HOMOGENEOUS CATALYTIC HYDROGENATION AND ISOMERIZATION OF LINEAR AND CYCLIC MONOENES AND DIENES IN THE PRESENCE OF THE HETEROMETALLIC CLUSTER (η^5-C$_5$H$_5$)NiRu$_3$(μ-H)$_3$(CO)$_9$

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Summary

The complex (η^5-C$_5$H$_5$)NiRu$_3$(μ-H)$_3$(CO)$_9$ catalyses the selective hydrogenation of the terminal double bond of conjugated linear dienes in homogeneous conditions; isomerization of non-conjugated to conjugated dienes and of pent-1-ene to pent-2-enes also occurs. Selective hydrogenation and isomerization of cyclic hexenes and hexadienes takes place without opening of the ring; a reaction scheme is proposed, and the activity of the cluster itself relative to that of its decomposition products is discussed. Its behaviour is compared with the analogous complex (η^5-C$_5$H$_5$)NiOs$_3$(μ-H)$_3$(CO)$_9$.

Introduction

The chemistry of the homo- and heterometallic transition metal carbonyl clusters has attracted much attention mainly because of the considerable potential of such species in homogeneous catalysis; the multi-site activation of small molecules [1] and the presence of different metal centres is expected to lead to selective reaction patterns different from those observed for mononuclear compounds [2]. However, owing to the relatively low stability of the carbonyl clusters under the conditions generally required for catalytic processes, their potential has not been fully exploited; there are however a few cases in which the catalytic activity of the intact cluster has been fully demonstrated [3]. In most cases cluster-derived fragments have been found to be responsible for the observed reactivity.

We found that (η^5-C$_5$H$_5$)NiOs$_3$(μ-H)$_3$(CO)$_9$ (complex 1) [4,5] and its phosphine substituted derivatives [6] act as intact cluster catalysts in the homogeneous, selective hydrogenation and isomerization of monoenes and dienes [7]. Cluster 1 is also a precursor of heterogeneous catalytic systems, when supported (after thermal treatment) on Al$_2$O$_3$ [8,9] or on gas-chromatographic packings [10–12].
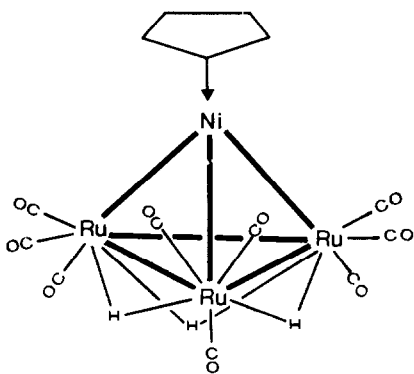
SCHEME 1. Structure of cluster **2**, hypothesized on analytical and spectroscopic results and on the analogy with the known structure of **1**.

We describe here another example of intact cluster catalysis, and we also show that the fragments have different catalytic properties from those of the parent complex. The ruthenium analogue of **1**, $(\eta^5\text{-}C_5H_5)NiRu_3(\mu\text{-}H)_3(CO)_9$ (complex **2**), [4,13] is known; originally it was obtained in only low yields but more convenient syntheses have recently been developed [14]. The suggested structure of the complex [4] is shown in Scheme 1.

The behaviour of **2** has been studied in the homogeneous catalytic hydrogenation and isomerization of linear and cyclic monoenes and dienes; the following substrates were examined, cis-1,3-pentadiene, 1,3-pentadiene, 1-pentene, cyclohexene, 1,3-cyclo-hexadiene, 1,4-cyclo-hexadiene and benzene. The activities and selectivities of clusters **1** and **2** towards the same substrates under identical conditions have been compared, and several similarities and some interesting differences found.

Complex **2** is less stable than **1** under the conditions used; it is less active in hydrogenation and more active in isomerization. This behaviour, together with other experimental evidence, points to intact cluster catalysis when hydrogenation occurs, and to "fragment" catalysis for isomerization. The behaviour of cyclic dienes, not previously examined, provides further support for the suggested reaction schemes.

Experimental

Materials

Complex **1** was prepared and purified as previously described [4]; complex **2** was obtained by a modification of known procedures [13,14]. This involved treatment of $Ru_3(CO)_{12}$ with $(Cp)_2Ni_2(CO)_2$ under hydrogen in Cellosolve at 95°C for 3 hours. Yields of about 75% based on ruthenium were reproducibly obtained; the complex was purified by preparative TLC (Kieselgel P.F. Merck, eluants light petroleum (40–70°C) and diethyl ether) and crystallized from hexane/chloroform at −10°C, under nitrogen, to give microcrystalline powder.

The dienes, monoenes and benzene were purchased from Fluka, Aldrich and C. Erba and were used as received, after ^{1}H NMR checks of purity; GLC was used for

detecting minor impurities in the ligands. n-Octane was distilled over sodium; carefully dried, ultrapure deuterium (Farmitalia Carlo Erba) and hydrogen (S.I.A.D.) were used.

Hydrogenation and deuteration experiments

The reactions were performed in sealed glass vials (volume 25 ml) each containing an n-octane (1–2 ml) solution of cluster **2** (2.5 mg) or **1** (5 mg) and the substrate to be hydrogenated (0.200 ml); the vials were filled with hydrogen (or deuterium) to 0.9 atm unless otherwise stated by standard vacuum techniques. Some isomerization experiments and the reactions of deuterated **2** with dienes and monoenes were performed similarly and with the same concentrations but in the absence of any gas.

The deuterated complex **2** was obtained, as reported for **1**, by exchange between complex **2** and D_2; complex **2** (40 mg) was dissolved in 50 ml n-octane and introduced into a vial (volume 250 ml). Deuterium (0.9 atm) was introduced and the sealed vial was thermostatted at 120°C for 40 minutes. After evaporation to dryness in vacuo, the residue was purified by preparative TLC as described above; about 85% of deuterated **2** was recovered and some decomposition products were observed. The ^1H NMR spectrum of deuterated **2** [15] showed only the cyclopentadienyl resonance, indicating a deuteration yield of ca. 99.8%.

Gas chromatographic analyses of the reaction solutions

The organic products in the solutions after isomerization and hydrogenation experiments were analysed with a Carlo Erba 4200 FID gas-liquid chromatograph equipped with 2 m × 0.6 cm i.d. columns and operated with N_2 (25 ml/min) as carrier gas, under the following conditions; linear C_5 molecules: n-octane/Porasyl C (100/120 mesh) column, 75°C for 10 min, then 20°C/min till 155°C. Cyclic C_6 molecules: bentonite column, 60°C for 6 min, then 5°C/min till 135°C. 1,3-cyclo-hexadiene: n-octane/Porasyl C (100/120 mesh) column, 60°C for 6 min, then 3°C/min till 135°C. The deuterated organic products and the unknown liquid or gaseous products from the homogeneous experiments were identified by means of a Carlo Erba 4200 FID and Kratos MS-50 linked GLC mass spectrometry system and in some cases by NMR studies, with a JEOL JNM GX 270 FT instrument.

Tentative identification of the organometallic products in the reaction solutions

The hydrogenation and isomerization solutions were checked by TLC for the decomposition of the catalyst and for the formation of new complexes. Complex **2** decomposes extensively after only 20–40 min reaction time, giving mainly insoluble (inorganic or polymeric) materials and very small amounts of organometallic products. The identification of the latter was thus based mainly on the comparison of their IR spectra with those of known products and, when possible, on mass spectrometric analysis. In the reaction solutions of linear monoenes and dienes, at least five different products in trace amounts were detected:

(a) A light-yellow complex (**A**); IR. (C_6H_{14}, $\nu(CO)$): 2096 m, 2070 vs, 2062 m(sh), 2050 m(sh), 2046 vs, 2027 s, 2017 s(sh), 2009 cm^{-1}. Mass spectrum $P^+ = 576$ m/e. Tentative identification $HRu_3(CO)_9(C_5H_7)$ by analogy with known derivatives [16];
(b) An unidentified yellow complex (**B**); IR (C_6H_{14}, $\nu(CO)$): 2064 vs, 1998 vs, 1987 vs(sh), 1950 m, cm^{-1}.

(c) A dark-brown violet complex (C);, IR (C_6H_{14}, ν(CO)): 2076 m, 2046 vs, 2010 s, 2006 s(sh), 1998 m, 1958 m, cm^{-1}. Mass spectrum $P^+ = 724$ m/e. Tentative identification (Cp)NiRu$_3$H$_3$(CO)$_8$(C$_5$H$_8$) by comparison with the analogous derivatives of complex 1 [7].

(d) An unidentified orange complex (D); IR (C_6H_{14}, ν(CO)): 2065 s, 2038 vs, 2026 s(sh), 2001 s, cm^{-1}.

(e) An unidentified dark-yellow, nearly insoluble complex (E); IR (C_6H_{14}/CHCl$_3$, ν(CO)): 2056–2020 m(vb), 2009 m, 1975 s, 1945 vs, cm^{-1}. The low frequency of the more intense carbonyl stretching band could indicate a mononuclear derivative.

Several isomers of complexes **A** and **C** (as well as other unidentified derivatives) may be present, depending on the *cis/trans* isomerism in the coordinated dienes.

The reaction solutions of cyclic substrates contained mainly decomposition materials; only one (a yellow) derivative in trace amounts was isolated (complex **F**): IR (C_6H_{14}, ν(CO)): 2111 m, 2083 s, 2056 s, 2036 s, 2025 s, 2010 s, 2000 s(sh), 1980 m, cm^{-1}, mass spectrum $P^+ = 636$ m/e, loss of 9 CO's: tentatively identified as $H_2Ru_3(CO)_9(C_6H_4)$ by analogy with known derivatives [17].

Finally, when $M_3(CO)_{12}$ (M = Ru, Os) were used in isomerizations, complexes HM$_3$(CO)$_9$(RCCHCR′) similar to those described in ref. 7 were found in the case of linear dienes, and complexes isostructural with F were tentatively identified in the solutions from cyclic dienes.

Results and discussion

Hydrogenation experiments

(a) cis-1,3-Pentadiene in the presence of 2: a comparison with the behaviour of 1. For an evaluation of the hydrogenating properties of cluster **2** we chose as substrate cis-1,3-pentadiene, which had already been extensively studied in the presence of cluster **1** [7]; the same solvent, temperature and procedures were used. The results of the hydrogenations in the presence of **2** are shown in Table 1.

A comparison between the behaviour of **1** and **2** in these reactions can be made from Table 2, where the turnovers, the 2-pentenes/1-pentene and *trans-/cis*-2-pentene ratios are shown, together with the extents of decomposition of the clusters.

Complex **2** gives a higher reaction rate (a turnover of 140 is observed after 1 h, compared with 21 for cluster 1); however, the overall catalytic efficiency is greater for **1**. In our opinion this is due to the greater stability of **1**, which is recovered almost unaltered after some hours, whereas **2** decomposes extensively after only 40 min; the slowing of the reaction rate in both cases with the decomposition of the clusters points to intact cluster catalysis *.

In the presence of **2** the main product is *trans*-2-pentene, with some *cis*-2-pentene and smaller amounts of 1-pentene. The 2-pentenes/1-pentene and the *trans-/cis*-2-pentene ratios are higher for **2** than for **1**; this indicates a greater isomerization ability for **2** (see discussion below).

For the hydrogenation of dienes in the presence of cluster **1** we had earlier suggested a reaction scheme [7] involving the formation of a free coordination site,

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* The lower reaction rate at 85°C, where the cluster is decomposed to a very small extent, also favours this hypothesis.

TABLE 1

HYDROGENATION REACTIONS OF *cis*-1,3-PENTADIENE IN THE PRESENCE OF **2**

Experiment	Reaction time (min)	Turnover [a]	Composition of the organic mixtures (organic products) (%)					Extent of decomposition of **2** (%) and organometallic products [b]
			pentane	1-pentene	*t*-2-pentene	*c*-2-pentene	substrate	
1 [c]	10	1	–	tr [d]	–	–	99.9	80%, **A, C, D**
	20	2	–	0.3	–	–	99.6	
	30	4	–	0.7	–	–	99.3	
	40	7	–	1.1	–	–	98.8	
2 [e]	10	15	0.2	0.2	1.4	0.4	97.8	70%, **A, C, D**
	20	48	0.2	1.2	5.2	1.4	91.9	
	40	117	0.2	2.1	14.6	3.6	79.4	
	60	140	0.8	7.3	12.5	4.5	74.8	
3 [f]	20	44	0.2	0.6	5.0	1.7	92.5	50%, **A, C, D**
	20	20	0.2	0.2	1.9	0.8	96.9	
	20	15	0.2	0.2	1.1	0.7	97.7	
	20	10	0.2	0.2	0.5	0.4	98.6	
4 [g]	20	105	0.3	1.9	12.7	3.6	81.5	40%, **C, D**
	20	160	0.3	3.8	18.6	5.6	71.6	
	20	221	0.6	5.3	23.4	10.1	60.6	
	20	226	1.4	7.3	18.4	13.1	59.8	
5 [h]	10	8	–	0.1	0.5	0.15	99.2	100%, **A, D**
	20	23	–	0.4	2.3	0.8	96.5	
	30	19	–	0.3	2.0	0.6	97.1	
	40	16	–	0.2	1.6	0.5	97.7	
6 [i]	10	12	0.8	–	0.2	tr	98.9	10%, none
	20	18	0.9	tr	0.5	0.1	98.4	
	30	26	1.0	0.1	0.9	0.2	97.7	
	40	31	1.0	0.2	1.3	0.3	97.2	

[a] Moles of substrate reacted per mole of **2**. [b] The extent of decomposition is the maximum observed for long reaction times; the organometallic products were always found in trace amounts. [c] At 120°C in the absence of hydrogen. [d] tr = traces. [e] Under 0.9 atm of dihydrogen, at 120°C. [f] At 120°C, hydrogen pressure 1.00, 0.75, 0.50, 0.25 atm respectively for the four entries. [g] At 120°C, diene concentration 1.70, 0.85, 0.42, 0.21 mol l^{-1} respectively for the four entries. [h] At 120°C in the presence of H_2 and CO (1 : 1 v/v) 0.9 atm. [i] At 85°C under 0.9 atm of hydrogen.

TABLE 2

COMPARISON OF THE BEHAVIOUR OF CLUSTERS 2 AND 1 IN THE HYDROGENATION OF
cis-1,3-PENTADIENE. Turnover numbers, 2-pentenes/1-pentene ratio (A), trans/cis-2-pentene ratio (B)
and approximate extent of decomposition of the clusters (C)

Experiment (cluster)	Reaction time	Turnover numbers	A	B	C [a] (%)	Reference
1 [b]	4 h	6	4.33	2.25	2	7
	6 h	12	5.40	3.50		
2 [b]	10 min	5	–	1.57	40	this work
	20 "	9	–	1.76		
	30 "	19	–	1.85		
	40 "	27	–	2.18		
1 [c]	1 h	21	3.08	1.37	20	7
	2 h	29	2.78	1.40		
	4 h	231	4.31	1.28		
	6 h	247	3.43	1.30		
	24 h	357	4.37	1.29	> 50	7
2 [c]	10 min	15	9.0	3.5	70	this work
	20 "	40	5.50	3.7		
	30 "	117	8.67	4.0		
1 [d]	4 h	282	3.50	1.67	15	7
	4 h	191	4.53	1.65		
	4 h	143	5.29	1.76		
	4 h	108	5.80	2.30		
2 [d]	20 min	44	11.2	3.0		this work
	20 "	20	13.5	2.4		
	20 "	15	9.0	1.6		
	20 "	10	4.5	1.2		
1 [e]	4 h	203	3.64	1.62	15	7
	4 h	259	3.17	1.23		
	4 h	337	3.16	1.36		
	4 h	386	4.50	1.37		
2 [e]	20 min	105	8.6	3.5	40	this work
	20 "	160	6.4	3.3		
	20 "	221	6.3	2.3		
	20 "	226	4.3	1.4		
1 [f]	1 h	2	3.0	2.0	15	7
	2 h	2	3.0	2.0		
	3 h	2	3.0	2.0		
	4 h	5	1.8	2.0		
2 [f]	10 min	8	6.5	3.3	100	this work
	30 "	23	7.7	2.87		
	30 "	19	8.7	3.3		
	40 "	16	10.5	3.2		

[a] Maximum extent of decomposition, after the longest reaction time. [b] In the absence of hydrogen. [c] Under 0.9 atm. of hydrogen. [d] Decreasing hydrogen pressure (see Table 1). [e] Decreasing diene concentration (see Table 1). [f] Under 0.9 atm. of CO/H_2 (1 : 1 v/v).

coordination of diene via the terminal double bond only, intermolecular hydrogen transfer, and formation of σ-alkyl derivatives, followed by release of the hydro-genated products in the presence of external hydrogen. Observations supporting this hypothesis were the easy exchange of the cluster-bound hydrides with external D_2, the decrease in the turnover number with decrease in the H_2 pressure and its
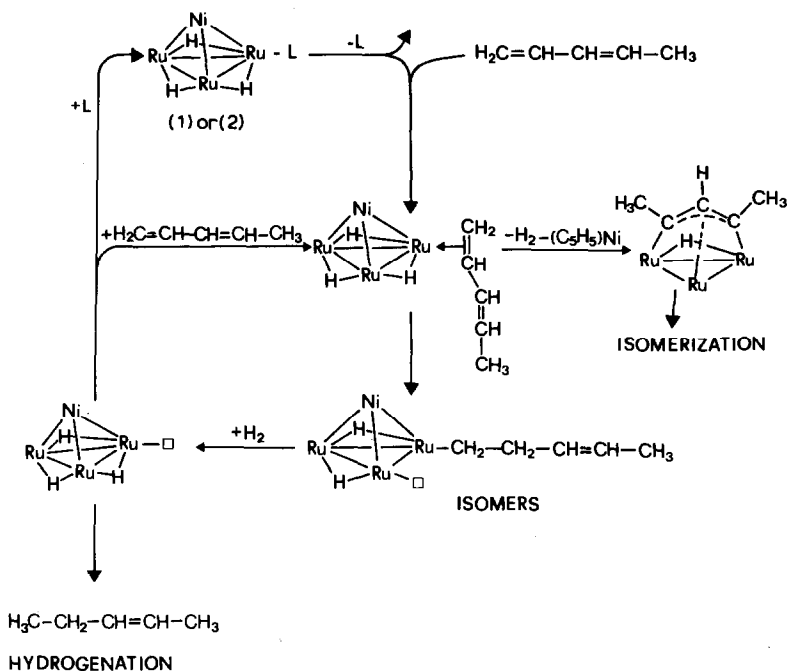
Fig. 1. Hypothesized hydrogenation and isomerization patterns for linear dienes, on cluster 2.

increase with decrease in the diene concentration, and the inhibition of the reaction in the presence of CO; further evidence was obtained from deuteration experiments and by the identification of intermediate products.

In the case of complex 2 we find comparable behaviour, namely: (i) ready exchange between the cluster-bound hydrides and external D_2; (ii) formation of small amounts of $(1,2-D_2)$ cis-1,3-pentadiene and some deuterated monoenes when $(Cp)NiRu_3D_3(CO)_9$ is used in the absence of hydrogen; (iii) decrease in the turnover number when the hydrogen pressure is reduced and increase in the turnover number on reducing the diene concentration; (iv) inhibition of the reaction in the presence of CO; (v) formation of trace amounts of complexes C in the reaction solutions. The latter complexes are homologues of the intermediate products found for 1 [7]. In spite of the easier decomposition of 1, which certainly requires metal–metal bond cleavage, we could not detect butterfly intermediates, although these were found in the presence of alkynes [18], which probably act as stabilizing ligands.

All the above evidence, together with the fact that 2 shows good selectivity for the hydrogenation of the terminal double bonds and that the activity decreases when the cluster starts to decompose point to intact cluster catalysis in the presence of 2. As expected, at 85°C the same products are obtained but the reactions are considerably slower. On the basis of the above results a reaction path similar to that proposed for 1 [7] can be suggested and is shown in Fig. 1.

Another point which deserves some comment is that there are minor differences in the pattern of 2-pentenes/1-pentene ratios (figures A) and trans-/cis-2-pentene

ratios (figures B) for **1** and **2**; this is shown below:

		Increasing reaction time			Same reaction time	
		Without H_2	With H_2	With CO/H_2	Decreasing H_2	Decreasing Diene
(A)	Cluster 1	increases	increases	decreases	increases	increases
	Cluster 2	no reaction	stable	increases	decreases	decreases
(B)	Cluster 1	increases	stable	stable	increases	increases
	Cluster 2	increases	increases	stable	decreases	decreases

This could indicate that alongside hydrogenations on the intact cluster there are other processes due to fragments whose formation is sensitive to the presence of ligands.

(b) Cyclic monoenes, dienes and benzene. Hydrogenation and isomerization experiments. These compounds (cyclohexene, 1,3- and 1,4-cyclohexadiene, benzene) had not been investigated previously; reaction conditions similar to those used for the linear substrates were adopted, in the presence of **2**. The results (except for benzene) are shown in Table 3.

The 1,3-cyclohexadiene, a conjugated molecule, is hydrogenated to cyclohexene with reaction rates and turnovers comparable with those found for *cis*-1,3-pentadiene in the presence of **2**. Once again only one double bond is hydrogenated, moreover, the hydrogenation of cyclohexene to cyclohexane occurs very slowly. Complex **2** can hence be considered a selective catalyst for hydrogenation of one double bond of cyclic hexadienes; steric arguments cannot provide a satisfactory explaination for this behaviour and so electronic factors have to be invoked. The conjugated dienes should be favoured in terms of coordinating ability compared with the non conjugated dienes and the monoenes. In fact, the behaviour of 1,4-cyclohexadiene lies between that of the 1,3-isomer and that of cyclohexene; the 1,4-cyclohexadiene is hydrogenated at a slower rate than the 1,3. It is noteworthy, however, that in the early stages of the reaction considerable amounts of 1,3-cyclohexadiene are observed; this compound begins to disappear after some time and the amounts of cyclohexene to increase. Hence, it seems that 1,4-cyclohexadiene is first isomerized to the 1,3-isomer and this is then hydrogenated to cyclohexene; comparable behaviour has been found for a linear non-conjugated substrate, 1,4-pentadiene (see below). The overall course of the reaction is shown in Scheme 2:
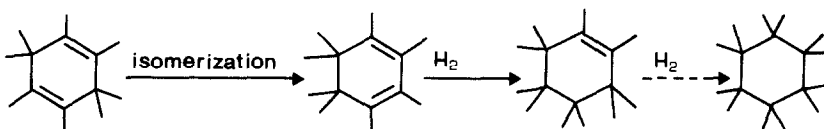
SCHEME 2.

Under these conditions benzene is hydrogenated very slowly; after 4 hours at 120°C there were only traces of cyclohexane and of 1,3-cyclohexadiene.

The behaviour of the cyclic dienes is further evidence for the hypothesis that the hydrogenation reactions occur on the intact cluster through coordination of only one double bond of the substrate, and that only one coordination site of the cluster is used. The suggested reaction path, similar to that proposed for linear substrates, is shown in Fig. 2.

Also noteworthy is that the hydrogenation of the conjugated linear and cyclic dienes is accompanied by extensive decomposition of cluster **2**; once again, however,

TABLE 3

HYDROGENATION (AND ISOMERIZATION) OF CYCLIC MONOENES AND DIENES IN THE PRESENCE OF **2**

Experiment	Reaction time (min)	Turnover [a]	Composition of the reaction mixtures (organic products) (%)						Extent of cluster decomposition (%) [c]
			Cracking [b]	hexenes	c-hexane	c-hexene	1,3-c-hexadiene	substrate	
Cyclohexene									
1 [d]	10	1	tr	tr	0.1	99.8 [e]	–	99.8	15
	20	3	tr	tr	0.4	99.5	–	99.5	
	30	11	tr	tr	1.8	98.0	–	98.0	
2 [f]	10	1	–	tr	0.1	99.8	–	99.8	10
	30	2	–	tr	0.2	99.7	–	99.7	
1,4-Cyclohexadiene									
1 [d]	10	15	tr	tr	–	0.7	1.8	97.4	20
	20	33	tr	tr	–	2.8	2.6	94.4	
	30	38	tr	tr	–	6.1	0.3	93.4	
2 [f]	10	3	–	tr	–	tr	0.4	99.5	20
	30	8	–	tr	–	0.3	0.8	98.7	
1,3-Cyclohexadiene									
1 [d]	10	17	tr	0.1	–	2.8	97.0 [e]	97.0	90
	20	70	tr	0.1	–	12.1	87.7	87.7	
	30	85	tr	0.2	–	14.4	85.2	85.2	
2 [f]	10	7	–	tr	–	1.0	98.8	98.8	80
	30	7	–	tr	–	1.2	98.7	98.7	

[a] Moles of substrate used per mole of **2**. [b] $C_1 + C_2$. [c] Maximum extent of decomposition observed after long reaction times. Only traces of complex **F** present in the solutions. [d] In the presence of 0.9 atm of dihydrogen. [e] When underlined, the same as the substrate. [f] In the absence of hydrogen.
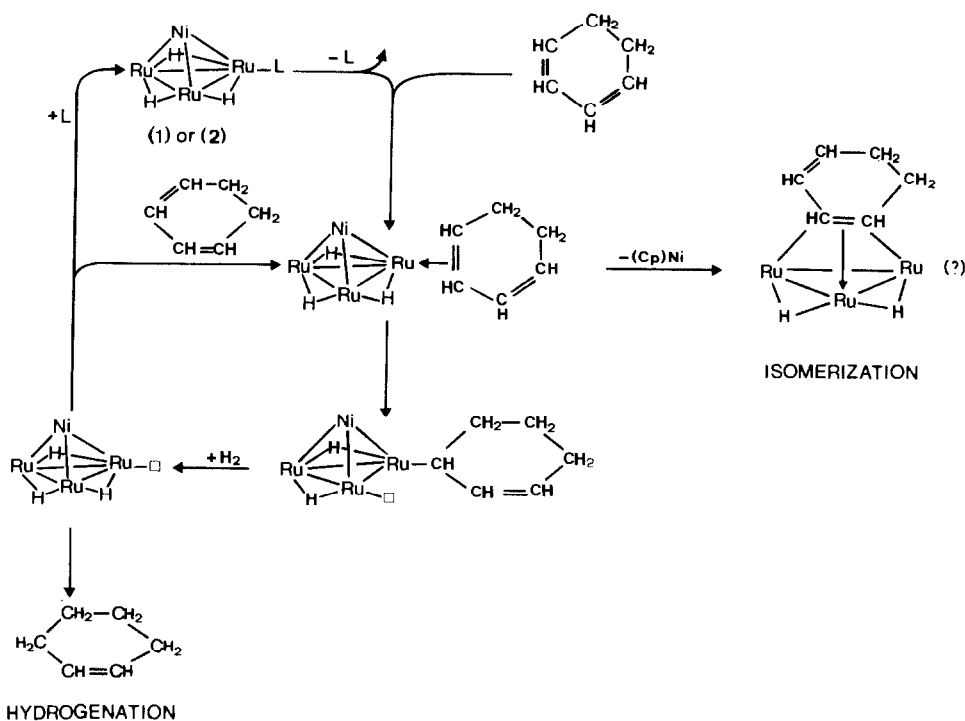
Fig. 2. Hypothesized hydrogenation and isomerization patterns for cyclic dienes on cluster **2**.

the reaction slows down when the cluster decomposes. Moreover, only traces of linear or of cracking products are observed; thus, apparently, the insoluble decomposition products have low hydrogenating activities. By contrast, cluster derived metal powders [18] readily cause C–C cleavage, and silica-supported ruthenium particles derived from clusters show considerable C–C bond cleavage ability with linear and cyclic hydrocarbons [19].

Isomerization experiments

(a) On linear dienes, in the presence of 2 and 1. Isomerization experiments were also carried out with 1-pentene (terminal monoene), 1,4-pentadiene (non-conjugated diene) and *cis*-1,3-pentadiene (in order to study *cis/trans* isomerization reactions) *; the results for complex **2** and of some experiments involving **1** are shown in Table 4. A comparison between the behaviour of cluster **2** and **1** in these reactions can be made from the results presented in Table 5.

The solutions containing **2** readily isomerize 1-pentene to *trans*- and *cis*-2-pentene with turnovers of 479 after 40 min and with a *trans/cis* ratio of 3 : 1, compared with a turnover of 142 after 6 hours and a 2 : 1 ratio for complex **1** [7] **. These

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* The hydrogenation/isomerization for cyclic substrates has been discussed above (see Table 3); that of the "fragment" is discussed in the next section.

** Both cluster **2** and $Ru_3(CO)_{12}$ catalyze the *cis/trans* isomerization of 2-pentene (see Table 6).

TABLE 4. ISOMERIZATION OF MONOENES AND DIENES IN THE PRESENCE OF CLUSTERS **2** AND **1**

Experiment	Reaction time (min)	Turnover [a]	Composition of the organic mixtures (organic products only) (%)					
			pentane	1-pentene	t-2-pentene	c-2-pentene	c-1,3-pentadiene	substrate
1-pentene								
1 [b]	40	–	–	–	–	–	–	100
2 [c]	10	17	tr	–	2.3	1.0	–	96.6
	20	235	tr	–	34.0	13.1	–	52.9
	30	473	tr	–	70.0	25.0	–	5.0
	40	479	tr	–	71.6	24.5	–	3.9
cis-1,3-pentadiene								
1 [b]	40	–	–	–	–	–	100 [d]	100
2 [c]	10	5	–	tr	0.11	0.07	99.81	99.81
	20	9	–	tr	0.60	0.34	99.05	99.05
	30	19	–	tr	1.70	0.92	97.38	97.38
	40	27	–	tr	2.81	1.29	95.90	95.90
1,4-pentadiene								
1 [b]	40	–	–	–	–	–	–	100
2 [c]	10	5	–	0.1	–	–	0.7	99.1
	20	34	–	0.7	–	–	5.7	93.6
	30	67	–	1.6	–	–	11.0	87.4
	40	79	–	2.1	–	–	12.8	85.1
3 [e]	1 h	0.5	–	–	–	–	tr	99.9
	2 h	1	–	–	–	–	0.2	99.7
	4 h	7	–	–	–	–	1.9	98.0
4 [f]	10	12	tr	0.2	–	–	1.9	97.8
	20	27	1.1	1.2	–	–	2.8	94.9
	30	42	1.4	1.7	–	–	4.7	91.3
5 [g]	1 h	77	0.2	5.50	15.10	–	–	79.20
	2 h	119	4.7	20.80	6.70	–	–	67.80
	4 h	106	3.2	22.40	3.30	–	–	71.10
	6 h	265	4.1	11.20	38.20	18.40	–	28.10

[a] Moles of substrate used per mole of cluster. [b] Experiment 1, in the absence of cluster. [c] Experiment 2, in the presence of **2** and in the absence of hydrogen. [d] When underlined, same as the substrate. [e] Experiment 3, in the presence of **1** and in the absence of hydrogen. [f] Experiment 4, in the presence of **2**, under 0.9 atm of hydrogen. [g] Experiment 5, in the presence of **1** under 0.9 atm of hydrogen (see ref. 7).

TABLE 5

COMPARISON OF THE BEHAVIOUR OF CLUSTERS 1 AND 2 IN THE ISOMERIZATION OF 1-PENTENE AND 1,4-PENTADIENE. Turnover numbers, isomerization products/substrate ratio (A), trans-/cis-2-pentene ratio (B) and approximate extent of decomposition of the cluster (C)

Experiment	Reaction time	Turnover	A	B	C [a] (%)	Reference
1-pentene						
Cluster 1 [b]	1 h	81	0.30	2.03	< 10	7
	2 h	111	0.47	1.60		
	4 h	133	0.62	1.57		
	6 h	142	0.69	1.39		
Cluster 2 [b]	10 min	17	0.034	2.3	20	this work
	20 "	253	0.89	2.6		
	30 "	473	19.0	2.8		
	40 "	479	24.60	2.9		
1,4-pentadiene						
Cluster 1 [b]	1 h	0.5	–	–	< 5	this work
	2 h	1	0.0002	–		
	4 h	7	0.019	–		
Cluster 2 [b]	10 min	5	0.028	–	90	this work
	20 "	34	0.064	–		
	30 "	67	0.12	–		
	40 "	79	0.14	–		
Cluster 1 [c]	1 h	77 [d]	– (0.26) [e]	–	< 10	7
	2 h	119	– (0.47)	–		
	4 h	106	– (0.41)	–		
	6 h	265	– (2.23)	–		
Cluster 2 [c]	10 min	12	0.019 (0.021)	–	30	this work
	20 "	27	0.029(0.054)	–		
	30 "	42	0.051(0.085)	–		

[a] Maximum extent of decomposition after the longest reaction time. [b] In the absence of hydrogen. [c] Under 0.9 atm of hydrogen. [d] Hydrogenation plus isomerization. [e] In parentheses the ratio of the hydrogenation plus isomerization products on the substrate.

solutions are also fairly active in the isomerization of 1,4-pentadiene to cis-1,3-pentadiene in the absence of hydrogen; in the presence of this gas, however, the isomerization/hydrogenation process is slower. By contrast, complex 1 shows a low isomerizing ability in the absence of hydrogen and a good isomerization-hydrogenation activity in the presence of it; however, a dramatic change in the reaction rate and in the type of products is observed after 4 h reaction time. This could indicate the presence of different catalytic species in the reaction solutions (e.g. mono- or poly-metallic cluster demolition fragments); evidence for this suggestion has been obtained from the experiments described below.

(b) Isomerization of linear and cyclic substrates in the presence of "cluster fragments". In an attempt to simulate the effect of cluster-derived fragments, we treated $Os_3(CO)_{12}$, $Ru_3(CO)_{12}$ and $(Cp)_2Ni_2(CO)_2$ with 1,4-pentadiene, 1,4-cyclohexadiene and cis-2-pentene; the results of these experiments are collected in Table 6.

In the presence of hydrogen, the trimetallic $M_3(CO)_{12}$ carbonyls (M = Ru, Os) display a considerable isomerizing ability towards the linear and cyclic substrates; $Ru_3(CO)_{12}$ has the higher activity and this is consistent with our suggestion that the

TABLE 6

HYDROGENATION AND/OR ISOMERIZATION EXPERIMENTS FOR NON-CONJUGATED DIENES AND *cis-2*-PENTENE IN THE PRESENCE OF $M_3(CO)_{12}$ (M = Ru, Os) AND $(Cp)_2Ni_2(CO)_2$.

Substrate and cluster	Turnover [a]	Composition of the reaction mixtures (organic substrates only) (%)				
1,4-pentadiene [b]		Cracking [c]	pentane	1-pentene	1,3-pentadiene	substrate
$Ru_3(CO)_{12}$	113	tr	—	6.5	38.9	54.5
$Os_3(CO)_{12}$	104	tr	—	7.4	22.0	70.5
$(Cp)_2Ni_2(CO)_2$	17	tr	0.3	12.9	0.8	85.9
1,4-cyclohexadiene [b]		Cracking	hexane	cyclohexene	1,3-cyclohexadiene	substrate
$Ru_3(CO)_{12}$	65	—	—	12.2	11.5	76.3
$Os_3(CO)_{12}$	42	—	—	6.5	4.4	89.1
$(Cp)_2Ni_2(CO)_2$	14	—	1.0	9.6	—	89.4
cis-2-pentene [d]		1-pentene	t-2-pentene			substrate
Cluster 2	414	1.9	79.8			18.3
$Ru_3(CO)_{12}$	177	5.2	69.4			25.4

[a] Moles of substrate reacted per mole of cluster. [b] at 120°C, under 0.9 atm hydrogen, for 40 min. [c] Unidentified $C_1 + C_2$. [d] at 120°C, for 40 min, without hydrogen.

isomerization reactions are due to fragments. These results, in our opinion, provide conclusive evidence for the isomerizing effect of "cluster fragments" and also indicate that the isomerization reaction occurs when more than one coordination site is available. Similarly some complexes of **A** and **F** type and allylic derivatives similar or homologues to those described for cluster **1** [7] were observed in the reaction solution. Further evidence for the above hypotheses, comes from the fact that *cis*-2-pentene, which can occupy only one coordination site, is in the absence of hydrogen isomerized better in the presence of cluster **2** than in the presence of $Ru_3(CO)_{12}$.

By contrast, the nickel "fragments" display only hydrogenation and (in part) C–C bond cleavage ability; thus it is again evident that the hydrogenation/isomerization sequences observed are due to the presence of the two different metals which form a well defined cluster structure.

Concluding remarks.

Cluster **2** is a selective hydrogenation catalyst either for linear and cyclic dienes, and acts as an intact entity in solution; its activity is lower than that of complex **1** because of its lower stability. When fragments are formed, good isomerization activity is observed. Furthermore the ruthenium or nickel containing "fragments" have different effects, which indicates that the presence of both metals is important. The effect of the (Cp)Ni unit is probably to stabilize the cluster by capping [20] the ruthenium atom triangle and also to favouring the release of some carbonyl groups from the cluster as a result of a *trans*-effect [21]. Indeed, all the phosphine-derivatives of cluster **1** give axial substitution, that is the ligands enter *trans* to the nickel [22], and this is apparently also the case for cluster **2** [23].

The reactions described represent a further example of homogeneous catalysis due to an intact cluster entity, and also provide sound evidence for a different behaviour of the cluster-derived fragments; there have, to our knowledge, been very few similar comparisons of the reactivities of clusters with those of the possible fragments.

Acknowledgements

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