



# Reactions of diphenylacetylene and dihydrogen with chalcogenide- or methylidyne-capped trinuclear iron, ruthenium and cobalt clusters Evidence for the formation and recombination of metal fragments

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Dedicated to Professor Renato Ugo on the occasion of his 65th birthday

## Abstract

We have studied the behaviour of transition metal carbonyl clusters in homogeneous and solid–gas hydrogenation catalysis trying to evidence structure–reactivity relationships. Here, we report on the behaviour of trinuclear homo- and hetero-metallic clusters containing “capping” sulphido or selenido ligands, as well as methylidyne ligands. Very modest results have been obtained in homogeneous hydrogenation reactions of diphenylacetylene. The low activity observed indicates that these complexes do not act as cluster catalysts. In effect of the capping ligands—which are supposed to stabilize the clusters and prevent fragmentation—do not act as expected. Formation and recondensation of metal fragments, to give inactive (and somewhat unexpected) reaction byproducts have been evidenced. These processes presumably occur at the expenses of fragment catalysis. Reaction pathways, supported by IR, <sup>1</sup>H NMR and mass spectrometric evidence are proposed.

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## 1. Introduction

Organometallic catalysis is known since long time [1]; it is also known that transition metal carbonyl

clusters catalyze homogeneous hydrogenation reactions [2,3]. Clusters have attracted much attention because of the presence of several (and/or different) metal centres, however, their use is limited by the following reasons: (i) under catalytic conditions they may decompose to mononuclear metal fragments with loss of synergistic effects between metals; (ii) this behaviour also makes difficult to distinguish between

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cluster and fragment catalysis; (iii) to our knowledge, even when cluster catalysis occurs only one metal centre is usually involved [4–7] and reaction pathways comparable with those of mononuclear catalysis are observed.

We undertook a study on the behaviour of homo- and hetero-metallic clusters in homogeneous catalytic hydrogenation reactions. We evidenced structure–reactivity relationships [8,9], we identified reaction intermediates or byproducts and—in some instances—we proposed reaction pathways [10]. In many reactions, cluster catalysis has been evidenced or hypothesized; in some instances, also fragment catalysis or competition between the two is likely to occur. In particular, the phosphine-substituted clusters  $\text{Ru}_3(\text{CO})_9(\text{PR}_3)_3$  ( $\text{R} = \text{Ph}$ , complex **1**,  $\text{R} = \text{Et}$  complex **2**) [11] are considerably active in the hydrogenation of diphenylacetylene<sup>1</sup> (TON<sup>2</sup> 155.9 for **1** and 119.5 for **2**; selectivity to monoenes 93.0 and 99.3%, respectively); however, in the solutions after the catalytic runs with complex **2**, the new complex  $\text{Ru}_3(\text{CO})_{10}(\text{PEt}_3)_2$  (**3**) was found. Presumably, it was obtained from **2** through intramolecular exchange of phosphine and CO ligands and/or formation and re-assembly of metal fragments. This led us to suspect that fragment catalysis occurred when complexes **1–3** were reacted.

In order to obtain further evidence on structure–reactivity relationships and on cluster or fragment catalysis, we have studied the behaviour of the diphosphine-substituted chalcogenide complexes  $\text{Fe}_3(\text{CO})_7(\text{PPh}_3)_2(\mu_3\text{-Se})_2$  (complex **4a**),  $\text{Fe}_3(\text{CO})_9(\mu_3\text{-Se})_2$  (complex **4b**, for comparison) and  $\text{Ru}_3(\text{CO})_7(\text{PPh}_2)_2(\mu_3\text{-Se})_2$  (complex **5**). All of the compounds are open clusters containing “capping” chalcogenide ligands, which—in principle—would prevent cluster fragmentation, as already observed for phosphinidene-bridged complexes [12]. The structures of complexes **4a**, **4b**, and **5** (X-ray crystallography) are shown in Fig. 1.

<sup>1</sup> The hydrogenation of diphenylacetylene is catalyzed by a considerable number of triruthenium clusters; we use this substrate as a probe for comparing the catalytic activity of triruthenium and related clusters in homogeneous hydrogenation catalysis (see [3,8,105,54]).

<sup>2</sup> TON: turnover number. TOF: turnover frequency ( $\text{TON} \times \text{h}^{-1}$ ). For comparison with previous results ([3,8,10,53]) we have chosen the hour as time unit.

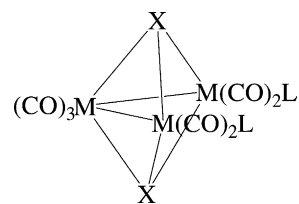


Fig. 1. Structures of complexes **4**, **4b**, and **5**.  $\text{M} = \text{Fe}$ ,  $\text{X} = \text{Se}$ ,  $\text{L} = \text{PPh}_3$ , complex **4**;  $\text{M} = \text{Fe}$ ,  $\text{X} = \text{Se}$ ,  $\text{L} = \text{CO}$ , complex **4b**;  $\text{M} = \text{Ru}$ ,  $\text{X} = \text{Se}$ ,  $\text{L} = \text{PPh}_3$ , complex **5**.

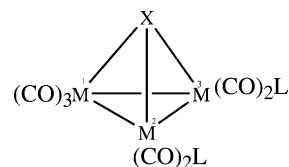


Fig. 2. Structures of complexes **6–10**.  $\text{M}^1 = \text{M}^2 = \text{M}^3 = \text{Co}$ ,  $\text{X} = \text{S}$ ,  $\text{L} = \text{CO}$ , complex **6a**;  $\text{M}^1 = \text{M}^2 = \text{M}^3 = \text{Co}$ ,  $\text{X} = \text{Se}$ ,  $\text{L} = \text{CO}$ , complex **6b**;  $\text{M}^1 = \text{M}^2 = \text{M}^3 = \text{Fe}$ ,  $\text{X} = \text{S}$ ,  $\text{L} = \mu\text{-H}$ , complex **7**;  $\text{M}^1 = \text{M}^2 = \text{M}^3 = \text{Co}$ ,  $\text{X} = \text{S}$ ,  $\text{L-L} = \mu\text{-C}_3\text{H}_5$ , complex **8**;  $\text{M}^1 = \text{M}^2 = \text{M}^3 = \text{Co}$ ,  $\text{X} = \text{S}$ ,  $\text{L}^2 = \text{CO}$ ,  $\text{L}^3 = \sigma\text{-C}_6\text{F}_5$ , complex **9**;  $\text{M}^1 = \text{Fe}$ ,  $\text{M}^2 = \text{M}^3 = \text{Co}$ ,  $\text{X} = \text{S}$ ,  $\text{L} = \text{CO}$ , complex **10**.

Clusters **4a** and **5** are poor hydrogenation catalysts, during the catalytic experiments unexpected organometallic derivatives were formed. This prompted us to extend our investigations to other chalcogenide-capped clusters, such as  $\text{Co}_3(\text{CO})_9\text{X}$  ( $\text{X} = \text{S}$ , **6a**;  $\text{X} = \text{Se}$ , **6b**),  $\text{H}_2\text{Fe}_3(\text{CO})_9\text{S}$  (complex **7**),  $\text{Co}_3(\text{CO})_7(\text{S})(\text{C}_3\text{H}_5)$  (complex **8**),  $\text{Co}_3(\text{CO})_7(\text{S})(\text{C}_6\text{F}_5)$  (complex **9**) and  $\text{FeCo}_2(\text{CO})_9\text{S}$  (complex **10**). Finally, we took into account also the methylidyne-capped tricobalt cluster  $\text{Co}_3(\text{CO})_9[\mu_3\text{-CCH}_2(\text{C}_6\text{H}_{10}\text{OH})]$  (complex **11**). The structures of complexes **6–10** are in Fig. 2 and that of complex **11** is in Fig. 3.

Again, we found that these clusters (but **11**) are very poor hydrogenation catalysts; evidence for their fragmentation has been obtained. Here, we discuss the processes alternative or competitive with catalysis, in particular, fragmentation and recondensation to new or already known products.

## 2. Experimental

### 2.1. General experimental details

Clusters **4–11** were obtained with established literature procedures [13–30]. Solvents heptane, octane,

Table 1

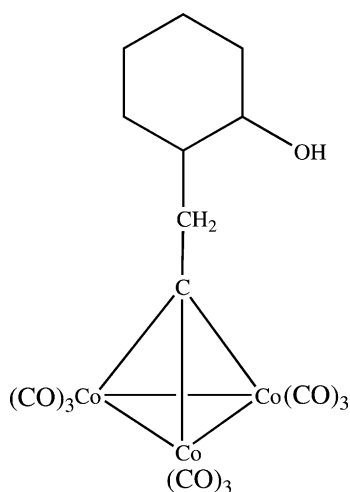
Organic and organometallic products obtained after the the hydrogenation reactions and in the 250 ml vials (V)

Reaction	Products and yields	Identification
<b>4</b> + C <sub>2</sub> Et <sub>2</sub> + H <sub>2</sub> (V)	Parent (40%) <sup>+</sup> , Fe <sub>2</sub> (CO) <sub>6</sub> L <sub>2</sub> (10%) <sup>+</sup> , Fe <sub>3</sub> (CO) <sub>9</sub> Se <sub>2</sub> (10%) <sup>×</sup> , (PPh <sub>3</sub> )Se <sup>*</sup>	(+) Comparison with known IR; (×) IR and MS; (*) IR, <sup>1</sup> H and MS
<b>5</b> + C <sub>2</sub> Ph <sub>2</sub> + H <sub>2</sub> (V)	Parent (80%), unidentified (tr)	(+)
<b>5</b> + C <sub>2</sub> Ph <sub>2</sub> + Me <sub>3</sub> NO (V)	Parent (40%) <sup>+</sup> , Ru <sub>2</sub> (CO) <sub>6</sub> L <sub>2</sub> <sup>+</sup> , C <sub>2</sub> Ph <sub>2</sub> <sup>°</sup> , hexaphenylbenzene <sup>°</sup>	(+) (°) Mass spectrometry
<b>4b</b> + C <sub>2</sub> Ph <sub>2</sub> + Me <sub>3</sub> NO (V)	Parent (90%) <sup>+</sup> , C <sub>2</sub> Ph <sub>2</sub> <sup>°</sup> , <i>t</i> -stilbene <sup>°</sup>	(+) (°)
H <sub>2</sub> Fe <sub>3</sub> (CO) <sub>9</sub> S ( <b>7</b> ) + C <sub>2</sub> Ph <sub>2</sub> + H <sub>2</sub> (experiments K–M)	Parent (80%) <sup>+</sup> , Fe <sub>3</sub> (CO) <sub>9</sub> S <sub>2</sub> <sup>+</sup> <sup>°</sup>	(+) (+)/(°)
Co <sub>3</sub> (CO) <sub>9</sub> X ( <b>6a</b> and <b>6b</b> ) + C <sub>2</sub> Ph <sub>2</sub> + H <sub>2</sub> (experiments H and J)	Co <sub>2</sub> (CO) <sub>6</sub> (C <sub>2</sub> Ph <sub>2</sub> ) (40%) <sup>+</sup> , decomposition	(+)
Co <sub>3</sub> (CO) <sub>7</sub> (S)(C <sub>3</sub> H <sub>5</sub> ) ( <b>8</b> ) + C <sub>2</sub> Ph <sub>2</sub> + H <sub>2</sub> (experiments O and P)	Co <sub>2</sub> (CO) <sub>6</sub> (C <sub>2</sub> Ph <sub>2</sub> ) (40%) <sup>+</sup> , C <sub>2</sub> Ph <sub>2</sub> <sup>°</sup> , hexaphenylbenzene <sup>°</sup>	(+) (°)
Co <sub>3</sub> (CO) <sub>9</sub> (S)(C <sub>6</sub> F <sub>5</sub> ) ( <b>9</b> ) + C <sub>2</sub> Ph <sub>2</sub> + H <sub>2</sub> (experiment R)	Co <sub>2</sub> (CO) <sub>6</sub> (C <sub>2</sub> Ph <sub>2</sub> ) (40%) <sup>+</sup> , C <sub>6</sub> F <sub>5</sub> H <sup>°</sup> , C <sub>6</sub> F <sub>5</sub> H <sub>5</sub> (?) <sup>°</sup>	(+) (°)
FeCo <sub>2</sub> (CO) <sub>9</sub> S ( <b>10</b> ) + C <sub>2</sub> Ph <sub>2</sub> + H <sub>2</sub> (experiment N)	Parent (50%) <sup>+</sup> , metal powder	(+)
Co <sub>3</sub> (CO) <sub>9</sub> [CCH <sub>2</sub> (C <sub>6</sub> H <sub>10</sub> OH)] ( <b>10</b> ) + C <sub>2</sub> Ph <sub>2</sub> + H <sub>2</sub> (experiments S and T)	Parent (10%) <sup>+</sup> , C <sub>2</sub> Ph <sub>2</sub> <sup>°</sup> , hexaphenylbenzene <sup>°</sup> , Co <sub>2</sub> (CO) <sub>6</sub> (C <sub>2</sub> Ph <sub>2</sub> ) (50%) <sup>+</sup> , cyclohexanol, methylcyclohexanol	(+) (°)

diethyl-ether and gases (dihydrogen, dinitrogen) were high-purity grade and were dehydrated before use.

## 2.2. Homogeneous hydrogenation reactions

The reactions were performed, as previously described [2,3], in 25 ml sealed glass vials each containing 2 ml of an *n*-octane solution of the complex

Fig. 3. Structure of complex **11**.

and diphenylacetylene under the appropriate pressure of dihydrogen and/or of other gaseous mixtures. The vials were sealed and then warmed in an oven at 120 °C for the required reaction time. Details of the reagent concentrations and of the reaction conditions are given as footnotes to Tables 1–3.<sup>3</sup>

The organic products in the reaction solutions were analyzed with a Carlo Erba FID 4200 gas chromatograph equipped with a (2 m × 0.6 mm i.d.) SE 30 5% on Chromosorb WAW (60/80 mesh) column operated under the following conditions: N<sub>2</sub> flow 46 ml min<sup>-1</sup>, 60 °C (6 min) then 10 °C min<sup>-1</sup> up to 240 °C.

## 2.3. Identification of the organometallic products after the hydrogenation reactions

The reaction solutions were analyzed by means of IR spectroscopy (Bruker Equinox 55, KBr cells) then chromatographed on TLC preparative plates on which the organometallic products were separated. These were analyzed by IR spectroscopy and—when possible—with <sup>1</sup>H NMR and mass spectrometry (JEOL JNM 270/89; Finnigan Mat TSQ-700 mass

<sup>3</sup> Tables 1–3 are available as supporting material upon request from the authors.

spectrometer [31]). When cooling after the experiments, in most of the reaction vials white crystals were deposited; these resulted to be unreacted diphenylacetylene, but—in some experiments—also *trans*-stilbene or hexaphenylbenzene were observed. The presence of these products in the reaction solutions made difficult the TLC separations and nearly impossible to read the IR spectra in the bridging carbonyl region.

#### 2.4. Other reactions

- (i) Reaction of **4a** with hex-3-yne. In a typical reaction, complex **4a** (500 mg, 2.1 mmol) and hex-3-yne (1 ml, 10 mmol ca.) were dissolved in octane, and sealed under 1 atm of dihydrogen in 250 ml vials, which were warmed for 30 min at 120 °C. The colour of the solution changed from purple to dark brown. TLC purification showed the presence of four bands: red, yellow (yields, ca. 10% each), purple-brown (40% ca.) and greenish (10% ca.). The red band was identified as  $\text{Fe}_3(\text{CO})_9\text{Se}_2$ ; the yellow one as  $\text{Fe}_2(\text{CO})_6\text{L}_2$  [ $\text{L} = \text{C}_2\text{Et}_2$ ]; the brown band was unreacted cluster **4a** and the greenish product was identified as (impure) triphenyl-phosphino-selenide [ $(\text{PPh}_3)\text{Se}$ ] ( $^1\text{H}$  NMR and mass spectrometry).
- (ii) Reaction of **4b** with diphenylacetylene. Complex **4b** (120 mg, 2.1 mmol ca.) and diphenylacetylene (1.0 g, 5.6 mmol) were dissolved in octane and sealed under 1 atm of dihydrogen in a 250 ml vial, which was warmed at 120 °C for 30 min. No evident change of colour could be observed. TLC purification showed the presence of one purple band only, which was shown to be unreacted **4b**. A large amount of diphenylacetylene crystals (containing about 5% of *trans*-stilbene) was also recovered upon cooling the vial.
- (iii) Reaction of **5** with diphenylacetylene. Complex **5** (101 mg, 0.85 mmol ca.) and diphenylacetylene (1.10 g, 5.7 mmol ca.) were dissolved in octane and sealed under 1 atm of dihydrogen in a 250 ml vial, which was warmed at 120 °C for 30 min. No change in colour was observed and TLC purification showed the presence of one orange band only; the IR spectrum showed the bands typical of unreacted **5** and one more band at  $2040\text{ cm}^{-1}$  (unknown).

The above reaction has been repeated, in the same conditions but under  $\text{N}_2$  atmosphere (in a three necked flask) and using  $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$  as a “promoter”. After 12 min, reflux TLC purification showed the presence of a yellow band identified as  $\text{Ru}_2(\text{CO})_6\text{L}_2$  [ $\text{L} = \text{C}_2\text{Ph}_2$ ] in a matrix of crystalline diphenylacetylene containing about 10% of hexaphenylbenzene (mass spectrometry), a red band (parent complex, about 50%) and some decomposition.

### 3. Results and discussion

#### 3.1. Hydrogenation reactions

- (a) Complexes **4** and **5** (Table 1). Complex **4b** (experiment A) gives low TON, decreasing during time; selectivity to *cis*-stilbene increases during time. Complex **4a** (experiments B–D) gives slightly greater TON; these decrease during time as well as the selectivity to *cis*-stilbene. When the dihydrogen pressure is decreased, the TON are nearly constant during time and *trans*-SB is the favoured product. When the S/C ratio is decreased, the TON decrease and *trans*-SB is again the favoured product. All these results point to cluster catalysis, at least at the beginning of the reactions; the “gap” observed, after 30 min time in experiments B–D, could mean, however, that there is a change from cluster to fragment catalysis.

With complex **5** (experiments E–G) low TON are obtained, slightly increasing during time whereas the selectivity to *cis*-SB decreases. The fully hydrogenated product increases steadily during time. Under reduced dihydrogen pressure an increase of the TON is observed and *trans*-SB is the favoured product. When the S/C ratio is decreased, the TON decrease and *trans*-SB is the favoured product, although the selectivity towards it decreases with time.

- (b) Complexes **6a**, **6b**, **7**, and **10** (Table 2). Complexes **6a** (experiment H) and **6b** (experiment J) show a very low activity, nearly constant with time. The di-hydridic complex **7** (experiments K–M) could insert alkynes into the Fe–H bonds, and hence behave as a good catalyst. It shows, instead, a very modest activity increasing during time, whereas

the *trans*-SB yields decrease. This could point for fragment catalysis; however, the inhibition of the catalytic activity when decreasing dihydrogen pressure is used or when CO is present would suggest cluster catalysis. Complex **10** (experiment N) shows a slightly better activity, with TON decreasing and *trans*-stilbene increasing regularly during time; these observations also accord with cluster catalysis.

- (c) Complexes **8**, **9**, and **11** (Table 3). The  $\pi$ -allylic complex **8** (experiments O–Q) shows again a modest activity, nearly constant during time and high selectivity towards *trans*-SB (cluster catalysis). The presence of dihydrogen inhibits and that of CO increases the activity (fragment catalysis). The  $\sigma$ -phenylic complex **9** (experiment R) shows a slightly better activity, increasing during time; increase of the fully hydrogenated product and of *cis*-SB during time are observed. As further discussed below, in the gas-chromatograms also (pentafluoro) benzene and hydrogenated benzene derivatives were detected.

### 3.2. Complex **11** (experiments S and T)

The methylidyne-capped closed triangular complex **11** is the most active among the clusters examined although its activity is quite modest and slightly decreasing with time; this and the selectivity to *trans*-stilbene (increasing during time) would point for cluster catalysis. Also, the decreased activity observed when the substrate/cluster ratio is decreased points for cluster catalysis.

### 3.3. Organometallic products in the reaction solutions

The reaction solutions were purified by TLC and—when possible—the products were subjected to IR<sup>4</sup> and <sup>1</sup>H NMR spectroscopies and to mass spectrometry. The results obtained are collected in Table 1.

<sup>4</sup> The identification of many products was mainly based on IR spectrophotometry. For this reason, we registered the blank spectra of the parent clusters and of most of the “fragments” or of proposed reaction products.

### 3.4. Reactions of **4b** and **5** with C<sub>2</sub>Ph<sub>2</sub>

The reaction of **4b** under dihydrogen yielded only large amounts of unreacted parent. The same happened for **5**; in the reaction solution of the latter a (unidentified) band at 2040 cm<sup>-1</sup> was also observed. This reaction was repeated in the presence of Me<sub>3</sub>NO and gave some Ru<sub>2</sub>(CO)<sub>6</sub>L<sub>2</sub> and hexaphenylbenzene.

### 3.5. Reaction of **4a** with hex-3-yne

This reaction has been studied on greater amounts of cluster, in order to better establish the formation pathway of organometallic compounds; hex-3-yne has been chosen at the place of diphenylacetylene because its <sup>1</sup>H NMR signals were easier to interpretate. Interestingly, not only recondensation of iron fragments (favoured by the chalcogen or by the alkynic substrate) to form Fe<sub>3</sub>(CO)<sub>9</sub>Se<sub>2</sub> was observed; also oligomerization of the alkyne to form Fe<sub>2</sub>(CO)<sub>6</sub>L<sub>2</sub> was found. Finally, “retrosynthesis” of the (PPh<sub>3</sub>)Se used for the synthesis of complex **4a** could be evidenced.

### 3.6. Complex **7**

The IR spectra of the reaction solutions showed the presence of large amounts of unreacted **7**. TLC purification showed the presence of two bands, one red and one brown. The mass spectrum of the red band showed a “parent” ion at 456 *m/z* corresponding to Fe<sub>3</sub>(CO)<sub>8</sub>S<sub>2</sub>, but a comparison of the IR with an authentic sample allowed the identification as Fe<sub>3</sub>(CO)<sub>9</sub>S<sub>2</sub>.

### 3.7. Complexes **6a** and **6b**

After TLC purification, in the reaction solutions of **6a** high yields of dark-red Co<sub>2</sub>(CO)<sub>6</sub>(C<sub>2</sub>Ph<sub>2</sub>), as the unique product, were obtained. The same behaviour has been observed for **6b**.

### 3.8. Complex **8**

The IR spectra of the reaction solutions showed the presence of Co<sub>2</sub>(CO)<sub>6</sub>(C<sub>2</sub>Ph<sub>2</sub>) in considerable amounts. The solutions were put together, brought to small volume and cooled (4 °C) for some days; a precipitate of whitish long needles (slightly contaminated

with organometallic products) was obtained. These resulted to be a mixture of unreacted diphenylacetylene and of hexaphenylbenzene (in about 10 to 1 ratio) as evidenced by  $^1\text{H}$  NMR and mass spectrometry. It is known that complexes  $\text{Co}_2(\text{CO})_6(\text{RC}_2\text{R}')$  catalyze the cyclotrimerization of alkynes [32–35].

### 3.9. Complex **9**

In the reaction solutions considerable amounts of  $\text{Co}_2(\text{CO})_6(\text{C}_2\text{Ph}_2)$  were found; GLC–MS analyses of these solutions also showed the presence of  $\text{C}_6\text{F}_5\text{H}$  and of  $\text{C}_6\text{F}_5\text{H}_5$  (tentative identification), coming from the hydrogenation of the  $\sigma$ -bound pentafluoro phenyl ligand.

### 3.10. Complex **10**

After the reactions, on the walls of the vials, a metallic mirror was observed. The IR spectra of the reaction solutions showed the presence of the parent cluster. TLC separation also showed one brown band only, corresponding to complex **10**, and some decomposition (metal powder).

### 3.11. Complex **11**

TLC purification of the reaction solutions showed the presence of small amounts (about 10%) of unreacted complex **11** and of considerable amounts of  $\text{Co}_2(\text{CO})_6(\text{C}_2\text{Ph}_2)$ ; a whitish precipitate was also collected in the vials after longer reaction times. This

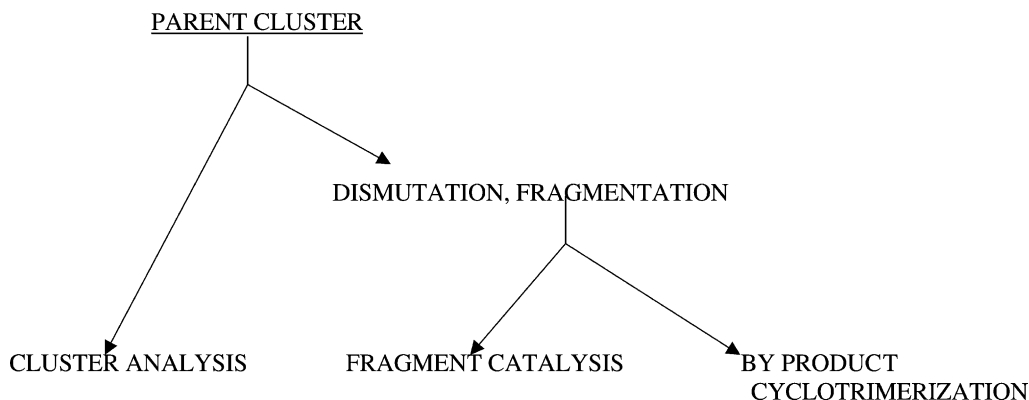
showed IR absorptions typical of diphenylacetylene and/or *trans*-stilbene (and of hexaphenylbenzene). The fate of the methylidyne ligand is also of interest; in the reaction products cyclohexanol, methylcyclohexanol and unidentified heavy organic products presumably coming from the linking of  $\text{C}_2\text{Ph}_2$  to the methylidyne (gas chromatography) were observed.

The tendency of several other cobalt clusters to form  $\text{Co}_2(\text{CO})_6(\text{C}_2\text{Ph}_2)$  when reacted in the presence of diphenylacetylene has been evidenced. Presumably, the driving force of the reaction is the formation of the very stable, tetrahedral, binuclear derivative. Obviously, this behaviour constitutes evidence for the formation of metal fragments in solution.

### 3.12. Reaction pathways

- (i) Formation of metal fragments. This has been observed, during catalytic experiments, for clusters **1–3** [11]. Evidence for the fragmentation of  $\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3$  to mononuclear hydridic fragments, under heating and UV light has been confirmed with *para*-hydrogen NMR experiments [36]. The stepwise formation of  $\text{Ru}_3(\text{CO})_9(\text{PCy}_3)_3$  starting from  $[\text{HRu}_3(\text{CO})_{11}]^-$  occurs in methanol, through the intermediacy of  $\text{H}_2\text{Ru}_3(\text{CO})_6(\text{PCy}_3)_3$  which adds CO and loses hydrogen to form the final product [37].

Formation and recombination of metal fragments also occurs for chalcogenide clusters. It is known that sulphur promotes the formation of  $\text{Fe}(\text{CO})_5$  via the formation of  $\text{Fe}_3(\text{CO})_9\text{S}_2$



Scheme 1. Proposed reaction pathways observed during the reactions with clusters **4–11** with diphenylacetylene and dihydrogen.



intermediates [38]; this is in accord with the results obtained in this work. An example of (ruthenium) fragment condensation promoted by the C–S bond cleavage of the ligand  $\text{SCH}_2\text{CH}=\text{CH}_2$  is known [39]; a comparable reaction is the formation of tri- and tetranuclear heterometallic clusters favoured by the P–Se cleavage of phosphine selenides [40]. Formation of tetranuclear complexes is observed during the reactions of  $\text{Fe}_3(\text{CO})_9(\mu_3\text{-Te})_2$  with  $\text{Fe}_2(\text{CO})_9$  [41].  $\text{Fe}_3(\text{CO})_9\text{S}_2$  (**4b**) is also formed (with other products coming from metal fragment condensation) when the anion  $[\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-}\eta^2\text{-CR}' = \text{CHR}'')]^-$  ( $\text{R} = \text{H, Me}$ ;  $\text{R}' = \text{H, Et, Ph}$ ) is reacted at low temperature with  $\text{Fe}_2(\text{CO})_6\text{S}_2$  [42].

- (ii) Reactivity of sulphido-capped clusters towards alkynes. Clusters **4–10** show a low hydrogenation activity. In addition, both clusters and fragments react with the alkyne substrate to form inactive species such as metalla-ferroles or complexes active in other reactions such as alkyne trimerization. Reductive coupling of alkynes (to give *cis*-dienes, which are precursors of ferroles) has been observed for  $\text{H}_2\text{M}_3(\text{CO})_8(\text{NCMe})(\mu_3\text{-X})$  [ $\text{M} = \text{Ru}$ ,  $\text{X} = \text{NSOOC}_6\text{H}_4\text{Me-4}$ ;  $\text{M} = \text{Os}$ ,  $\text{X} = \text{S}$ ] [43]. The reaction of  $\text{Fe}_3(\text{CO})_7(\mu\text{-PPh}_2)_2(\mu_3\text{-S})$  with alkynes leads to bimetallic derivatives containing alkynes inserted into the Fe–P and Fe–S bonds [44].<sup>5</sup>

It is also worth noting that the sulphido-capped  $[\text{CpMo}(\text{CO})_2]_2\text{Ru}(\text{CO})_3(\mu_3\text{-S})$  catalyzes the cyclotrimerization of phenylacetylene to 1,3,5-triphenyl-benzene through an intermediate containing a six-carbon atom chain on the opposite face of the cluster with respect of the  $\mu_3\text{-S}$  [45]. For complexes **8** and **11** we have found comparable behaviour, the difference being that, in our case, cluster fragmentation occurred and the catalytic species was  $\text{Co}_2(\text{CO})_6(\text{PhC}_2\text{Ph})$ .

Thus, the results obtained would indicate that capped complexes undergo cluster catalysis; the low activities observed could be ascribed to the

electronic saturation and stability of the clusters. The presence of capping ligands would prevent (but not exclude) fragmentation of the clusters and therefore the possibility of fragment catalysis. In addition, the ligands or substrates would favour recondensation of the metal fragments formed giving stable and catalytically inactive species. The proposed reaction pathways are shown in Scheme 1.

- (iii) Behaviour of cluster **11**. This cluster shows a moderate hydrogenation activity and the tendency to fragment to form  $\text{Co}_2(\text{CO})_6(\text{C}_2\text{Ph}_2)$ . Methylidyne derivatives are models for the hydrogenation of alkynes and alkenes on clusters; such structures have also been isolated in some hydrogenation experiments [46]. On the other hand,  $\text{Co}_3(\text{CO})_9(\mu_3\text{-CPh})$  was tested in the hydroformylation of 1- and 2-pentene under pressure; cluster catalysis was proposed [47]. Later on it was found that, under CO/dihydrogen, fragmentation and monometallic catalysis occurs [48,49]. After the hydroformylation of 1-hexene in the presence of  $\text{Co}_3(\text{CO})_9(\mu_3\text{-CPh})$  Seyferth observed extensive decomposition; with cross-experiments he concluded that fragment catalysis is likely to occur [50]. In contrast,  $\text{Co}_3(\text{CO})_7(\mu\text{-dppm})(\mu_3\text{-CCH}_3)$  acts as a cluster catalyst in the hydroformylation of 1-pentene under pressure [51].

There are several examples of the reactivity of methylidyne-capped clusters towards alkynes; usually ferrole-like derivatives are obtained [52–54].

#### 4. Conclusion

In this work, we evidenced that competitive processes, that is cluster and fragment catalysis, as well as recombination of metal fragments, occur when clusters **4–11** are reacted with  $\text{C}_2\text{Ph}_2$  under dihydrogen. Our results suggest that: (i) the type and bonding of the cluster substituent has a strong influence on the activity; (ii) the nature of the metal is considerably important (e.g. iron versus ruthenium); (iii) in nearly all the experiments made there is competition between cluster and fragment catalysis; (iv) recondensation of metal fragments is favoured by the cluster ligands or by the alkyne substrate; (v) the new

<sup>5</sup> According with these results, we have found that complex **5** reacts with terminal alkynes  $\text{HC}\equiv\text{CR}$  ( $\text{R}=\text{Ph}$ ,  $\text{Bu}^t$ ) to give the complexes  $\text{Ru}_3(\text{CO})_6(\text{PPh}_3)_2(\mu_3\text{-Se})[\mu_3\text{-}\eta^1\text{-C}=\text{C}(\text{H})\text{R}]$  with a vinyl on the opposite side of Se. Predieri and Sappa, unpublished results.

complexes formed may be catalytically inactive or favour reactions different from hydrogenation.

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