Rhodium Complexes with Phosphine and Diazabutadiene Ligands. Their Properties as Hydrogenation Catalysts. Molecular Structure of RhCl(COD)P(p-C$_6$H$_4$F)$_3$

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Abstract

The complexes RhCl(COD)L (I), [Rh(COD)(R-DAB-R')L]ClO$_4$ (II), and [RhH$_2$(R-DAB-R')L$_2$]·ClO$_4$ (III), (COD = 1,5-cyclooctadieno, R-DAB-R' = NH$_2$N=C(CH$_3$)C(CH$_3$)=NNH$_2$, L = P(p-C$_6$H$_4$F)$_3$), have been obtained and characterized by IR and ^{1}H NMR.

The molecular structure of I was elucidated by X-ray study. Crystals are monoclinic, space group $P2_1/c$. Unit cell parameters are: a = 11.145(2), b = 11.991(4), c = 18.356(5) Å, β = 99.35(1)°, Z = 4, R = 0.072, R_w = 0.081, for 5081 reflections with $I > 2\sigma(I)$.

The catalytic activity of complexes I, II and III in the n-hexene hydrogenation processes has been studied, at different temperatures at a constant pressure of H$_2$, in acetone.

Compound I presents an induction period that decreases with the increase of temperature. At room temperature (23 °C) the activity follows the order I < II < III. When T increases this order changes to II < III < I.

A selectivity towards *cis*-2-hexene formation has been observed.

Introduction

It is well known that binuclear complexes [RhX-Diene]$_2$ react smoothly with group V donor ligands L to give compounds whose composition depends upon the ratio L/Rh, the nature of the diene of L and of the solvent.

When L/Rh < 1, for L = tertiary phosphine, neutral, mononuclear complexes of general formula 'Rh X Diene L' are obtained [1–3]. If the ratio L/Rh > 1, pentacoordinated neutral intermediate 'Rh Cl diene L$_2$' are formed, [4] which, in the presence of a suitable anion, give cationic species [Rh Diene L$_2$]$^+$ [5].

NMR studies of ^{1}H and ^{31}P have helped to elucidate the stereochemistry of these compounds [6].

Their stability depends on the relative stability of the Rh–diene bond which varies in the order nbd > cod > cot [7]. The size and the electronic factors of the phosphorus ligands play their roles in the stability of the complex, the steric effect being more important than the electronic one.

Complexes of Rh(I), with 16 electrons coordinatively insaturated, have been intensively studied as catalyst precursors in the hydrogenation of olefins. By its reaction with molecular hydrogen, intermediate hydrides are formed, which are responsible for the catalytic activity of these systems [8, 9].

In our study of rhodium–COD–phosphine systems, we have isolated good crystals of [RhCl(COD)-P(p-FC$_6$H$_4$)$_3$] (I), a good starting material for the synthesis of penta- or hexacoordinated derivatives.

Compound I reacts with 1,4-diaza-1,3-butadiene, R-DAB-R', R-N=C(R')C(R')=N-R, when R = NH$_2$, R' = CH$_3$ and molecular hydrogen with the formation of [Rh(COD)(NH$_2$-DAB-CH$_3$)P(p-C$_6$H$_4$F)$_3$]ClO$_4$ (II) and [RhH$_2$(NH$_2$-DAB-CH$_3$)(P(p-C$_6$H$_4$F)$_3$)$_2$]$_2$ClO$_4$, (III) [10]. The activity of I, II and III as catalyst precursors in olefin hydrogenation processes has been studied.

Experimental

Reactions were carried out in a dry oxygen-free, nitrogen atmosphere, at room tempera-

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ture. Solvents were dried and distilled before use.

Preparation of the Compounds

The starting complex [Rh(COD)Cl]$_2$ and the α-diimine ligand, NH$_2$DAB-CH$_3$, were prepared according to the literature [11, 12].

Synthesis of RhCl(COD)P(p-C$_6$H$_4$F)$_3$ (I)

By addition of P(p-C$_6$H$_4$F)$_3$ to a suspension of [Rh(COD)Cl]$_2$ in methanol, yellow crystals of RhCl(COD)P(p-C$_6$H$_4$F)$_3$ were obtained.

Anal. Found (calc.): C, 55.1 (55.5); H, 4.1 (4.3)%.

X-ray Analysis: The crystals were found to belong to the monoclinic system, space group $P2_1/c$; cell dimensions and intensity data were measured with an Enraf-Nonius CAD-4 four-circle diffractometer with Mo Kα radiation. a = 11.145(2), b = 11.991(4), c = 18.356(5) Å, β = 99.35(1)$^\circ$; V = 2421(1) Å^3, D_x = 1.544 g/cm^3 and Z = 4, F(000) = 1136.

A total of 7364 independent reflections were measured in the range of $2^\circ < \theta < 30^\circ$, of which 5081 were considered as observed when $I > 2\sigma(I)$, σ being determined from counting statistics, and were therefore used in refining the structural parameters.

The structure was resolved by the heavy atom method and by Fourier and difference Fourier synthesis, refined by full matrix least-squares method, with anisotropic thermal parameters for non- H atoms. All H atoms located in a difference Fourier synthesis are included in the calculations with isotropic temperature factors. Final R = 0.072, R_w = 0.081. The final shift did not exceed 0.016, the empirical weighting scheme giving no trends in $\langle w\Delta^2 F \rangle$ [13]. There are significant features in the final ΔF synthesis.

Synthesis of [Rh(COD)(NH$_2$DAB-CH$_3$)P(p-C$_6$H$_4$-F)$_3$]ClO$_4$ (II)

A solution of DAB ligand in methanol is added to a suspension of complex I in methanol, in 1/1 molar ratio, to give a yellow solution. On addition of an aqueous solution of NaClO$_4$, a microcrystalline orange solid precipitates. Yield 60–65%. *Anal.* Found (calc.): C, 48.6 (48.6); H, 4.7 (4.6); N, 7.5 (7.6)%.

Synthesis of [RhH$_2$(NH$_2$DAB-CH$_3$){P(p-C$_6$H$_4$F)$_3$}$_2$]ClO$_4$ (III)

Compound III can be obtained from compounds I or II.

(a) When a solution of compound I in methanol is treated with NH$_2$-DAB-CH$_3$ (3 mmol, 0.3 g) and an ethereal solution of P(p-C$_6$H$_4$F)$_3$ (1.5 mmol, 0.5 g), the solution acquires a pale yellow colour; molecular hydrogen was bubbled through for 3 h; with addition of an aqueous solution of NaClO$_4$ and partial evaporation of the solvent a yellow solid

precipitates. Recrystallization from methanol–ethylether. Yield 70–80%.

(b) When an excess of P(p-C$_6$H$_4$F)$_3$ in ethylether is added to a methanolic solution of compound II, followed by a molecular hydrogen bubbling (3 h) a yellow solid of composition III is obtained. Yield 70–80%.

Anal. Found (calc.): C, 50.0 (50.5); H, 3.7 (3.8); N, 6.0 (5.9)%.

Techniques

^{1}H NMR spectra were recorded at room temperature with a Brucker WM-360 using deuterochloroform as solvent and TMS as internal standard.

IR spectra were recorded in the 4000–200 cm^{-1} region using KBr discs on a Nicolet 60 SX (FTIS) spectrometer.

Elemental analysis for C, H, N, were performed by the Inorganic Chem. Dept. in Alcalá de Henares University (Madrid).

Hydrogenation Catalysis

Hydrogenation was carried out in a 300 ml capacity stainless steel 'Magnedrive' autoclave at 500 rev/min. Acetone was used as standard solvent. Solvent, catalyst and 1-hexene, were deaerated with nitrogen before use.

Once the desired temperature was reached, H$_2$ was admitted up to 4 atmospheres; to maintain constant pressure, more H$_2$ was admitted to the reaction vessel as the reaction proceeded.
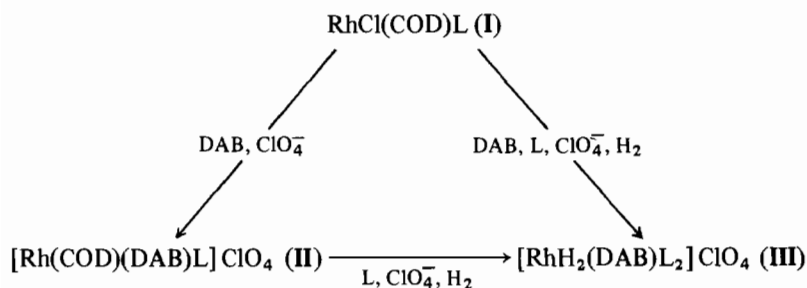
In order to measure reactant and products, samples were taken at different times and analyzed by GLC using a column 1/8 in, packed with 15 wt.% β,β'-oxydipropionitrile on Chromosorb P(80/100 mesh connected).

Results and Discussion

Complexes of rhodium, tetra- (I), penta- (II) and hexa- (III) coordinates have been obtained, in accordance with Scheme 1.

The stoichiometries of these compounds have been determined by spectroscopic methods (IR, ^{1}H NMR) and elemental analysis. The spectroscopic results for II and III are detailed in Table I. Both complexes give in their ^{1}H NMR spectra only one signal for the methyl protons and one signal also for the NH$_2$ groups of the diazabutadiene ligand, which is an indication that it is symmetrically coordinated to Rh — through 4 ϵ — by the two nitrogen atoms.

In absence of other effects, signals are expected to shift downfield upon coordination, but the ring-current effects originated by the aromatic rings of the phosphine can shift the signal in the opposite sense (upfield), (Δ values −0.71, −0.48, Table I).

RhCl(COD)L (I)

DAB, ClO$_4^-$ DAB, L, ClO$_4^-$, H$_2$

[Rh(COD)(DAB)L] ClO$_4$ (II) $\xrightarrow{\text{L, ClO}_4^-\text{, H}_2}$ [RhH$_2$(DAB)L$_2$] ClO$_4$ (III)

Scheme 1. L = P(p-C$_6$H$_4$F)$_3$. DAB = diazabutadiene, NH$_2$N=C(CH$_3$)C(CH$_3$)=NNH$_2$; COD = 1,5-cyclooctadiene.

TABLE I. Spectroscopic Data for [Rh(COD){NH$_2$N=C(CH$_3$)C(CH$_3$)=NNH$_2$}P(p-C$_6$H$_4$F)$_3$]$^+$ (II) and [RhH$_2${NH$_2$N=C(CH$_3$)-C(CH$_3$)NNH$_2$}{P(p-C$_6$H$_4$F)$_3$}$_2$]$^+$ (III)

Compound	Infrared				^{1}H NMR[d]						
	ν(N–H)	ν(C–H)$_{CH_3}$	ν(C–H)$_{COD}$	ν(Rh–H)	Hydride[a]	NH$_2$DAB-CH$_3$		COD[b]		P(p-C$_6$H$_4$F)$_3$[c]	
						δ (ppm)	Δ[e]	δ (ppm)	Δ[e]	δ (ppm)	Δ[e]
II	3400m	2940w	2920m			NH$_2$ 5.31 (s, 4H)	0.02	CH 5.74 (d, 4H)	0.18	7.54 (m, 6H)	0.28
	3300m		2900m			CH$_3$ 1.26 (s, 6H)	−0.71				
			2880m 2860sh 2830m								
III	3420m	2940w		2120w	−15.7 (q, 2H)	NH$_2$ 5.38 (s, 4H)	0.05			7.55 (m, 12H)	0.29
	3320m			2040m		CH$_3$ 1.49 (s, 4H)	−0.48			7.16 (m, 12H)	0.16

[a] ^1J(H, Rh) $\simeq$ ^2J(H,P) = 14.3 Hz.   [b] ^5J(H,H) = 8 Hz.   [c] ^3J(H,F) = 8.2 Hz, ^2J(o,m) = 6 Hz.   [d]Chemical shift (δ ppm, from TMS in ClDCl$_3$).   [e]Δ = δ complex − δ free ligand.

The spectrum of compound **III** gave a signal at −15.7 ppm of which the multiplicity, a quartet, is in agreement with two equivalent *cis* protons coupled to Rh and also to two phosphorus atoms with very similar coupling constant values ^2J(H,P) $\simeq$ ^1J(H, Rh) $\simeq$ 14.3, [10]. The IR spectrum shows a ν(Rh–H) signal at 2047 cm^{-1}.

We have studied the molecular structure of **I**, shown in Fig. 1, with its atoms labelled. Positional parameters are given in Table II; bond lengths and angles are shown in Table III.

Bond lengths and angles in the coordination sphere of the rhodium are regular and compare well with the corresponding values found in other complexes of rhodium with phosphine and Cl.

The rhodium atom has the expected square planar coordination with the COD bidentate ligand, π-coordinated, which implies a plane defined by Rh, Cl, P and the mid-point of both olefin bonds in COD (C22–C23; C19–C26).

The rings of the phosphine move away to accommodate the bulky COD ligand.

We have not been able to isolate a good size single crystal of compound **II**, to determine its molecular structure.

Compound **III** crystallizes well but we have not studied its structure, as we have already done so with a similar one, with a different DAB ligand (Ph-DAB) and PPh$_3$ [14]. The structure is a deformed octahedron with the two hydride-hydrogen atoms in the *cis* position and the two phosphine ligands *trans*, bended towards the two hydride hydrogens.

Catalytic Hydrogenation of 1-Hexene

Hydrogenation and isomerization of 1-hexene using the complexes **I**, **II** and **III** as catalysts have
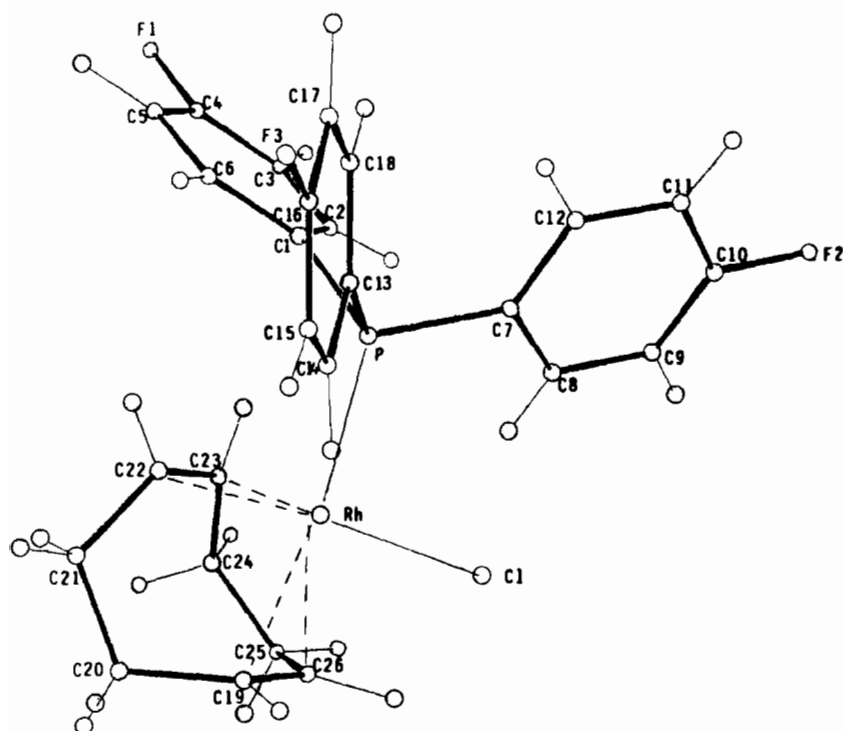
Fig. 1. Molecular structure of RhCl(COD)P(p-C$_6$H$_4$F)$_3$.

TABLE II. Atomic Parameters for RhCl(COD)P(p-C$_6$H$_4$F)$_3$. Thermal Parameters as: $U_{eq} = (1/3)[U_{ij}a_i^*a_j^*a_ia_j \cdot \cos(a_ia_j) \times 10^4]$

Atom	x/a	y/b	z/c	U_{eq}
Rh	0.03040(4)	0.22066(4)	0.34020(2)	389(1)
P	−0.17320(11)	0.22625(11)	0.29240(7)	308(3)
Cl	0.06808(15)	0.32718(15)	0.23777(10)	538(5)
F1	−0.47137(40)	−0.10124(40)	0.42614(27)	684(16)
F2	−0.27336(84)	0.07674(64)	−0.01791(28)	1319(36)
F3	−0.38653(51)	0.67181(38)	0.32483(37)	904(23)
C1	−0.27160(42)	0.13093(42)	0.33182(28)	317(13)
C2	−0.27388(51)	0.01889(45)	0.31113(32)	379(15)
C3	−0.33930(53)	−0.06025(47)	0.34267(38)	446(18)
C4	−0.40348(51)	−0.02507(53)	0.39552(35)	441(17)
C5	−0.40356(63)	0.08388(60)	0.42018(42)	553(23)
C6	−0.33615(59)	0.16075(51)	0.38741(38)	475(19)
C7	−0.20620(52)	0.18767(44)	0.19481(30)	370(15)
C8	−0.12620(64)	0.11441(64)	0.16868(39)	539(22)
C9	−0.14938(84)	0.07761(66)	0.09749(45)	643(27)
C10	−0.24923(108)	0.11424(77)	0.05260(42)	801(36)
C11	−0.33010(112)	0.18728(97)	0.07638(45)	936(41)
C12	−0.30842(84)	0.22281(75)	0.14783(39)	691(28)
C13	−0.24325(47)	0.36187(39)	0.30035(30)	335(14)
C14	−0.16777(56)	0.45278(49)	0.31954(36)	441(18)
C15	−0.21589(68)	0.55862(50)	0.32671(42)	541(23)
C16	−0.33878(67)	0.56912(50)	0.31697(45)	549(23)
C17	−0.41730(60)	0.48268(58)	0.29924(46)	584(23)
C18	−0.36823(54)	0.37745(49)	0.29089(39)	471(18)
C19	0.21170(60)	0.26426(66)	0.40500(45)	578(23)
C20	0.20788(87)	0.25995(96)	0.48646(54)	820(35)
C21	0.08377(102)	0.24532(123)	0.50510(50)	1005(47)
C22	−0.00490(66)	0.18453(84)	0.44645(40)	637(26)

(continued)

TABLE II. *(continued)*

Atom	x/a	y/b	z/c	U_{eq}
C23	0.01633(57)	0.08141(65)	0.41036(43)	573(23)
C24	0.13426(79)	0.01560(79)	0.42700(68)	895(40)
C25	0.23132(78)	0.05325(76)	0.38745(58)	736(31)
C26	0.22486(53)	0.17269(70)	0.36302(41)	549(22)

TABLE III. Bond Distances (A) and Valency Angles (°)

Rh–P	2.297(1)	Rh–Cl	2.366(2)
Rh–C19	2.234(7)	Rh–C22	2.097(8)
Rh–C23	2.130(8)	Rh–C26	2.216(6)
C23–Rh–C26	81.3(3)	C22–Rh–C26	95.5(3)
C22–Rh–C23	39.8(3)	C19–Rh–C26	35.7(3)
C19–Rh–C23	90.6(3)	C19–Rh–C22	81.0(3)
Cl–Rh–C26	89.8(2)	Cl–Rh–C23	160.7(2)
Cl–Rh–C22	159.2(3)	Cl–Rh–C19	92.0(2)
P–Rh–C26	162.8(2)	P–Rh–C23	95.1(2)
P–Rh–C22	92.2(2)	P–Rh–C19	161.5(2)
P–Rh–Cl	88.4(1)		

been studied at 23, 35 and 50 °C at a hydrogen pressure of 4 atm. The catalyst concentration was 1×10^{-3} mol/l. A typical run employs 0.1 mmol of **I**, **II** or **III**, and 40 mmol of olefin.

Details of the method can be found in 'Experimental'. Experimental results are presented in Table IV.

In Fig. 2(a,b,c) the evolution of the reactant and products with reaction time at 23, 35 and 50 °C is given for catalysts **I**, **II** and **III** respectively. Several features can be observed there: first of all there exists an induction period for catalyst **I**, clearly observed at lower reaction temperatures, indicating that the compound $RhCl(COD)P(p\text{-}C_6H_4F)_3$ (**I**) is not the catalyst but just a precursor that in the presence of hydrogen is transformed into an active intermedia that can act as catalyst.

The induction period decreases with temperature as the hydrogen incorporation reaction becomes faster. No induction period is observed with catalysts **II** and **III**.

The relative activity of the catalyst follows the order: **III** > **II** > **I** at 23 and 35, but at 50 °C the most active catalyst is **I** followed by **II** and **III**. The low activity shown by catalyst **I** at the lower temperatures would be a consequence of the fact that in these conditions the controlling step is the formation of the active catalytic species from the precursor. On the other hand, and due to the higher activation energy of this process with respect to the hydrogenation of 1-hexene, at 50 °C the rate of hydrogenation of 1-hexene becomes faster than the formation of the catalytic species, the induction period disappears and consequently the catalyst shows its real catalytic capacity. In these conditions catalyst **I** is indeed the most active, as one would expect from the structure, electronic and coordinatively unsaturated.

TABLE IV. Catalytic Hydrogenation of 1-Hexene

Compound	T (°C)	30 Minutes			60 Minutes			180 Minutes		
		% HO	% H2C	% H2T	% HO	% H2C	% H2T	% HO	% H2C	% H2T
I	35	1.5	0.7	1.8	2.4	0.4	0.7	6.0	2.0	0.6
	50	64.0	1.1	0.1	91.1	1.0	0.4	100		
	70	75.0	5.3		88.0	1.7		100		
II	23	8.6	0.3	0.6	13.9	0.7	1.1	22.9	2.6	0.5
	35	10.2	1.4	0.5	16.2	2.7	0.5	27.3	6.9	0.2
	50	18.1	3.6	0.4	28.3	7.7	0.2	50.6	11.9	0.1
III	23	11.9	1.3	0.5	18.5	2.6	0.5	43.0	8.1	1.2
	35	18.6	2.7	0.5	29.0	4.6	0.4	59.7	9.8	1.1
	50	33.7	7.6	0.2	38.5	10.3	1.1	64.3	9.6	0.1

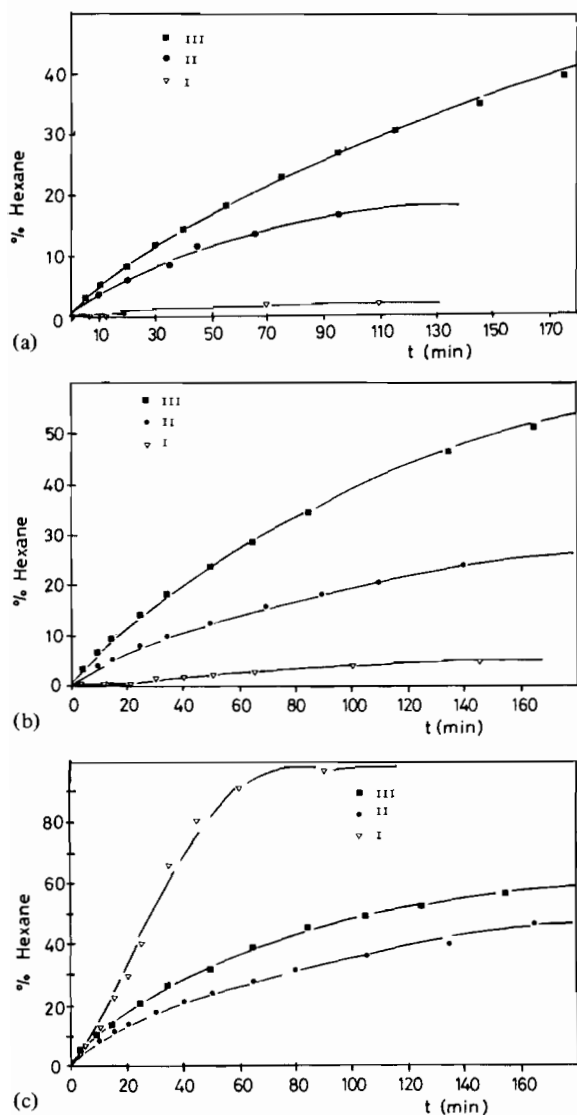HO = hexane, H2C = 2-*cis*-hexene, H2T = 2-*trans*-hexene.

(a)

(b)

(c)

Fig. 2. Catalytic hydrogenation of 1-hexene with **I, II** and **III** complexes as catalysts; (10^{-3} M) in acetone (a) T = 23 °C; (b) T = 35 °C; (c) T = 50 °C.

From the curve giving the yield of hexane at different reaction times its initial rate of formation can be calculated at 23, 35 and 50 °C for catalysts **II** and **III**, and at 50 and 70 °C for catalyst **I**. From these values and the Arrhenius equation the apparent activation energies for catalysts **I, II** and **III** have been calculated to be 5.8, 6.0 and 5.6 respectively. These results show that the mechanism of hydrogenation of 1-hexene on the three catalysts is the same.

In Fig. 3, as an example, we show the increase of activity with temperature, for catalyst **III**.

In Fig. 4(a,b,c) the selectivity curves for the different reaction products are given at 35 °C. The same selectivity behaviour is observed for the three catalysts which is further proof of the similar mecha-
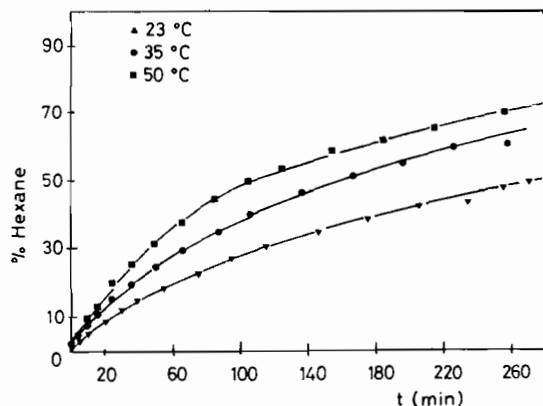

Fig. 3. Variation of activity with temperature for catalyst **III**, in the process of n-hexene hydrogenation.
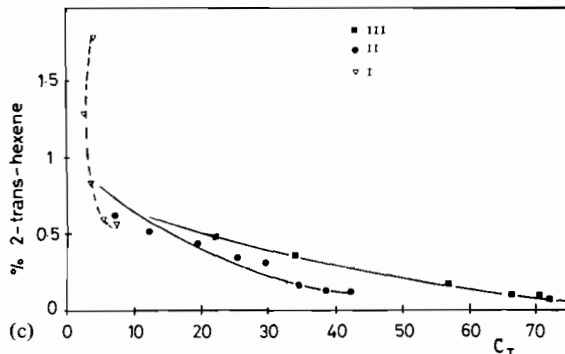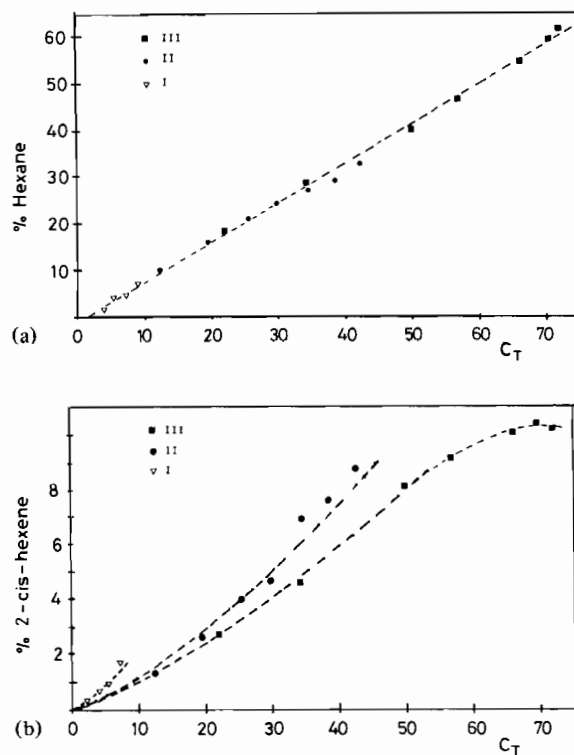

(a)

(b)

(c)

Fig. 4. Selectivity curves at 35 °C.

nism operating on the three of them. Furthermore, in this figure it is possible to see that hexane is a primary plus secondary stable product, *cis*-2-hexene is a primary plus secondary unstable product and *trans*-2-hexene is an unstable product. The primary character of hexane is easily explained from the direct hydrogenation of 1-hexene. In a similar way, the primary character of the *cis*-2-hexene can be explained by isomerization of 1-hexene. The secondary behaviour of hexane must be due to the hydrogenation of the *cis*-2-hexene formed in a first step. However, the secondary character of hexane is very slight, while the corresponding instability of the *cis*-2-hexene, generated by hydrogenation to hexane, is only apparent at high levels of conversion when the concentration of 1-hexene is highly depleted. This is a clear indication that on these catalysts *cis*-2-hexene is hydrogenated to hexane at a lower rate than 1-hexene. On the other hand, in Fig. 3c it can be observed that the initial amount of *trans*-2-hexene present as an impurity in the feed not only does not increase with the level of conversion, as would be expected if *trans*-2-hexene were to be formed by isomerization of 1-hexene, but decreases when increasing the total 1-hexene conversion. This observation can be explained by considering that *trans*-2-hexene is rapidly isomerized to *cis*-2-hexene and also that it is probably not formed by isomerization of 1-hexene. This in turns shows the very high selectivity of catalysts **I**, **II** and **III** as *cis* directing in the double bond isomerization process. Therefore, taking into account the product selectivity behaviour described above, the following common reaction network for the three catalysts can be written.
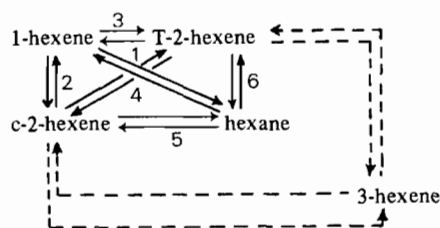
Scheme 2.

It is apparent from the experimental results that the rate of the different steps listed in Scheme 2 could be the following

$$r_1 > r_5, r_6; r_2 \gg r_3 \text{ and } r_4 \gg r_{4'}$$

Compound **I** behaves as a catalyst precursor in the process of hydrogenation of n-hexene, and it has an induction period that decreases with temperature. Once this period is over it is reasonable to presume the formation of an intermediate hydrogenated species, that we have not been able to isolate, which produces a rapid hydrogenation (it only takes a few minutes), and once the olefin reduction is over the catalyst decomposes giving Rh in the reaction vessel.

Compounds **II** and **III** do not have induction periods and their total activity is moderate.

Compound **II**, pentacoordinated without a hydrogen—hydride ligand, shows, after reaction, a hydride signal in its IR and ^{1}H NMR spectra at 23 °C, which confirms the presence of a solvated hydride species in solution after reaction with molecular hydrogen.

Catalyst **III**, a dihydride hexacoordinate complex, analyzed after the hydrogenation process, appears to be unaltered, its IR and ^{1}H NMR spectra are identical to the starting complex at different temperatures.

Acknowledgements

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