1. Structure of III with the numbering scheme for the cyclooctadiene protons.

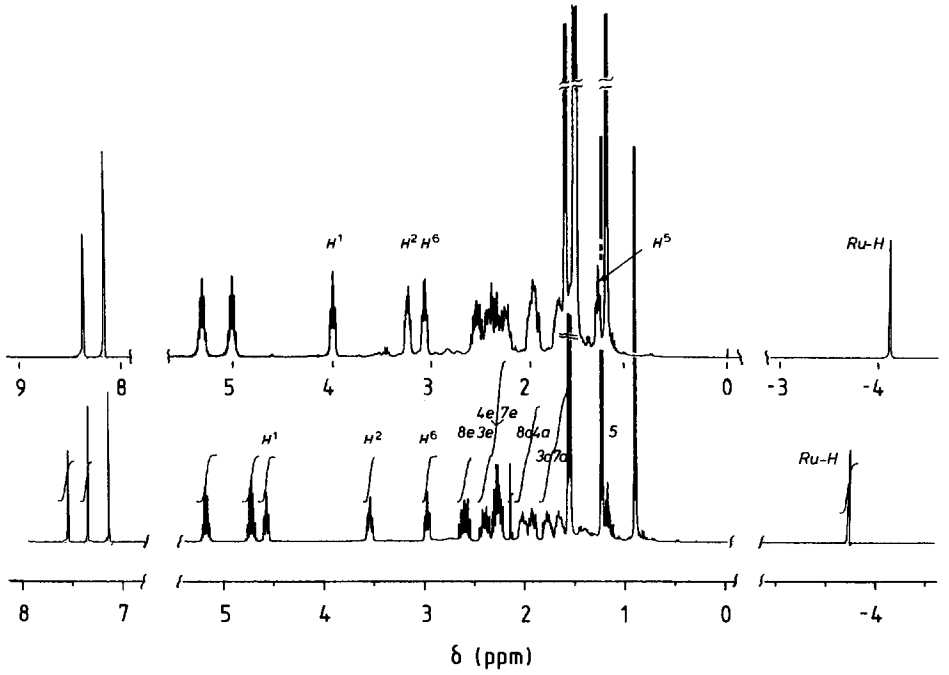



Fig. 2. 360 MHz-$^1$H NMR spectra of IIIb (top: $CDCl_3$; bottom: $C_6D_6$) with COD proton assignments.

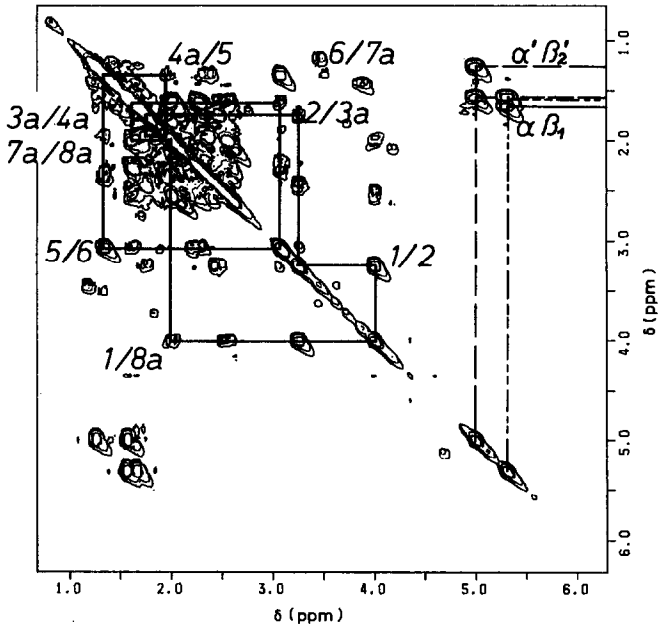
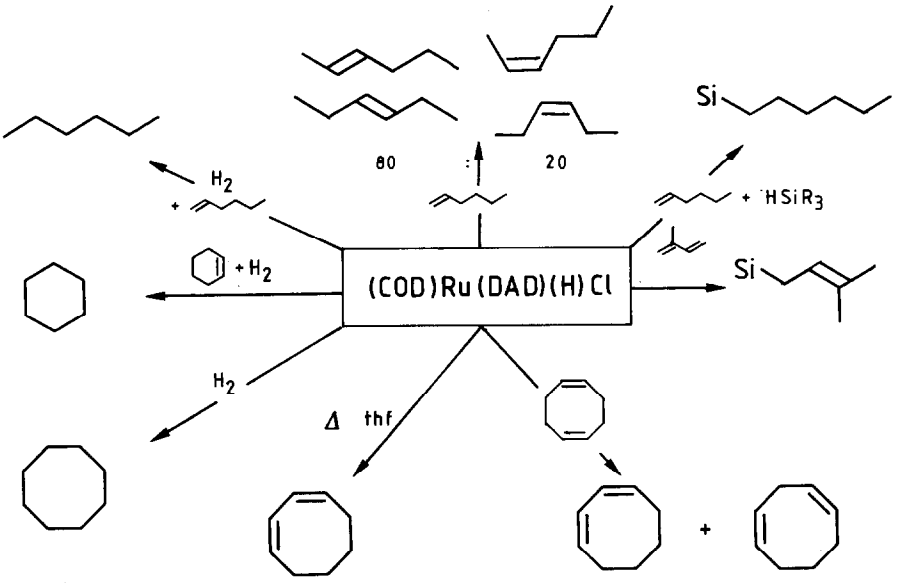


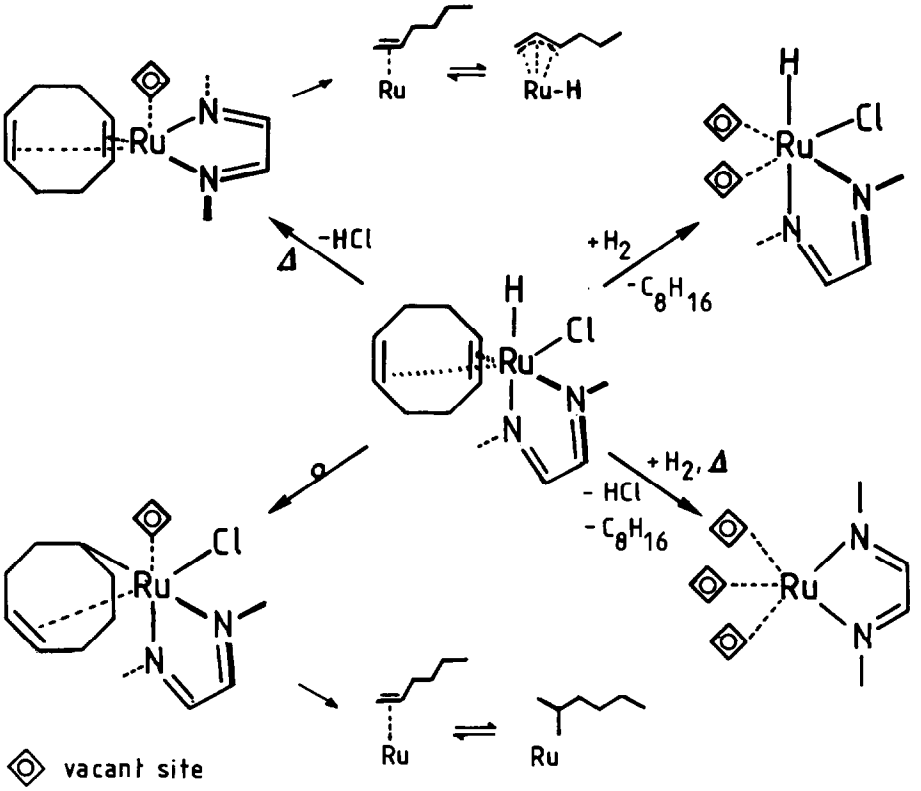

Fig. 3. 2D-H/H-COSY spectrum of IIIb. One cyclic connectivity of eight cross peaks is indicated.




SCHEME 2

Thermal decomposition of the complex IIIb in tetrahydrofuran gave free 1,3-cyclooctadiene, and that under an atmosphere of hydrogen gave cyclooctane. Therefore we also examined the effectiveness of IIIb in isomerization of 1,5-cyclooctadiene. At 50°C in dichloromethane 1,5-COD is slowly transformed to 1,3-COD (80%) and 1,4-COD (20%), the proportion of the latter decreasing on prolonged reaction. Singleton et al. [30] and Tkatchenko et al. [31] have shown that hydridoruthenium complexes $[RuH(COD)(PR_3)_3]^+$ or $[RuH(COD)(1\text{–}6\text{-}\eta\text{-}C_8H_{10})]^+$ isomerize via $\pi$-allylic intermediates; from 1,5-COD ligands, 1,3-COD ligands and even a monohapto cyclooctenyl ligand can be formed. The stepwise hydrogen transfer, which is catalytic in our case, does not depend on the charge of the starting complexes nor on a special type of ligand (olefin, $PR_3$, DAD). The initial step in this isomerization, $HRu(1,2;5,6\text{-}\eta\text{-}C_8H_{12}) \rightarrow Ru(1,2;5\text{-}\eta\text{-}C_8H_{13})$, which creates a vacant coordination site, is probably also the activation step for the other catalytic reaction considered above. An alternative mechanism would involve hydrogen chloride elimination from III, giving rise to a vacant site at a $Ru^0$ center. Complexes III show no catalytic activity in tetrahydrofuran, but this does not help in deciding between the possible mechanisms.

It is noteworthy that complexes of norbornadiene, $(nor\text{-}C_7H_8)Ru(DAD)Cl_2$, which are very similar to $(1,5\text{-}COD)Ru(DAD)Cl_2$ (V) can be reduced with lithium sand in tetrahydrofuran [1] to give a $Ru^0$ species, probably $(nor\text{-}C_7H_8)Ru(DAD) \cdot THF$. This complex is again inactive in tetrahydrofuran, but shows catalytic activity in non-coordinating solvents. In the hydrosilylation there is no induction period, and in the isomerization of 1-hexene only *trans*-hexenes are formed. This difference from the reaction of 1-hexene catalysed by III can be explained by $\pi$-allyl/alkene interconversion in the former case and an alkyl/alkene interconversion in the latter (Scheme 3).




SCHEME 3

In principle there are four ways in which the hydrido complexes III can initiate reaction directly or undergo activation in catalytic reactions: (i) hydride transfer from Ru to the COD ligand; (ii) HCl elimination at elevated temperatures; (iii) elimination of COD by hydrogenation; (iv) elimination of COD by hydrogenation after thermal elimination of hydrogen chloride. This last process has been observed with formation of stoichiometric amounts of cyclooctane, and of an amine hydrochloride at 80°C under hydrogen during the hydrogenation of alkenes in the presence of an amine [29]. Investigations of the possible catalytic cycles are in progress.

## Experimental

All experiments were performed by standard inert atmosphere techniques. Solvents were dried and stored under nitrogen and freshly distilled before use. The following systems were used for analysis and spectroscopy: IR: Perkin–Elmer 325 and Pye Unicam 1100; VIS/UV: Perkin–Elmer 554 spectrometer; GC: Hewlett-Packard Model 5840A with 12.5 m capillary column (dimethylsilicone); NMR: Bruker WP 80 SYFT and Bruker AM 360.

Cyclooctadienedichlororuthenium was prepared by a published procedure [32], as was the analogous cycloheptatriene complex $[(c\text{-}C_7H_8)RuCl_2]_2$ [20]. Complex I

(1,5-COD)Ru(piperidine)$_2$(H)Cl, in 63% yield, by the method described by Potvin et al. [19]; it gave a strong $\nu$(Ru–H) band at 2060 cm$^{-1}$.

*Chloro-cycloheptatriene-piperidido-bis(piperidine)ruthenium (Ib)*

To a suspension of 1.5 g of Ru(c-$C_7H_8$)$Cl_2$ (5.5 mmol) in a mixture of methanol (20 ml) and acetone (20 ml) was added a large excess of piperidine (10 ml). A spontaneous exothermal reaction took place as the complex dissolved. After 10 h stirring at ambient temperature the solvents were evaporated and the product extracted from the residue with a total of 50 ml of benzene (yellow solution), from which after concentration to 15 ml, the product was precipitated with pentane. Yield 65%. Ib is very air sensitive, soluble in benzene, methanol and acetone, and poorly soluble in hexane and ether. It decomposes in dichloromethane. There are no hydride signals in the NMR or Ru–H bands in the IR.

Analysis: Found: C, 54.08; H, 9.22; N, 8.84. $C_{22}H_{40}ClN_3Ru$ calc: C, 54.7; H, 8.35; N, 8.70%. The product reacts cleanly with DAD IIb to give a complex of composition (c-$C_7H_8$)Ru(DAD)($C_5H_{10}N$)Cl, which is shown by its NMR spectra to be asymmetric, as are the corresponding COD-hydrido complexes III [26].

*Chloro-cyclooctadiene-diazadiene-hydridoruthenium (III)*

The starting complex I (0.5 g, 1.2 mmol) is suspended in diethyl ether. A slight excess of the corresponding DAD II in ether is added. The solution is stirred below 25°C for 24 h (*N*-aliphatic DAD) or 3 d (*N*-aromatic DAD). The products are then filtered off and taken up in dichloromethane. The solution is filtered and pentane added to precipitate the product. Yield 65–75%. Analyses:

IIIa. Found: C, 56.47; H, 8.28; N, 5.99. $C_{22}H_{37}ClN_2Ru$ calc: C, 56.72; H, 7.95; N, 6.02%.

IIIb. Found: C, 49.17; H, 7.57; N, 7.22. $C_{16}H_{29}ClN_2Ru$ calc: C, 49.81; H, 7.28; N, 7.26%.

IIIc. Found: C, 59.65; H, 6.08; N. 5.85. $C_{24}H_{29}ClN_2Ru$ calc: C, 59.82; H, 5.82; N, 5.80%.

IIId. Found: C, 60.57; H, 6.93; N, 5.45. $C_{26}H_{33}ClN_2Ru$ calc: C, 61.24; H, 6.28; N, 5.50%.

$^{13}$C NMR data for IIIb (in $CDCl_3$): $\delta$ 22.2, 24.0, 24.6, 25.8 28.4, 31.4, 32.4, 33.4 (C(3), C(4), C(7), C(8) of the COD, $CH_3$ i-propyl); 59.0, 66.1, 68.7, 82.6 (C(1), C(2), C(5), C(6) of the COD); 72.3, 72.8 (CH, i-propyl); 153.5, 156.5 (CH=N) ppm.

*Thermal decomposition of III*

Heating a complex of type III in tetrahydrofuran results in slow decomposition and formation of a new complex of type IV, which has not yet been identified. After 60 min heating the thf is evaporated in vacuo and the solid residue extracted with hexane. No crystals can be isolated from the extract. The residual IV (in $C_6D_6$) shows a hydride resonance at $\delta$ −10 ppm and new signals near 0 ppm. Analysis indicates that IV contains no chloride.

*trans-Dichloro-1,5-cyclooctadiene-diacetylbis(phenylimine)ruthenium(II) (Vc) and -diacetylbis(p-tolylimine)ruthenium(II) (Vd)*

550 mg (1.1 mmol) of Ru(COD)(toluidine)$_2Cl_2$, (prepared in the way described for the corresponding norbornadiene complex [32]) is heated for 30 min with 1.5

mmol of the DAD (350 mg of IIc, 390 mg of IId) in 40 ml of thf under reflux. A gentle stream of air is passed through the warm solution for 10 min in order to oxidize some undesired by-products. The solvent is then evaporated and the solid residue washed with $2 \times 50$ ml of petroleum ether to remove remaining DAD. By fractional crystallization from acetone/petroleum ether or dichloromethane/petroleum ether the desired products can be separated from complexes $(DAD)_2RuCl_2$ which are also formed [22]. Analyses:

Vc. Found: C, 56.05; H, 5.52; N, 5.46. $C_{24}H_{28}Cl_2N_2Ru$ calc: C, 55.81; H, 5.46; N, 5.42%.

Vd. Found: C, 57.35; H, 6.01; N, 5.18. $C_{26}H_{32}Cl_2N_2Ru$ calc: C, 57.35; H, 5.92; N, 5.14%.

*Catalytic reactions*

The catalytic reactions were performed with complex IIIb (40 mg, 0.1 mmol) and 40 mmol of each substrate (1-hexene, 1,5-cyclooctadiene, or isoprene plus triethoxysilane) in 20 ml of dichloromethane. The products were characterized by capillary GC, comparison being made with authentic samples. The hydrosilylation products are described elsewhere [7].

The hydrogenation was performed (at the ENSC laboratory of Prof. Ph. Kalck in Toulouse) in a 150 ml Sotelem pressure reactor, again with 0.1 mmol of catalyst IIIb, and a total of 40 ml of liquid components (35 ml of $C_2H_4Cl_2$, 5 ml of 1-hexene or cyclohexene). The initial pressure in the 500 ml reservoir (Prolabo) was set to 20 bar and the hydrogen uptake in the stirred solution (at temperatures 20 and 80°C) was monitored automatically by recording of the change pressure in the reservoir (J.P.B. instrument type E6031).

*Preparation of (DAD)(norbornadiene)Ru · THF*

The starting complex (DAD)(norbornadiene)$RuCl_2$ (with DAD IIb) is obtained, in the same way as V, from Ru(nor)(toluidine)$Cl_2$ [32] and DAD IIb in refuxing thf. After 8 h reflux the solvent is evaporated, the residual DAD IIb extracted with petroleum ether, and the product chromatographed on neutral $Al_2O_3$ (activity V) with dichloromethane as eluant. The yellow initial fraction is collected and, after reduction of the solvent volume, addition of petroleum ether precipitates the product. Yield 40%. Analysis: Found: C, 44.54, H, 6.08; N, 6.86. $C_{15}H_{24}Cl_2N_2Ru$ calc: C, 44.56; H, 5.98; N, 6.93%.

This product (1 mmol, 404 mg) is then stirred in 50 ml of tetrahydrofuran at ambient temperature for 24 h with an excess of lithium sand (50 mg; 7 mmol). The solution becomes brown-orange ($\lambda_{max}$ 425 nm). The lithium chloride and the residual lithium sand are removed by filtration, and the thf solution then yields a triphenylphosphine complex and a carbonyl complex of the type (DAD)(nor)Ru(L) [1]. The solutions are stable for hours at room temperature. Evaporation of the solvent at reduced pressure gives a brownish raw product, which cannot be sufficiently purified to give satisfactory analyses but is active for the addition reaction with CO or $P(C_6H_5)_3$, and in the type of catalyses studied with IIIb.

15 ml of a solution containing 0.1 mmol of "(norbornadiene)Ru(DAD) · THF" in dichloromethane is stirred with 25 mmol (3 ml) of isoprene and 4 ml (26 mmol) of $HSi(OC_2H_5)_3$. After 48 h hydrosilylation is complete. (For product analysis see [7]). The isomerization reaction of 1-hexene gave a mixture of *trans*-2-hexene and *trans*-3-hexene, but no *cis* isomers.

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