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# Metal carbonyl clusters in homogeneous catalysis. Hydrogenation and isomerization of cyclic dienes in the presence of $[H_4Ru_4(CO)_{12}]$, $[H_2Ru_4(CO)_{13}]$, $[H_2FeRu_3(CO)_{13}]$ and $[Fe_2Ru(CO)_{12}]$. Identification of organometallic products and a discussion of their role

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## Abstract

The hydridic tetrahedral clusters $[H_4Ru_4(CO)_{12}]$ (**1**), $[H_2Ru_4(CO)_{13}]$ (**2**) and $[H_2FeRu_3(CO)_{13}]$ (**3**), and the related $[Fe_2Ru(CO)_{12}]$ (**4**), have been tested as homogeneous catalysts for the hydrogenation–isomerization of 1,3- and 1,4-cyclohexadiene. Catalytic activity was found but there is evidence for metal species rather than intact clusters to account for the observed behaviour.

After the hydrogenation experiments, diene- and arene-substituted clusters and organometallic derivatives were found in solution. Their nature was confirmed by spectroscopic analyses, mass spectrometry and, in some instances, by independent synthesis. Their role in the hydrogenation reactions is discussed. Deuteration experiments showed that hydrogen adds first to the cluster metals and is then transferred to the coordinated substrate.

*Keywords:* Iron; Ruthenium; Clusters; Hydrogenation; Cyclohexadienes; Catalysis

## 1. Introduction

We are interested in the behaviour of homo- and hetero-metallic carbonyl clusters as homogeneous hydrogenation and isomerization catalysts of alkynes, alkenes and dienes. We have found that tri-and tetranuclear ruthenium clusters are active in these reactions [1] and we recently reported that $[H_4Ru_4(CO)_{12}]$ (**1**), $[H_2Ru_4(CO)_{13}]$ (**2**) and $[H_2FeRu_3(CO)_{13}]$ (**3**), and the related $[Fe_2Ru(CO)_{12}]$ (**4**), hydrogenate diphenylacetylene to *cis*- and *trans*-stilbene in the presence of dihydrogen [2]. Our study was aimed at detecting the role of the alkyne-substituted complexes found in the reaction mixtures. We showed that most of these complexes are inactive side-products and that only the dihydride $[H_2Ru_3(CO)_9(C_2Ph_2)]$ (A) [3] is an intermediate.

We have investigated the reactivity of complexes **1**–**4** towards cyclic dienes and compared their behaviour with that of the tetrahedral hydride $[(CpNi)Ru_3(\mu\text{-}H)_3(CO)_9]$ (**5**) [4] and of $[Ru_3(CO)_{12}]$. The structures of complexes **1**–**5** are shown in Fig. 1.

The substitution reactions of $[Ru_3(CO)_{12}]$ with 1,3-cyclohexadiene have already been studied (vide infra). This made easier the identification of some organometallic complexes found in the hydrogenation solutions. These were $[Ru(CO)_3(C_6H_8)]$ (B), $[H_2Ru_3(CO)_9(C_6H_6)]$ (E), $[H_2Ru_3(CO)_9(C_6H_4)]$ (F), $[HRu_3(CO)_9(C_6H_7)]$ (G), $[Ru_3(CO)_9(C_6H_6)]$ (H), $[Ru_4(CO)_9(C_6H_6)(C_6H_8)]$ (I) and $[H_2Ru_4(CO)_{10}(C_6H_6)]$ (L); this last identification is only tentative.

We again found that most of these derivatives, except B, are side-products and not intermediates in the hydrogenation reactions, despite the fact that E and F have structures comparable with that of A.

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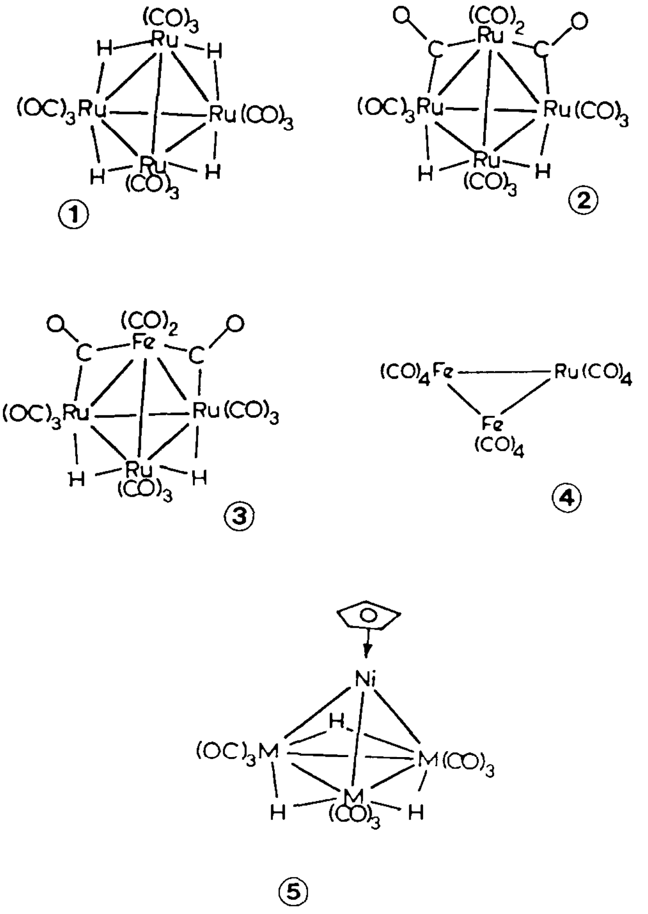

Fig. 1. Structures of complexes 1–5.

## 2. Experimental details

### 2.1. General experimental procedures, materials and analysis of the products

Clusters **1–4** were prepared as already described [2]. The dienes (Fluka) were commercial products used as received after purity checks. Dihydrogen and dinitrogen were dried prior to use. Deuterium was purchased from Union Carbide (UCAR, Belgium). The independent syntheses of complexes B, E–H and L were performed in conventional glassware consisting of three-necked flasks equipped with gas inlet, condenser, mercury pressure-release valve and magnetic stirrer. The solvents (heptane, octane, toluene) were dried over sodium. The reaction mixtures were taken to small volume under reduced pressure and purified by TLC (Kieselgel Merck, mixtures of diethyl ether and light petroleum as eluants). When possible, the complexes were crystallized from suitable solvents.

Compounds were analyzed with a F & M CHN Analyzer and a Perkin-Elmer atomic absorption spectrometer. Some analyses were performed by F. Pascher (Remagen, Germany). The complexes were characterized by IR (Perkin-Elmer 580), $^1H$ and $^{13}C$ NMR (JEOL EX-400 FT) spectroscopy and EI or CI mass spectrometry [5].

### 2.2. Hydrogenation and isomerization of 1,3- and 1,4-cyclohexadiene

The hydrogenation and isomerization reactions were performed in sealed vials (25.0 ml volume) as described earlier [2]. The organic products in the reaction solutions were analyzed with a Carlo Erba FID 4200 gas–liquid chromatograph equipped with 2 m × 0.6 mm n-octane/Porasil C, 80–100 mesh, columns used as follows: 60°C (6 min) then 3°C min$^{-1}$ up to 135°C; $N_2$ 25 ml min$^{-1}$.

### 2.3. Identification of organometallic products in the hydrogenation and isomerization solutions

After GLC, the solutions were purified on TLC plates and the fractions analyzed by spectroscopy and/or by elemental analyses.

In a great number of experiments, complexes F–H, together with a mixture of B and of other complexes tentatively identified as $[H_2Ru_3(CO)_9(C_6H_6)]$ (E, two isomers) and $[H_2Ru_4(CO)_{10}(C_6H_6)]$ (L) were obtained; L 'disappeared' during TLC elution, probably forming E and B. An analysis of a fresh specimen of L was made possible by collecting the complex after rapid elution.

Complex B [6]: IR ($\nu_{co}$, $C_7H_{16}$) (cm$^{-1}$): 2064 (vs); 1995 (vs, b). MS (EI) *m/z*: $P^+ = 266$, loss of three COs.

Complex E: IR ($\nu_{co}$, $C_7H_{16}$) (cm$^{-1}$); 2096 (m–s); 2070 (vs); 2042 (vs); 2026 (vs); 2012 (vs); 2002 (sh); 1985 (m–s). $^1H$ NMR ($CDCl_3$, rt)δ: 9.04 (s,1H,CH); 4.84 (s,1H,CH); 3.65 (s,4H,$CH_2$); −18.51 (s,2H,hydrides) ppm. MS (NICI and PICI) *m/z*: '$P^+$' = 633 (li [7]: expected 638); 568 (i, $Ru_3$ pattern); 543 (vi); 514 (i).

Complex E′: IR ($\nu_{co}$, $C_6H_{14}$) (cm$^{-1}$): 2114 (m); 2075 (m); 2053 (vs); 2012 (s); 2003 (m); 1986 (m). $^1H$ NMR ($CDCl_3$, rt)δ: 3.83 (s,4H,$CH_2$); 3.06 (s,2H,CH); −14.85 (s,2H,hydrides) ppm. MS (PICI, NICI): see E.

Complex F [4]: IR ($\nu_{co}$, $C_7H_{16}$) (cm$^{-1}$): 2111 (m); 2083 (s); 2056 (s); 2036 (s); 2025 (s); 2010 (s); 2000 (s sh); 1980. MS (EI) *m/z*: $P^+ = 636$, loss of 9 CO/s, then complex fragmentation.

Complex G: MS (PICI) *m/z*: 633 (li); 594 (li, $Ru_3$ pattern); 556 ($P^+ - 3CO$, i); 529 (vi); 500 (vi); 473 (vi). MS (NICI): comparable fragmentation starting from *m/z* 594.

Complex H: MS (PICI) *m/z*: 635 (li); 594 (li, isotopic pattern $Ru_3$); 556, 528, 500, 473 (vi/i). MS (NICI) *m/z*: 556, 528, 500, 473 (vi/i).

Complex L: IR ($\nu_{co}$, $C_7H_{16}$) (cm$^{-1}$): 2064 (vs); 2050 (s sh); 1996 (vs); 1989 (vs sh); 1970 (s b). $^1H$ NMR ($CDCl_3$, rt); see that of E. MS (NICI and PICI) *m/z*:

712 (i, $Ru_4$ pattern); 690, 670, 630, 583, 555 (i/vi); 527, 499 (mi). Starting from $m/z$ 583, isotopic pattern $Ru_3$.

### 2.4. Independent syntheses of the organometallic complexes B and E–L. Reactions of $[Ru_3(CO)_{12}]$ and complexes 1 and 2 with 1,3-cyclohexadiene

Treatment of complex **1** (200 mg, 0.27 mmol) with $Me_3NO$ (100 mg, 1.33 mmol) and 2.0 ml (21.0 mmol) of 1,3-cyclohexadiene (1,3-CHD) under $N_2$ in toluene, at reflux for 3 min yielded an orange–brown suspension. This was taken to small volume under reduced pressure and purified by TLC. The yellow complexes (F, 5%), (G, 5%) and (H, 5%) were collected but small amounts of the B, E–E′, L mixture were also observed.

Treatment of cluster **2** (100 mg, 0.13 mmol) with 1,3-CHD (2 ml, 21.0 mmol) in octane, under $N_2$ for 1 min with reflux, yielded a dark yellow solution. After TLC purification the complexes referred to above, were recovered in comparable yields.

Treatment of $[Ru_3(CO)_{12}]$ (400 mg, 0.63 mmol) with $Me_3NO$ [8] (0.5 g, 6.7 mmol) and 1,3-CHD (2.0 ml, 20.1 mmol) under $N_2$ in toluene for 3 min at reflux yielded a clear red–brown solution and a metallic deposit. TLC purification of the filtrate gave unreacted $[Ru_3(CO)_{12}]$ (20%) and complexes F, G and H (5%–10% each) as described above. The reaction was repeated under similar conditions using heptane as a solvent. The results were similar.

### 2.5. Hydrogenation of the organometallic complexes

Complexes E, G F were treated under $H_2$ in sealed vials as previously described [2]. Complex G was also tested as a catalyst for the hydrogenation of 1,3-CHD. Among the organometallic products of the hydrogenation reactions of G we observed well-formed red–purple crystals which were sparingly soluble in hydrocarbons (complex I), identified by IR and mass spectra.

Complex I IR ($\nu_{CO}$, $C_7H_{16}$) ($cm^{-1}$): 2090 (m); 2062 (vs); 2040 (s); 2033 (vs); 2013 (s); 2003 (m–w). MS (PICI) $m/z$: 796 (li, $P^+-CO$); 748 (i); 716 (i); 688 (i). MS (NICI) $m/z$: 716 (vi, isotopic pattern $Ru_4$); 688 (li).

### 2.6. Deuteration experiments

(a) *Attempted synthesis of deuterated clusters* **1–3**.

The synthetic method used for complexes **1–4** [2] involves water. However, attempts to obtain deuterated clusters **1–3** by adding $D_2O$ to the reaction mixture led to non-deuterated clusters **1–3** (IR and $^1H$ NMR spectra). $[H_4Ru_4(CO)_{12}]$ (**1**) (0.5 g, 0.67 mmol) was suspended in toluene (100 ml) in a 250 ml vial and 1.5 ml of $CH_3OD$ added. After sealing under vacuum, the vial was heated at 120°C for 1 h and on cooling a reddish insoluble material was deposited. The yellow solution was taken to small volume and purified by TLC; considerable decomposition was observed and only 100 mg of non-deuterated **1** could be collected. Deuterated cluster **1** was obtained by reaction of $[Ru_3(CO)_{12}]$ under $D_2$, as described for the original synthesis of **1** [9].

(b) *Homogeneous deuteration experiments*

An octane suspension of 100 mg (0.13 mmol) of deuterated cluster **1** was added to 0.5 ml (5.0 mmol) of 1,3-CHD and sealed in a 25.0 ml vial under vacuum. The vial was warmed to 120°C for 30 min. A mixture of complexes B, E-E′, L was obtained; E contained $\mu_2$-D.

A 100 ml octane suspension of 53 mg (0.07 mmol) of **1** was added to 1.8 ml (19.0 mmol) of 1,3-CHD and sealed in a 250 ml vial under 1 atm of $D_2$. The vial was warmed to 120°C for 30 min. Complexes E and G (with $\mu_2$-D) together with partially deuterated organic products were identified (GC–MS).

## 3. Results and discussion

### 3.1. Hydrogenation and isomerization experiments

The results of the hydrogenation experiments for 1,3-cyclohexadiene (1,3-CHD) are collected in Table 1. The organometallic complexes and the decomposition observed in the reaction solutions from these experiments and from those discussed below are listed in Table 2.

Complexes **1–4** hydrogenate 1,3-CHD to cyclohexene with 100% selectivity, albeit with relatively low turnover numbers (TON). In all experiments, except those with $[Ru_3(CO)_{12}]$, TON increased with time. Apparently, the catalytic activity of the clusters follows the order: $[H_4Ru_4(CO)_{12}] < [Ru_3(CO)_{12}] < [Fe_2Ru(CO)_{12}] \leqslant [H_2FeRu_3(CO)_{13}] < [H_2Ru_4(CO)_{13}]$.

Complexes **1–4** also hydrogenate 1,4-CHD to cyclohexene with higher TON but lower selectivity (Table 3). In all experiments, except those with $[H_2Ru_4(CO)_{13}]$, TON values increased regularly with time, the order of catalytic activities being: $[H_4Ru_4(CO)_{12}] < [H_2FeRu_3(CO)_{13}] \leqslant [Fe_2Ru(CO)_{12}] < [H_2Ru_4(CO)_{13}] \leqslant [Ru_3(CO)_{12}]$.

The selectivity towards cyclohexene follows the order: $[Ru_3(CO)_{12}] = [H_4Ru_4(CO)_{12}] < [H_2FeRu_3(CO)_{13}] < [H_2Ru_4(CO)_{13}] < [Fe_2Ru(CO)_{12}]$. The ease of hydrogenation of the substrates follows the order: 1,3-CHD > 1,4-CHD > cyclohexene. One would therefore expect benzene and toluene to be very easily hydrogenated, but they did not undergo hydrogenation under the conditions employed [10].

The results obtained may be interpreted in terms of catalysis by metal fragments, the active catalyst being presumably B which is found in nearly all reaction mixtures. Fragmentation of the tetranuclear derivatives would give the active mononuclear complex and the inactive trinuclear derivatives F–L, as further discussed below. This would explain the high activity of $[H_2Ru_4(CO)_{12}]$ and the low activity of $[Ru_3(CO)_{12}]$ towards 1,3-CHD.

We believe that 1,4-CHD isomerizes first to 1,3-CHD presumably catalyzed by a polynuclear species. The latter is then hydrogenated. This would explain the

Table 1

Hydrogenation of 1,3-cyclohexadiene (1,3-CHD) in the presence of clusters **1–4** [a]

| Parent cluster (experiment) | Reaction time (min) | Conversion (%) | TON | Composition of reaction solutions (%) | |
|---|---|---|---|---|---|
| | | | | Cyclohexene | 1,3-CHD [b] |
| $[H_4Ru_4(CO)_{12}]$ (A) | 15 | 2.29 | 4.14 | 2.29 | 97.71 |
| | 30 | 2.68 | 4.84 | 2.68 | 97.32 |
| | 45 | 3.65 | 6.60 | 3.65 | 96.35 |
| $[H_2Ru_4(CO)_{13}]$ (B) | 15 | 21.58 | 38.67 | 21.58 | 78.42 |
| | 30 | 22.42 | 40.18 | 22.42 | 77.58 |
| | 45 | 22.72 | 40.71 | 22.72 | 77.28 |
| $[H_2Ru_4(CO)_{13}]$ (B′) | 30 | 18.43 | 39.78 | 18.43 | 81.57 |
| | 30 | 6.27 | 13.53 | 6.27 | 93.73 |
| | 30 | 3.73 | 8.05 | 3.73 | 96.27 |
| $[H_2Ru_4(CO)_{13}]$ (B″) | 30 | 24.75 | 53.42 | 24.75 | 75.25 |
| | 30 | 21.35 | 23.04 | 21.35 | 78.65 |
| | 30 | 48.55 | 26.15 | 48.55 | 51.45 |
| $[H_2FeRu_3(CO)_{13}]$ (C) | 15 | 6.94 | 25.30 | 6.94 | 93.06 |
| | 30 | 6.99 | 25.49 | 6.99 | 93.01 |
| | 45 | 7.35 | 26.80 | 7.35 | 92.65 |
| $[H_2FeRu_3(CO)_{13}]$ (C′) | 30 | 7.33 | 17.60 | 7.33 | 92.67 |
| | 30 | 6.13 | 7.36 | 6.13 | 93.87 |
| | 30 | 9.68 | 5.81 | 9.68 | 90.32 |
| $[H_2FeRu_3(CO)_{13}]$ (C″) | 30 | 7.69 | 19.50 | 7.69 | 92.31 |
| | 30 | 7.93 | 20.10 | 7.93 | 92.07 |
| | 30 | 6.02 | 15.26 | 6.02 | 93.98 |
| $[Fe_2Ru(CO)_{12}]$ (D) | 15 | 1.88 | 8.11 | 1.88 | 98.12 |
| | 30 | 5.47 | 23.60 | 5.47 | 94.53 |
| | 45 | 6.64 | 28.64 | 6.64 | 93.36 |
| $[Fe_2Ru(CO)_{12}]$ (D′) | 30 | 5.36 | 16.80 | 5.36 | 94.64 |
| | 30 | 6.48 | 10.15 | 6.48 | 93.52 |
| | 30 | 12.12 | 9.50 | 12.12 | 87.88 |
| $[Fe_2Ru(CO)_{12}]$ (D″) | 30 | 5.27 | 14.00 | 5.27 | 94.73 |
| | 30 | 4.86 | 12.91 | 4.86 | 95.14 |
| | 30 | 4.58 | 12.17 | 4.58 | 95.42 |
| $[Ru_3(CO)_{12}]$ (E) | 15 | 3.62 | 15.30 | 3.62 | 96.38 |
| | 30 | 2.84 | 12.00 | 2.84 | 97.16 |
| | 45 | 2.15 | 9.09 | 2.15 | 97.85 |
| $[Ru_3(CO)_{12}]$ (E′) | 30 | 1.95 | 7.85 | 1.95 | 98.05 |
| | 30 | 1.78 | 7.16 | 1.78 | 98.22 |
| | 30 | 1.45 | 5.84 | 1.45 | 98.55 |

[a] Details of cluster and substrate concentrations in the experiments: Solvent, octane, 2 ml vial$^{-1}$; $T = 120$°C.

A: [cluster] = $1.6 \times 10^{-5}$ mol; [1,3-CHD] = $2.10 \times 10^{-3}$ mol; substrate/cluster = 179.5; $H_2 = 1.0$ atm. B: [cluster] = $1.17 \times 10^{-5}$ mol; [1,3-CHD] = $2.10 \times 10^{-3}$ mol; substrate/cluster = 181.0; $H_2 = 1.0$ atm. B′: [cluster] = $9.73 \times 10^{-6}$ mol; [1,3-CHD] = $2.10 \times 10^{-3}$ mol; substrate/cluster = 215.8; $H_2 = 1.0$, 0.5, 0.25 atm. B″: [cluster] = $9.73 \times 10^{-6}$ mol; $H_2 = 1.0$ atm; [1,3-CHD] = $2.10 \times 10^{-3}$, $1.05 \times 10^{-3}$, $5.24 \times 10^{-4}$ mol; substrate/cluster = 215.8, 107.9, 53.9. C: [cluster] = $5.75 \times 10^{-6}$; [1,3-CHD] = $2.10 \times 10^{-3}$ mol; substrate/cluster = 365.2; $H_2 = 1.0$ atm. C′: [cluster] = $8.73 \times 10^{-6}$ mol; $H_2 = 1.0$ atm; [1,3-CHD] = $2.10 \times 10^{-3}$, $1.05 \times 10^{-3}$, $5.24 \times 10^{-4}$ mol; substrate/cluster = 240.6, 120.3, 60.0. C″: [cluster] = $8.27 \times 10^{-6}$; [1,3-CHD] = $2.10 \times 10^{-3}$ mol; substrate/cluster = 253.9; $H_2 = 1.0$, 0.5, 0.25 atm. D: [cluster] = $4.86 \times 10^{-6}$ mol; [1,3-CHD] = $2.10 \times 10^{-3}$ mol; substrate/cluster = 432.1; $H_2 = 1.0$ atm. D′: [cluster] = $6.69 \times 10^{-6}$ mol; $H_2 = 1$ atm; [1,3-CHD] = $2.10 \times 10^{-3}$, $1.05 \times 10^{-3}$, $5.24 \times 10^{-4}$ mol; substrate/cluster = 313.9, 157.0, 78.3. D″: [cluster] = $7.89 \times 10^{-6}$ mol; [1,3-CHD] = $2.10 \times 10^{-3}$ mol; substrate/cluster = 266.2; $H_2 = 1.0$, 0.5, 0.25 atm. E: [cluster] = $4.96 \times 10^{-6}$ mol; [1,3-CHD] = $2.10 \times 10^{-3}$ mol; substrate/cluster = 423.4; $H_2 = 1.0$ atm. E′: [cluster] = $5.21 \times 10^{-6}$ mol; [1,3-CHD] = $2.10 \times 10^{-3}$ mol; substrate/cluster = 403.1; $H_2 = 1.0$, 0.5, 0.25 atm.

[b] Selectivity to 1,3-CHD was always 100%.

high activity of $[Ru_3(CO)_{12}]$ and of $[H_2Ru_4(CO)_{13}]$ with TON nevertheless decreasing with time. The latter is the best isomerization catalyst for 1,4-CHD (see below). The decrease of the TON may be related therefore to the formation of 1,3-CHD which would react to form an inactive species.

Further evidence for metal-fragment catalysis is as follows: (i) The complexes F–L identified in the catalytic experiments were prepared independently either from clusters **1** or **2** and from $[Ru_3(CO)_{12}]$ (ii) The iron-containing clusters **3** and **4** are quite active although generally iron is a very modest hydrogenation catalyst. This could indicate that loss and recondensation of fragments [11] favours the formation of mononuclear ruthenium species. (iii) In the hydrogenation of complex G, the tetranuclear complex I is formed.

Finally, deuteration experiments indicate that $D_2$ enters as an hydride, presumably into complexes **1**–**3**, and is then shifted in part on to the organic moieties.

The results of the isomerization experiments of 1,4-CHD are collected in Table 4. Relatively low TON values were observed and these increase in the order: $[H_4Ru_4(CO)_{12}] < [H_2FeRu_3(CO)_{13}] = [Ru_3(CO)_{12}] < [H_2Ru_4(CO)_{13}]$. As already observed for complex **5** [4], some cyclohexane was found in the isomerization experiments. This can be accounted for by a disproportionation reaction of the dienes to benzene and cyclohexane, as discussed below.

### 3.2. Some comments on the hydrogenation results

The results obtained contrast strongly with those with $C_2Ph_2$ in the presence of clusters **1**–**4** [2]. For $C_2Ph_2$, 'irregular' TON numbers were observed at intermediate reaction times, and the catalytic efficiency for the iron-containing derivatives was lower than that for the ruthenium complexes. Competition between metal-fragment formation under $H_2$ and metal-fragment condensation favoured by the alkyne has been suggested. In the present case, we propose a complex pathway leading either to hydrogenation (with metal fragments) or to contemporaneous formation of inactive trinuclear organometallic products obtained upon oxidative addition of the substrate.

We reported that cluster **5** catalyzes the hydrogenation of 1,3- and 1,4-CHD to cyclohexene [maximum TON = 85 (1,3-CHD) and = 38 (1,4-CHD), respectively] and that cyclohexene is hydrogenated to cyclohexane with a maximum TON of only 2 [4]. The proposed mechanism involves isomerization of 1,4-CHD to

Table 2
Organometallic products and decomposition in hydrogenation and isomerization reactions with complexes **1**–**4** and F, G and H

| Parent cluster (experiment) | Colour change | Organometallic products and yields | Decomposition (%) |
|---|---|---|---|
| *Hydrogenation of 1,3-CHD* | | | |
| $[H_4Ru_4(CO)_{12}]$ (A) | no change | F (10%), G (5%), B, E, L (tr.) | 20 |
| $[H_2Ru_4(CO)_{13}]$ (B, B′, B″) | red to yellow | F (10%), G (5%), B, E, L (2%) | 20–30 |
| $[H_2FeRu_3(CO)_{13}]$ (C) | red to colourless | – | 100 |
| $[Fe_2Ru(CO)_{12}]$ (D) | blue to green | $[Fe_3(CO)_{12}]$ (10%) | 90 |
| *Hydrogenation of 1,4-CHD* | | | |
| $[H_4Ru_4(CO)_{12}]$ (F) | no change | F (2%), G (2%), B, E, L (tr.) | 40 |
| $[H_2Ru_4(CO)_{13}]$ (G, G′) | red to yellow | parent (5%), F (15%) G (5%), B, E, L (3%) | 60 |
| $[H_2FeRu_3(CO)_{13}]$ (H) | red to yellow | parent (5%), F (3%), G, B, E, L (tr.) | 80 |
| $[Fe_2Ru(CO)_{12}]$ (I) | blue to yellow | – | 70 |
| *Isomerization of 1,4-CHD* | | | |
| $[H_4Ru_4(CO)_{12}]$ (K) | no change | parent (80%) | 10 |
| $[H_2Ru_4(CO)_{13}]$ (M, M′) | no change | F (8%), G (tr.) | 15 |
| $[H_2FeRu_3(CO)_{13}]$ (L) | red to yellow | parent (60%), F (tr.)<br>$[Fe_2Ru(CO)_{12}]$ (tr.)<br>$[H_2Ru_4(CO)_{13}]$ (10%) | 20 |
| *Hydrogenation of organometallic complexes F, G and H* | | | |
| Complex G (R) | no change | complex I (10%) | 10 |
| Complex G (S) | no change | parent (60%) | 30 |
| Complex F (P) | yellow to orange | $[H_2Ru_4(CO)_{13}]$ (10%) | 70 |
| Complex H (T) | yellow to orange | $[H_2Ru_4(CO)_{13}]$ (5%) | 70 |

NB When small vials were used for the hydrogenation reactions, the TLC separation was performed with the products of a series of vials. The products and their concentration therefore represent an average situation.

1,3-CHD followed by hydrogenation, in a reaction sequence requiring coordination of the dienes to one ruthenium, followed by hydride transfer and release of the hydrogenation products. In the reaction solutions only decomposition products and traces of complex F could be detected. The formation of F lowered the catalytic activity. These results are in substantial accord with those reported here. Apparently **5** shows a greater tendency to decompose to metal, whereas clusters **1**–**3** give inactive organometallic products and lower-nuclearity fragments.

As discussed previously, the intact clusters are present only in the first reaction steps. The literature supports this hypothesis. Kinetic studies on the homogeneous hydrogenation and isomerization of olefins catalyzed by $[Ru_3(CO)_{12}]$ under $H_2$ flow [12a] showed that low nuclearity species were responsible for hydrogenation, whereas higher-nuclearity derivatives gave

Table 3
Hydrogenation of 1,4-cyclohexadiene in the presence of clusters **1**–**4** [a]

| Parent cluster (experiment) | Reaction time (min) | Conversion (%) | TON | Composition of reaction solutions (%) [b,c] | | |
|---|---|---|---|---|---|---|
| | | | | Cyclohexene | 1,3-CHD | 1,4-CHD |
| $[H_4Ru_4(CO)_{12}]$ (F) | 15 | 7.69 | 28.20 | 2.82<br>(36.7) | 4.87<br>(63.3) | 92.31 |
| | 30 | 9.34 | 34.25 | 3.76<br>(40.3) | 5.58<br>(59.7) | 90.66 |
| | 45 | 10.01 | 36.70 | 4.13<br>(41.3) | 5.88<br>(58.7) | 89.99 |
| $[H_2Ru_4(CO)_{13}]$ (G) | 15 | 21.09 | 86.72 | 5.13<br>(24.3) | 15.96<br>(75.7) | 78.91 |
| | 30 | 10.70 | 44.00 | 5.73<br>(53.5) | 4.87<br>(46.5) | 89.30 |
| | 45 | 11.96 | 49.18 | 6.51<br>(54.4) | 5.45<br>(45.6) | 88.04 |
| $[H_2Ru_4(CO)_{13}]$ (G′) | 30 | 11.59 | 45.72 | 5.29<br>(45.6) | 6.30<br>(54.4) | 88.41 |
| | 30 | 11.18 | 44.10 | 4.45<br>(39.8) | 6.73<br>(60.2) | 88.82 |
| | 30 | 8.53 | 33.65 | 2.15<br>(25.2) | 6.38<br>(74.8) | 91.47 |
| $[H_2FeRu_3(CO)_{13}]$ (H) | 15 | 6.67 | 24.75 | 2.85<br>(44.2) | 3.72<br>(55.7) | 93.33 |
| | 30 | 8.70 | 32.29 | 3.37<br>(38.7) | 5.33<br>(61.3) | 91.30 |
| | 45 | 11.35 | 42.12 | 4.50<br>(39.7) | 6.85<br>(60.4) | 88.65 |
| $[Fe_2Ru(CO)_{12}]$ (I) | 15 | 6.59 | 28.94 | 2.04<br>(31.0) | 4.55<br>(69.0) | 93.41 |
| | 30 | 9.18 | 40.31 | 5.78<br>(63.0) | 3.40<br>(37.0) | 90.82 |
| | 45 | 13.03 | 57.21 | 10.30<br>(79.0) | 2.73<br>(21.0) | 86.97 |
| $[Ru_3(CO)_{12}]$ (J) | 15 | 18.25 | 78.52 | 7.39<br>(40.5) | 10.86<br>(59.5) | 81.75 |
| | 30 | 21.19 | 91.17 | 7.14<br>(33.7) | 14.05<br>(66.3) | 78.81 |
| | 45 | 21.53 | 92.63 | 7.02<br>(32.6) | 14.51<br>(67.4) | 78.47 |

[a] Reaction conditions, see Table 1. Details of the cluster and substrate concentrations are as follows.

F: [cluster] = $5.82 \times 10^{-6}$ mol; [1,4-CHD] = $2.13 \times 10^{-3}$ mol; substrate/cluster = 366.0; $H_2$ = 1 atm. G: [cluster] = $5.19 \times 10^{-6}$ mol; [1,4-CHD] = $2.13 \times 10^{-3}$ mol; substrate/cluster = 410.4; $H_2$ = 1.0 atm. G′: [cluster] = $5.41 \times 10^{-6}$ mol; [1,4-CHD] = $2.13 \times 10^{-3}$ mol; substrate/cluster = 393.7; $H_2$ = 1.0, 0.5, 0.25 atm. H: [cluster] = $5.75 \times 10^{-6}$ mol; [1,4-CHD] = $2.13 \times 10^{-3}$ mol; substrate/cluster = 370.4; $H_2$ = 1.0 atm. I: [cluster] = $4.86 \times 10^{-6}$ mol; [1,4-CHD] = $2.13 \times 10^{-3}$ mol; substrate/cluster = 438.3; $H_2$ = 1.0 atm. J: [cluster] = $4.96 \times 10^{-6}$ mol; [1,4-CHD] = $2.13 \times 10^{-3}$ mol; substrate/cluster = 429.4; $H_2$ = 1.0 atm.

[b] Selectivities in parentheses.

[c] Difference = cyclohexane.

isomerization after an induction period. In the isomerization–hydrosylilation of olefins, evidence for cluster catalysis was found only during the first few minutes [12b].

We note also that [$HRu_3(CO)_9(PhNC_6H_4N)$] is a hydrogenation catalyst for alkynes. In the alkyne–ethylene codimerization, the cluster is the catalyst and the vinyl derivative [$Ru_3(CO)_9(PhNC_6H_4N)\{\mu$-(Ph)C =C(Ph)H}] is an intermediate [13]. [$HRu_3(CO)_9$(Hampy)] (Hampy = 2-amino-6-methylpyridine) has been considered an efficient catalyst for the hydrogenation of 1,3-CHD [14] and of $C_2Ph_2$. However, further studies indicated that the proposed trinuclear or binuclear diphenylvinylidene intermediates are inactive. Kinetic experiments showed that mononuclear species were the active catalysts [14b]. However, [$HRu_3(CO)_9$(Hampy)] reacts with dihydrogen to give a hexa-hydridic dimer which is an active catalyst precursor for the hydrogenation of $C_2Ph_2$ under mild conditions [15], thus confirming the role of cluster-bound hydrides in this type of catalysis.

### *3.3. Characterization and role of the organometallic complexes in the reaction solutions*

It has been reported that cluster 1 catalyzes the hydrogenation of pent-2-yne and the isomerization of pentenes [16]. [$Ru_3(CO)_{12}$] isomerizes 1-pentene to *cis*- and *trans*-2-pentene. The complexes [$HRu_3(CO)_9$(MeC=C=CHMe)] (M) and [$HRu_3(CO)_9$(MeCCHC-Me)] (N) were found in the reaction mixtures along with [$H_2Ru_4(CO)_{13}$] and [$H_4Ru_4(CO)_{12}$], the latter arising from dehydrogenation of 1-pentene. In contrast with our findings for E and F, complexes M and N

Table 4
Isomerization of 1,4-cyclohexadiene in the presence of clusters 1–3 [a]

| Parent cluster (experiment) | Reaction time (min) | Conversion (%) | TON | Composition of reaction solutions (%) | | |
|---|---|---|---|---|---|---|
| | | | | Cyclohexene | 1,3-CHD | 1,4-CHD |
| [$H_4Ru_4(CO)_{12}$] (K) | 15 | 0.84 | 2.86 | 0.04<br>(4.8) | 0.80<br>(95.2) | 99.16 |
| | 30 | 1.61 | 5.48 | 0.07<br>(4.3) | 1.54<br>(95.7) | 98.39 |
| | 45 | 1.93 | 6.57 | 0.09<br>(4.7) | 1.84<br>(95.3) | 98.07 |
| [$H_2FeRu_3(CO)_{13}$] (L) | 15 | 0.96 | 4.46 | 0.05<br>(5.2) | 0.91<br>(94.8) | 99.04 |
| | 30 | 2.39 | 11.11 | 0.18<br>(7.5) | 2.21<br>(92.5) | 97.61 |
| | 45 | 4.04 | 18.78 | 0.28<br>(6.9) | 5.90<br>(93.1) | 95.96 |
| [$H_2Ru_4(CO)_{13}$] (M) | 15 | 8.51 | 26.24 | 0.26<br>(3.1) | 8.25<br>(96.9) | 91.49 |
| | 30 | 8.72 | 26.89 | 0.31<br>(3.6) | 8.41<br>(96.4) | 91.28 |
| | 45 | 9.21 | 28.40 | 0.44<br>(4.8) | 8.77<br>(95.2) | 90.79 |
| [$H_2Ru_4(CO)_{13}$] (M′) | 30 | 6.18 | 24.38 | 0.28<br>(4.5) | 5.90<br>(95.5) | 93.82 |
| | 30 | 6.16 | 12.15 | 0.76<br>(12.3) | 5.40<br>(87.7) | 93.84 |
| | 30 | 8.20 | 8.09 | 1.56<br>(19.0) | 6.64<br>(81.0) | 91.80 |
| [$Ru_3(CO)_{12}$] (N) | 15 | 2.16 | 4.23 | 0.16<br>(7.4) | 2.00<br>(92.6) | 97.84 |
| | 30 | 7.24 | 14.17 | 0.54<br>(7.5) | 6.70<br>(92.5) | 92.76 |
| | 45 | 10.78 | 21.11 | 0.73<br>(6.8) | 10.05<br>(93.2) | 89.22 |

[a] Details of substrate and cluster concentrations in the experiments: Solvent, octane, 2 ml vial$^{-1}$; $T = 120$°C;

K: [cluster] = $6.27 \times 10^{-6}$ mol; [1,4-CHD] = $2.13 \times 10^{-3}$ mol; substrate/cluster = 339.7. L: [cluster] = $4.59 \times 10^{-6}$ mol; [1,4-CHD] = $2.13 \times 10^{-3}$ mol; substrate/cluster = 464.1. M: [cluster] = $6.92 \times 10^{-6}$ mol; [1,4-CHD] = $2.13 \times 10^{-3}$ mol; substrate/cluster = 307.8. M′: [cluster] = $5.41 \times 10^{-6}$ mol; [1,4-CHD] = $2.13 \times 10^{-3}$, $1.07 \times 10^{-3}$, $5.34 \times 10^{-4}$ mol; substrate/cluster = 393.7, 197.8, 98.7. N: [cluster] = $1.09 \times 10^{-5}$ mol; [1,4-CHD] = $2.13 \times 10^{-3}$ mol; substrate/cluster = 195.4.

were both intermediates and catalysts in these reactions [17]. Finally $[H_2Ru_4(CO)_{13}]$ isomerizes pentenes via allylic intermediates [17a–c].

Reports on the reactions of 1,3-CHD with $[Ru_3(CO)_{12}]$ have also appeared. In refluxing heptane [18], the formation of $[HRu_3(CO)_9(C_6H_9)]$ (D) [19] was reported. With a considerable excess of 1,3-CHD, complex B could be obtained. Complex B acted as a hydrogen-transfer catalyst and with 1,3-CHD under reflux gave 1,4-CHD, benzene, cyclohexene and complex C [18]. Reaction of $[Ru_3(CO)_{12}]$ with a large excess of 1,3-CHD (10–31 : 1) for long time in refluxing cyclohexane or octane gave complexes B and E, and the butterfly I [20]. Finally, reaction of an excess of 1,3-CHD with $[Ru_3(CO)_{10}(MeCN)_2]$ gave considerable yields of $[HRu_3(CO)_9(C_6H_7)]$ (G), which could be deprotonated to complex H [21]. The 1,3-CHD derivatives mentioned above and those found in our catalytic experiments are depicted in Fig. 2.

In the solutions from the catalytic experiments (Table 2) we could identify the complexes B, E–H and L whose nature was confirmed by independent syntheses. The butterfly I [20] was also formed during the hydrogenation of G. The structure of L could not be determined univocally. In our opinion it shows analogies to $[H_2Os_4(CO)_{10}(C_6H_5Me)]$ [22].

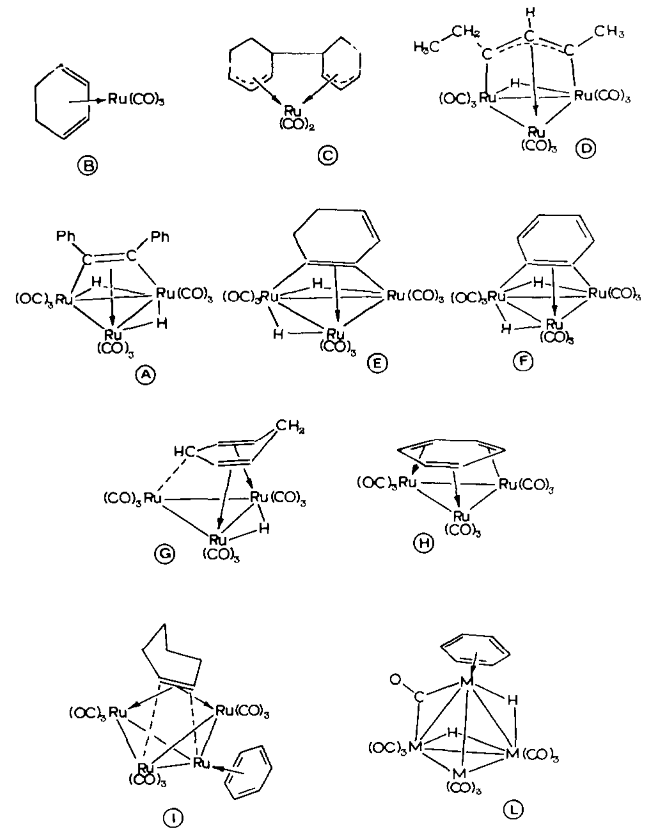

Fig. 2. Found or proposed structures for complexes (A)–(L), as discussed in the text.

Table 5
Hydrogenation of organometallic complexes E, F, G, H and L [a]

| Complex (experiment) | Reaction time (min) | TON | Composition of reaction solutions (%) | |
|---|---|---|---|---|
| | | | Cyclohexene | 1,3-CHD |
| Complex F (P) | 15–30 | – | – | – |
| Complex E (Q) | 15–30 | – | 15.3 | 84.7 |
| Complex G (R) | 15 | – | 100 [b] | – |
| | 30 | – | – | – |
| | 45 | – | – | – |
| Complex G (S) | 15 | 5.2 | 1.2 | 98.8 |
| | 30 | 3.8 | 0.9 | 99.1 |
| Complex H (T) | 15–30 | – | – | – |
| Complex L (U) | 15–30 | – | – | – |

[a] Details of complex nd substrate concentrations in the experiments: Solvent, octane, 2 ml $vial^{-1}$; $T = 120°C$. Experiments P,Q,R,T,U: complex ca. 50 mg, 1 atm $H_2$. Experiment S: $[cluster] = 4.72 \times 10^{-6}$ mol; $[1,3\text{-CHD}] = 2.10 \times 10^{-3}$ mol; substrate/cluster = 445; $H_2 = 1$ atm.

[b] The cyclohexene obtained is presumably from the cluster, which undergoes modification, deposing insoluble red crystals of I.

The complexes F, G, H, L and I result from oxidative addition reactions involving dehydrogenation of the dienes and hydrogen-transfer to the cluster or, in some instances, disproportionation to benzene and saturated hydrocarbons. These processes occur even under an excess of dihydrogen. Dehydrogenation of linear and cyclic dienes upon coordination to tri- or polymetallic clusters is a well-known reaction [23]. In order to verify if the trinuclear products were catalytic intermediates, we hydrogenated or treated some derivatives with 1,3-CHD as shown in Table 5.

None of these is a reaction intermediate or a catalyst, despite the fact that the structures of E and F are closely comparable with that of A, which is a homogeneous hydrogenation intermediate [2]. Several other examples are known of hydridic tri- and poly-nuclear clusters with alkynes coordinated parallel to a cluster edge acting as catalysts, catalyst precursors or intermediates in hydrogenation reactions [24]. $[H_2Ru_3(CO)_9(RC_2R)]$ (R = Me or Et) and $[HRu_3(CO)_9(MeCCHCEt)]$, obtained upon dehydrogenation of alkenes, are key intermediates in the homogeneous oligomerization of ethylene in the presence of $[Ru_3(CO)_{12}]$ or $[H_4Ru_4(CO)_{12}]$ [25]. Finally, cyclohexene [26a] and diphenylacetylene were hydrogenated on tetranuclear phosphinidene-bridged ruthenium clusters. 'Parallel' coordination of the alkyne to three metals was again observed among the intermediates leading to *cis*- and *trans*-stilbene [26b].

An explanation for the apparently anomalous behaviour of complexes E and F is easily found. Complex A is formed from the alkyne upon CO substitution and the hydrides are provided by external dihydrogen. Easy release of the hydrogenated ligand occurs in the presence of extra dihydrogen. In contrast, complexes E and

F are formed upon oxidative addition and consequent dehydrogenation. In the presence of external dihydrogen, re-formation of the original substrate is expected to occur.

## 4. Concluding remarks

The results reported here, represent an example of clusters as models of chemisorption and heterogeneous catalysis. Preliminary results obtained by supporting clusters **1** and **2** on inorganic oxides and transforming the derivatives into small metal particles indicate a very high hydrogenating and dehydrogenating activity. There is evidence for complex hydrogenation–dehydrogenation patterns, closely comparable with those found in homogeneous conditions [27]. Further examples of this behaviour have been found for supported $[(CpNi)Ru_3(CO)_9(\mu\text{-}H)_3]$ both in heterogeneous hydrogenation [28] and in ammonia synthesis [29].

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## References and notes

[1] (a) M. Castiglioni, R. Giordano, E. Sappa, A. Tiripicchio and M. Tiripicchio Camellini, *J. Chem. Soc., Dalton Trans.*, (1986) 23; (b) M. Castiglioni, R. Giordano and E. Sappa, *J. Organomet. Chem., 342* (1988) 111; *ibid., 362* (1989) 399; *ibid., 407* (1991) 377.

[2] R. Giordano and E. Sappa, *J. Organomet. Chem., 448* (1993) 157.

[3] (a) O. Gambino, E. Sappa and G. Cetini, *J. Organomet. Chem., 44* (1972) 185; (b) D. Cauzzi, R. Giordano, E. Sappa, A. Tiripicchio and M. Tiripicchio Camellini, *J. Cluster Sci., 4* (1993) 279.

[4] M. Castiglioni, R. Giordano and E. Sappa, *J. Organomet. Chem., 319* (1987) 167.

[5] EI: Kratos MS 80, 70 eV. The CI mass spectra were obtained on a Hewlett Packard 9589A MS Engine system under the conditions reported in M. Careri, A. Mangia, P. Manini, G. Predieri, V. Raverdino, G. Tsoupras and E. Sappa, *J. Chromatogr., 647* (1993) 79.

[6] All these complexes (excluding perhaps one isomer of E) are already known and are discussed in the text with the appropriate references. The analyses reported were made to confirm their nature. In some instances (e.g. the CI mass spectra), these were not given in the original papers.

[7] The following notations for the intensity of the peaks have been adopted: vi = very intense, i = intense, mi = medium intensity, li = low intensity.

[8] A.J. Blake, P.J. Dyson, B.F.G. Johnson, C.M. Martin, J.G.M. Nairn, E. Parisini and J. Lewis, *J. Chem. Soc., Dalton Trans.*, (1993) 981.

[9] (a) S.A.R. Knox, J.W. Koepke, M.A. Andrews and H.D. Kaesz, *J. Am. Chem. Soc., 97* (1975) 3942; (b) M.I. Bruce, M.L. Williams, G. Lavigne and T. Arliguie, *Inorg. Synth., 26* (1989) 262.

[10] Hydrogenation of toluene was attempted with $[H_2Ru_4(CO)_{13}]$. Three vials; 1 atm. $H_2$, 120°C, $[\text{cluster}] = 7.36 \times 10^{-6}$ mol, $[\text{toluene}] = 1.88 \times 10^{-3}$ mol, substrate/cluster = 255.4. No hydrogenation products were observed. $[H_2Ru_3(CO)_9(C_6H_3Me)]$ was tentatively identified in the reaction mixtures.

[11] With complex **4**, triiron dodecacarbonyl was observed, Table 2.

[12] (a) H.S. Hilal, W. Jondi, S. Khalaf and R. Abu-Halawa, *J. Organomet. Chem., 452* (1993) 161; H.S. Hilal, S. Khalaf and W. Jondi, *J. Organomet. Chem., 452* (1993) 167.

[13] N. Lugan, F. Laurent, G. Lavigne, T.P. Newcomb, E.W. Limatta and J.-J. Bonnet, *J. Am. Chem. Soc., 112* (1990) 8607.

[14] (a) J.A. Cabeza, J.M. Fernàndez-Colinas, A. Llamazares and V. Riera, *J. Mol. Catal., 71* (1992) L7; (b) J.A. Cabeza, J.M. Fernàndez-Colinas, A. Llamazares and V. Riera, *Organometallics, 11* (1992) 4355.

[15] J.A. Cabeza, J.M. Fernàndez-Colinas, S. Garcìa-Granda, A. Llamazares, F. Lòpez-Ortiz, V. Riera and J.F. Van der Maelen, *Organometallics, 13* (1994) 426.

[16] (a) P. Michelin Lausarot, G.A. Vaglio and M. Valle, *Inorg. Chim. Acta, 25* (1977) L107; (b) P. Michelin Lausarot, G.A. Vaglio and M. Valle, *Inorg. Chim. Acta, 36* (1979) 213; (c) P. Michelin Lausarot, G.A. Vaglio and M. Valle, *Transition Met. Chem., 4* (1979) 39; (d) G.A. Vaglio and M. Valle, *Inorg. Chim. Acta, 30* (1978) 161.

[17] (a) G.A. Vaglio, D. Osella and M. Valle, *Transition Met. Chem., 2* (1977) 94; (b) M. Valle, D. Osella and G.A. Vaglio, *Inorg. Chim. Acta, 20* (1976) 213; (c) G.A. Vaglio and M. Valle, *Inorg. Chim. Acta, 36* (1979) 213; (d) M. Castiglioni, L. Milone, D. Osella, G.A. Vaglio and M. Valle, *Inorg. Chem., 15* (1976) 394.

[18] T.H. Whitesides and R.A. Budnik, *J. Chem. Soc., Chem. Commun.*, (1973) 87.

[19] M. Evans, M. Hursthouse, E.W. Randall, E. Rosenberg, L. Milone and M. Valle, *J. Chem. Soc., Chem. Commun.*, (1972) 545.

[20] S. Aime, L. Milone, D. Osella, G.A. Vaglio, M. Valle, A. Tiripicchio and M. Tiripicchio Camellini, *Inorg. Chim. Acta, 34* (1979) 49.

[21] (a) B.F.G. Johnson, J. Lewis, M. Martinelli, A.H. Wright, D. Braga and F. Grepioni, *J. Chem. Soc., Chem. Commun.*, (1990) 364; (b) D. Braga, F. Grepioni, B.F.G. Johnson, J. Lewis, C.E. Housecroft and M. Martinelli, *Organometallics, 10* (1991) 1260; (c) D. Braga, F. Grepioni, E. Parisini, B.F.G. Johnson, C.M. Martin, J.G.M. Nairn, J. Lewis and M. Martinelli, *J. Chem. Soc., Dalton Trans.*, (1993) 1891.

[22] D. Braga, F. Grepioni, B.F.G. Johnson, H. Chen and J. Lewis, *J. Chem. Soc., Dalton Trans.*, (1991) 2559.

[23] (a) A.J.P. Domingos, B.F.G. Johnson and J. Lewis, *J. Organomet. Chem.*, 36 (1972) C43; (b) R.D. Adams and W. Wu, *Polyhedron, 11* (1992) 2123; (c) R.D. Adams and W. Wu, *Organometallics, 12* (1993) 1243; (d) B.F.G. Johnson, J. Lewis, C.E. Housecroft, M. Gallup, M. Martinelli, D. Braga and F. Grepioni, *J. Mol. Catal., 74* (1992) 61; (e) D. Braga, F. Grepioni, P.J. Dyson and B.F.G. Johnson, *J. Cluster Sci., 3* (1992) 297; (f) H. Chen, B.F.G. Johnson, J. Lewis, D. Braga, F. Grepioni and E. Parisini, *J. Chem. Soc., Dalton Trans.*, (1991) 215; (g) D. Braga, F. Grepioni, S. Righi, P.J. Dyson, B.F.G. Johnson, P.J. Bailey and J. Lewis, *Organometallics, 11* (1992) 4042, and references therein.

[24] (a) M. Castiglioni, G. Gervasio and E. Sappa, *Inorg. Chim. Acta, 49* (1981) 217; (b) R. Amadelli, C. Bartocci, V. Carassiti, S. Aime, D. Osella and L. Milone, *Gazz. Chim. Ital., 115* (1985) 337; (c) S. Aime, R. Gobetto, L. Milone, D. Osella, L. Violano, A.J. Arce and Y. De Sanctis, *Organometallics, 10* (1991) 2854;

(d) M. Castiglioni, R. Giordano and E. Sappa, *J. Organomet. Chem., 369* (1989) 419; (e) A. Basu, S. Bhaduri, K. Sharma and P.G. Jones, *J. Chem. Soc., Chem. Commun.*, (1987) 1126; (f) R.D. Adams, Z. Li, P. Swepston, W. Wu and J. Yamamoto, *J. Am. Chem. Soc., 114* (1992) 10 657.

[25] M. Bianchi, G. Menchi, U. Matteoli and F. Piacenti, *J. Organomet. Chem., 451* (1993) 139, and references therein.

[26] (a) F. Van Gastel, J.F. Corrigan, S. Doherty, N.J. Taylor and A.J. Carty, *Inorg. Chem., 31* (1992) 4492. (b) J.F. Corrigan, personal communication (to E.S.).

[27] (a) M. Castiglioni, R. Giordano and E. Sappa, Communication to *Vth Conf. Chem. Platinum Group Metals*, St. Andrews, Scotland, July 11–16, 1993; (b) M. Castiglioni, R. Giordano, E. Sappa, P. Baistrocchi, P. Moggi and G. Predieri, Communication to *XXIIIth Inorg. Chem. Meet. (SCI)*, Villasimius, Sept. 26–Oct. 1st, 1993, Paper CO 06.

[28] (a) M. Castiglioni, R. Giordano and E. Sappa, *J. Mol. Catal., 40* (1987) 65; (b) idem, *ibid., 42* (1987) 307.

[29] A. Armigliato, S. Bigi, P. Moggi, S. Papadopoulos, G. Predieri, G. Salviati and E. Sappa, *Mater. Chem. Phys., 29* (1991) 251.