

## METAL CLUSTERS IN CATALYSIS. THE REACTIVITY OF ALKYNE- AND VINYLIDENE-SUBSTITUTED HOMO- AND HETERO-METALLIC CLUSTERS TOWARDS MOLECULAR HYDROGEN IN HOMOGENEOUS CONDITIONS

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### Summary

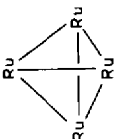
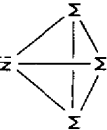
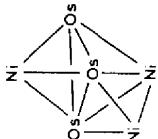
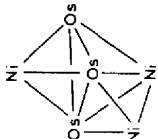
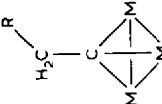
The reactivity of alkyne- and vinylidene-substituted clusters towards molecular hydrogen in homogeneous conditions has been studied by means of GC and GC/MS techniques. The reactivity of the homo- and hetero-metallic cluster frames (containing nickel and one of the iron triad metals) is discussed, as well as that of the coordinated ligands. Under hydrogen the cluster cores are modified, sometimes as a part of a catalytic cycle. The products obtainable from the coordinated small molecules seem to depend mainly on the overall electronic situation of the clusters or on the C-C distances in the alkynes, and to a lesser extent on the number of coordinating metal centres. In some instances it was observed that when both free alkynes and substituted clusters were present, only the coordinated alkynes were hydrogenated.

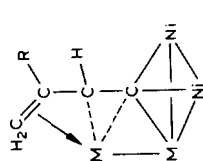
### Introduction

Selective hydrogenation of alkenes and alkynes under homogeneous conditions in the presence of metal clusters has been recently reported;  $\text{Pt}_2\text{Co}_2$  clusters selectively catalyse hydrogenation of phenylacetylene to styrene [1]. In the presence of  $\text{Ru}_3(\text{CO})_{12}$  styrene is hydrogenated to ethylbenzene and alkyne-substituted butterfly clusters have been identified as intermediates [2]. The hydrogenation of alkynes to alkenes in a catalytic cycle based on  $\text{HRu}_3(\text{CO})_9(\text{PPh}_2)$  has been described [3]. The mechanism of the hydrogenation of ethylene to ethane catalyzed by  $\text{H}_4\text{Ru}_4(\text{CO})_{12}$  has been discussed [4]. Finally, a full hydrogenation cycle, starting from hexafluorobutyne and leading to *cis*- and *trans*-hexafluorobutene catalyzed by osmium clusters, has been established [5].

We previously found that *t*-butylalkyne is hydrogenated to neohexane in the presence of  $\text{HRu}_3(\text{CO})_9\text{C}_2\text{Bu}^t$  [6] and that the heterometallic derivative  $(\eta\text{-C}_5\text{H}_5)_3\text{Ni}_3\text{Os}_3(\text{CO})_9$ , complex 1, and  $(\eta\text{-C}_5\text{H}_5)\text{NiM}_3(\text{CO})_9(\mu\text{-H})_3$  ( $\text{M} = \text{Ru}$ , com-

TABLE 1  
HOMO- AND HETERO-METALLIC SUBSTITUTED CLUSTERS AND RELATED COMPLEXES CONSIDERED IN THIS WORK

	Cluster frame	Coordination of the ligand and C-C bond length	Reference	Structure <sup>a</sup>
<i>Unsubstituted clusters</i> $H_4Ru_4(CO)_{12}$	homometallic tetrahedron	-	16	
$(Cp)NiRu_3(CO)_9(H)_3$ (complex 2a)	heterometallic tetrahedron	-	7	
$(Cp)NiOs_3(CO)_9(H)_3$ (complex 2b)	heterometallic tetrahedron	-	7	
$(Cp)_3Ni_3Os_3(CO)_9$ (complex 1)	heterometallic capped trigonal bipyramid	-	7	
<i>Substituted clusters</i> <i>(a) Apical substituents</i> $Fe_3(CO)_8(HC_2Et)_4$ (complex 10) $H_3Ru_3(CO)_9(CCH_2Bu^1)$ (complex 11)	homometallic triangle homometallic triangle	apical, $\mu_3$ (1.509(5)) apical, $\mu_3$ (1.525(9))	17 6	

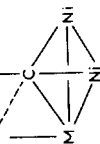


11

apical,  $\mu_3$   
(see also text)  
(1.42)

heterometallic  
"spiked triangle"

$(\text{Cp})_2\text{Ni}_2\text{Fe}_2(\text{CO})_6(\text{C}_5\text{H}_6)$   
(complex 5a)

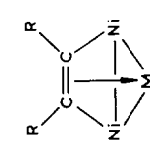


13

apical,  $\mu_3$   
(see also text)  
(1.45(4))

heterometallic  
"spiked triangle"

$(\text{Cp})_2\text{Ni}_2\text{Ru}_2(\text{CO})_6(\text{C}_5\text{H}_6)$   
(complex 5b)

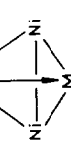


18

$\mu_3\text{-}\eta$   
alkyne  
(1.34(2)) (R = Ph)

heterometallic  
triangle

(b) *Alkyne substituents*  
 $(\text{Cp})_2\text{Ni}_2\text{Fe}(\text{CO})_3(\text{C}_2\text{R}_2)$   
(R = Ph, complex 7a)

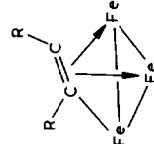


18

$\mu_3\text{-}\eta$   
alkyne  
(1.40(3)) (R = Ph)

heterometallic  
triangle

$(\text{Cp})_2\text{Ni}_2\text{Ru}(\text{CO})_3(\text{C}_2\text{Ph}_2)$   
(complex 7c)

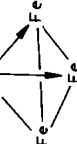


19

$\mu_3\text{-}\eta^2$   
alkyne  
(1.409(22))

homometallic  
triangle

$\text{Fe}_3(\text{CO})_9(\text{C}_2\text{Ph}_2)$   
(complex 8a)

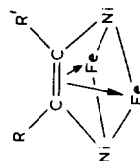


20

$\mu_3\text{-}\eta^2$   
alkyne

homometallic  
triangle

$\text{Fe}_3(\text{CO})_9(\text{C}_2\text{Et}_2)$   
(complex 8b)



15

$\mu_4\text{-}\eta^2$   
alkyne  
(1.431(23)) (R = Et)

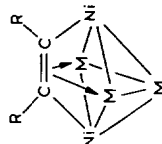
heterometallic  
square  
(see also text)

$(\text{Cp})_2\text{Ni}_2\text{Fe}_2(\text{CO})_6(\text{RC}_2\text{R}')$

(R = R' = Ph, complex 6b)

(R = R' = Et, complex 6c)

(R = H, R' = isopropenyl  
complex 6a)



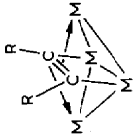
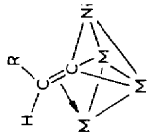
11

$\mu_4\text{-}\eta^2$   
alkyne  
(1.41(1))

heterometallic  
square pyramid

$(\text{Cp})_2\text{Ni}_2\text{Ru}_3(\text{CO})_8(\text{C}_2\text{Ph}_2)$   
(complex 4)

TABLE 1 (continued)

	Cluster frame	Coordination of the ligand and C-C bond length	Reference	Structure <sup>a</sup>
$\text{Ru}_4(\text{CO})_{12}(\text{C}_2\text{Ph}_2)$ (complex 9)	homometallic butterfly	$\mu_4\text{-}\eta^2$ alkyne (1.46(2))	21	
c) $\mu_4\text{-}\eta^2$ Vinylidene substituents (Cp)NiRu <sub>3</sub> (CO) <sub>9</sub> (H) (C = CHR)	heterometallic butterfly	$\mu_4\text{-}\eta^2$ vinylidene (1.436(13) R = Bu <sup>t</sup> ) (1.417(8) R = Pr <sup>t</sup> )	8 10 this work 9	
(R = Bu <sup>t</sup> complex 3a) (R = Pr <sup>t</sup> complex 3c) (R = Ph complex 3d) (Cp)NiOs <sub>3</sub> (CO) <sub>9</sub> (HX)(C=CHR) (R = Bu <sup>t</sup> complex 3b)	heterometallic butterfly	$\mu_4\text{-}\eta^2$ vinylidene (1.44(3))		

<sup>a</sup> (Cp), H, and CO ligands omitted for clarity.

plex **2a**; M = Os, complex **2b**) selectively hydrogenate t-butylacetylene and t-butylethylene under homogeneous conditions [7]. The mechanism of, and the intermediates in the latter reactions were not established, but it was suggested that possible intermediates could be the vinylidene substituted butterfly clusters  $(\eta\text{-C}_5\text{H}_5)_2\text{NiM}_3(\mu\text{-H})(\text{CO})_9(\text{C}=\text{CHR})$  (M = Ru, R = Bu<sup>t</sup> complex **3a** [8]; M = Os, R = Bu<sup>t</sup>, complex **3b** [9]). The complex with M = Ru, R = Pr<sup>i</sup> complex **3c** has also been characterized [10]).

The use of H<sub>2</sub> instead of N<sub>2</sub> as the reaction atmosphere considerably increased the yields of **3a** and **3c**, and was critical for the synthesis of **3b**. The presence of molecular hydrogen was shown to influence markedly both the yields and the nature of the vinylidene- and alkyne-substituted heterometallic clusters containing nickel and one metal of the iron triad; an example of this behaviour is the synthesis of  $(\eta\text{-C}_5\text{H}_5)_2\text{Ni}_2\text{Ru}_3(\text{CO})_8(\text{C}_2\text{Ph}_2)$ , complex **4**, which was not obtained under N<sub>2</sub> [11]. Furthermore, the yields of the "spiked triangular"  $(\eta\text{-C}_5\text{H}_5)_2\text{Ni}_2\text{M}_2(\text{CO})_6\text{-}[\text{CC}(\text{H})\text{C}(\text{=CH}_2)(\text{CH}_3)]$  (M = Fe, complex **5a** [12]; M = Ru, complex **5b** [13]) and of the "square planar" isomer  $(\eta\text{-C}_5\text{H}_5)_2\text{Ni}_2\text{Fe}_2(\text{CO})_6[\text{HC}_2\text{C}(\text{=CH}_2)(\text{CH}_3)]$ , complex **6** [12] are hydrogen dependent. This led us to suspect that the above clusters play a role as intermediates in the selective hydrogenation of alkynes in homogeneous conditions.

The role of clusters in homogeneous catalysis is still under discussion. Only a few examples of true cluster catalysis have been reported, whereas several examples of catalysis by the decomposition products have been found. On the other hand, the multi-site coordination of small molecules on several metal centres, such as are present in clusters, has been used as a "model" for the chemisorption (and "activation") of the same small molecules on surfaces [14]. For these reasons, we considered it to be of interest to study the reactions of clusters substituted with alkynes and vinylidenes towards H<sub>2</sub>, under the same conditions as are used for the reactions of clusters **1** and **2** with alkynes.

The clusters chosen for this study are listed in Table 1; the structures of the majority of them have been determined by X-ray methods. The table also gives the C-C bond lengths where these are available.

We studied both the reactivity of the cluster frames towards H<sub>2</sub> and the hydrogenation products obtained from the coordinated ligands. The variation in the behaviour of a given alkyne in different coordination environments was also investigated.

## Experimental

### Products and reactants

The clusters listed in Table 1 were made as reported in earlier papers (see references in the table) and were recrystallized before use. The hydrocarbon solvents (Carlo Erba pure grade) were distilled from sodium and stored over molecular sieves; before use they were saturated with dry nitrogen. The organometallic derivatives produced in the reactions were separated by preparative TLC plates (Kieselgel G or PF Merck; eluants: mixtures of ethyl ether and light petroleum). High purity diphenylacetylene (Fluka), *trans*-stilbene (Fluka) and diphenylethane (bibenzyl, Schilling) were used as GC standards. *trans*-Stilbene contained trace amounts of the *cis*-isomer and of diphenylethane (GC/MS evidence); this was particularly useful for the identification of *cis*-stilbene in the GC chromatograms.

### *Hydrogenation experiments*

These were performed in sealed glass vials of 100 or 50 ml volume, each containing either 10 or 5 ml of a 10 mM heptane solution of the complex. After freezing, the vials were evacuated and the solutions were then allowed to reach room temperature. Hydrogen (SIAD, ultrapure grade) (0.9 atm) was then introduced and after refreezing the vials were sealed off. They were then kept in a thermostated oven at  $120 \pm 2^\circ\text{C}$ . After the reaction, the solutions were examined either by GC/MS to identify the organic products, and by TLC (followed by IR or mass spectrometric analyses) to identify the organometallic species. The gas content of the vials was not investigated.

For some hydrogenations smaller vials, 25 ml in volume, were used; these were filled with 2.5 ml of a 10 mM heptane solution of the complex and 0.9 atm of hydrogen, by the procedure described above. The organic products were analysed by GC and the organometallic products by TLC.

### *Blank tests. Metallic powders as catalysts*

In all the experiments we observed the formation of metallic powder in varying amounts, and this was especially noticeable in the longer runs. Elemental analysis of these powders (Perkin–Elmer 303 Atomic Absorption Spectrophotometer) showed the presence of iron and nickel (or ruthenium and nickel) in ratios depending on the stoichiometry of the starting clusters.

Heptane (10 ml) containing diphenylacetylene (10 mmol/l) were placed into two 100 ml vials, containing either Fe/Ni or Ru/Ni powder (obtained as a precipitate from the hydrogenation of the clusters, and carefully washed with heptane). The vials were then filled with 0.9 atm of hydrogen sealed as described above, and kept in an oven at  $120^\circ$  for 18 h. The solutions were then analyzed by GC. In both cases no diphenylacetylene remained; the main product was diphenylethane and about 10% of *trans*-stilbene was also present.

### *Reactions of complexes 1 and 2b*

The reaction of complexes **1**,  $(\eta\text{-C}_5\text{H}_5)_3\text{Ni}_3\text{Os}_3(\text{CO})_9$  and **2b**,  $(\eta\text{-C}_5\text{H}_5)\text{NiOs}_3(\mu\text{-H})_3(\text{CO})_9$  with *t*-butylacetylene in presence of hydrogen (sealed vials, homogeneous conditions) has previously been reported [7]. The reaction of **1** and **2b** with alkynes under hydrogen and nitrogen were carried out in conventional glass apparatus by refluxing heptane or octane solutions of the complexes with a twofold molar excess of alkynes, as indicated below.

(a) *Reactions of complex 1.* Treatment of **1** with *t*-butylalkyne under  $\text{N}_2$  in heptane for 90 min yielded small amounts of  $\text{HOs}_3(\text{CO})_9\text{C}_2\text{Bu}^t$  (ca. 1%) [10],  $(\eta\text{-C}_5\text{H}_5)\text{NiOs}_3(\text{CO})_9(\mu\text{-H})(\text{C}=\text{CHBu}^t)$  (ca. 1%) and three, unidentified trace products.

Treatment of **1** in heptane, for 340 min under  $\text{N}_2$  with diphenylalkyne yielded very small amounts of 5 products, of which we identified  $\text{Os}_3(\text{CO})_{10}(\text{C}_2\text{Ph}_2)$  [22] and  $\text{Os}_3(\text{CO})_9(\text{C}_2\text{Ph}_2)_2$  [23]. The same reaction under  $\text{H}_2$  yielded about 15% of complex **2b**, together with small amounts of  $\text{HOs}_3(\text{CO})_{10}[\text{HC}(\text{Ph})=\text{CPh}]$  [24] and four unidentified trace products.

(b) *Reactions of complex 2b.* Treatment of **2b** with *t*-butylalkyne under  $\text{N}_2$  in octane for 120 min gave small amounts of  $\text{HOs}_3(\text{CO})_9\text{C}_2\text{Bu}^t$  and  $(\eta\text{-C}_5\text{H}_5)\text{NiOs}_3(\text{CO})_9(\mu\text{-H})(\text{C}=\text{CHBu}^t)$  (about 1% each). The same reaction under CO

gave higher yields of these products (about 3% of each) and 7 unidentified trace products, probably arising from decomposition. Treatment of **2b** in heptane, under  $N_2$  for 8 h with diphenylalkyne gave, besides large amounts of unchanged **2b**, only 4 trace products (not investigated). A GC/MS investigation of the solution showed the exclusive presence of diphenylalkyne.

The same reaction, for 7 h in octane under  $N_2$  gave about 80% of unchanged **2b**, some decomposition, and small yields of  $Os_3(CO)_{10}(C_2Ph_2)$  and  $Os_3(CO)_9(C_2Ph_2)_2$ ; GC/MS investigation of the product solution showed the presence of diphenylalkyne and trace amounts of diphenylalkenes.

The same reaction, under  $H_2$ , gave about 80% of unreacted **2b**, and 2% each of  $Os_3(CO)_{10}(C_2Ph_2)$  and  $HOs_3(CO)_{10}[H(Ph)C=CPh]$ ; GC/MS of the reaction solution showed the presence of equimolar amounts of diphenylalkyne and (*trans* + *cis*)-stilbene.

#### *Physical measurements and GC separation of diphenylacetylene and its hydrogenation products*

The organometallic products were generally obtained in very small amounts, and so not all of them could be characterized. This also precluded elemental analysis. The complexes were identified by spectroscopy.

The IR spectra were recorded on a Perkin-Elmer 580 B(KBr optics) instrument. The mass spectra were recorded on an Hitachi-Perkin-Elmer RMU 6H single focusing instrument, equipped with a direct inlet system and operating in E.I. at 70 eV.

The GC/MS analyses were performed with a Carlo Erba chromatograph (with SE 54 capillary columns, injections at 50°C, temperature program 10°C/min till 280°C), Kratos MS-50 instrument (Laboratorio di Gascromatografia-Spettrometria di Massa, Università-Provincia di Torino).

The GC analyses were performed on a Carlo Erba 4200 F.I.D. instrument operating with a 2 m, n-octane/Porasil C 100/120 mesh column, carrier  $N_2$ , 25 ml/min, in temperature programmed separations; the injections were at 60°C and the temperature was then raised at 5°C/min to 155°C. These conditions allowed the separation and identification of hexane and hexynes, and also of benzene, toluene, ethyl-benzene etc.

The separation of diphenylalkyne, stilbenes and diphenylethane was carried out with the same instrument using a 2 m SE 30 5% on Chromosorb W, AW, 60/80 mesh column, carrier  $N_2$ , 46 ml/min, temperature program 60–240°C, 10°C/min. The order of elution of the components was: *cis*-stilbene, diphenylethane, diphenylacetylene and *trans*-stilbene. (The order seems to be related, at least in part to the boiling points of the hydrocarbons. To our knowledge, the GC separation of such a mixture has not been previously reported, in spite of its importance for hydrogenation studies with the widely used diphenylalkyne ligand.)

The nature of the products was unequivocally established by the use of standard solutions containing the hydrocarbons in various proportions; the trace amounts of *cis*-stilbene in the *trans*-stilbene standard allowed the identification of the isomers by means of GC/MS. Accurate comparison between the mass results and the GC results then enabled the detection of *cis*-stilbene in the GC chromatograms also.

TABLE 2. ORGANIC AND ORGANOMETALLIC PRODUCTS FORMED IN HYDROGENATION OF COMPLEXES 1-11

Complex	Reaction conditions	Organic products (GC/MS)	Metal containing fragments in solution (GC/MS)	Organometallic products (TLC) <sup>a</sup>	Reference
<i>Apical ligands</i> Fe <sub>3</sub> (CO) <sub>9</sub> (HC <sub>2</sub> Et) <sub>4</sub> (complex 10)	A <sup>b</sup>	H <sub>3</sub> CCH <sub>2</sub> CH <sub>3</sub> <sup>c</sup> , C <sub>11</sub> H <sub>19</sub> <sup>d</sup> , C <sub>9</sub> H <sub>16</sub> <sup>d</sup> neohexane	Fe(CO) <sub>3</sub> <sup>+</sup>	decomposition (metal powder) <sup>e</sup> H <sub>4</sub> Ru <sub>4</sub> (CO) <sub>12</sub>	this work 6
H <sub>3</sub> Ru <sub>3</sub> (CO) <sub>9</sub> (CCH <sub>2</sub> Bu) <sup>f</sup> (complex 11)	see ref.6				
(Cp) <sub>2</sub> Ni <sub>2</sub> Fe <sub>2</sub> (CO) <sub>8</sub> (C <sub>3</sub> H <sub>6</sub> ) (complex 5a)	A	<i>methylbutane</i> hydrogenated dimer cyclopentadiene <i>methylbutane</i> hydrogenated oligomers ( <i>n</i> = 2-4)	Fe(CO) <sub>3</sub> <sup>+</sup> Fe <sub>2</sub> <sup>+</sup> Fe <sup>+</sup>	decomposition H <sub>4</sub> Ru <sub>4</sub> (CO) <sub>12</sub> (IR) (Cp)NiRu <sub>3</sub> (CO) <sub>9</sub> (H) <sub>3</sub> (IR)	this work this work
(Cp) <sub>2</sub> Ni <sub>2</sub> Ru <sub>2</sub> (CO) <sub>6</sub> (C <sub>5</sub> H <sub>6</sub> ) (complex 5b)	A	<i>methylbutane</i> , <i>hydrogenated oligomers</i> ( <i>n</i> = 2-4)	-		this work
μ <sub>3</sub> -η-Alkynes (Cp) <sub>2</sub> Ni <sub>2</sub> Fe(CO) <sub>3</sub> (C <sub>2</sub> Ph <sub>2</sub> ) (complex 7a)	D	<i>benzene</i> , <i>ethylbenzene</i> , <i>styrene</i> <i>diphenylethylene</i> ( <i>cis</i> + <i>trans</i> ) <i>diphenylethane</i> , <i>diphenylalkyne</i>	-		this work
(Cp) <sub>2</sub> Ni <sub>2</sub> Ru(CO) <sub>3</sub> (C <sub>2</sub> Ph <sub>2</sub> ) (complex 7c)	A	<i>ethylbenzene</i> , <i>stilbene</i> ( <i>cis</i> + <i>trans</i> ) <i>diphenylalkyne</i> , <i>diphenylethane</i> , C <sub>14</sub> H <sub>30</sub>	(Cp) <sub>2</sub> Ru <sup>+</sup>	decomposition (Cp) <sub>2</sub> Ni <sub>2</sub> Ru <sub>3</sub> (CO) <sub>8</sub> (C <sub>2</sub> Ph <sub>2</sub> ) (IR)	this work (see also Table 4) this work
μ <sub>3</sub> -η <sup>2</sup> -Alkynes Fe <sub>3</sub> (CO) <sub>9</sub> (C <sub>2</sub> Ph <sub>2</sub> ) (complex 8a)	A	<i>diphenylalkyne</i> , <i>diphenylethylene</i> ( <i>cis</i> + <i>trans</i> ), <i>diphenylethane</i> <i>3-hexyne</i> , <i>hexene</i> , <i>hexane</i> , <i>hydrogenated</i> <i>oligomers</i> ( <i>n</i> = 2, 3)	Fe(CO) <sub>3</sub> <sup>+</sup>	decomposition	this work
Fe <sub>3</sub> (CO) <sub>9</sub> (C <sub>2</sub> Et <sub>2</sub> ) (complex 8b)	A		-	decomposition	this work
μ <sub>4</sub> -η <sup>2</sup> -Alkynes (Cp) <sub>2</sub> Ni <sub>2</sub> Fe <sub>2</sub> (CO) <sub>6</sub> (C <sub>2</sub> Ph <sub>2</sub> )	A	<i>benzene</i> , <i>ethylbenzene</i>	-	(Cp) <sub>2</sub> Ni <sub>2</sub> Fe <sub>2</sub> (CO) <sub>6</sub> (C <sub>2</sub> Ph <sub>2</sub> ) (10%)	this



(complex 6b)	tetracyclone, diphenylethane, diphenylethylene ( <i>cis</i> + <i>trans</i> ), diphenylalkyne	(IR)	work
B	diphenylalkyne, diphenylethylene ( <i>cis</i> + <i>trans</i> ), diphenylethane	(Cp) <sub>2</sub> Fe <sup>+</sup> (Cp)Ni <sup>+</sup> Ni <sub>2</sub> (C <sub>2</sub> Ph <sub>2</sub> ) <sup>+</sup> (Cp) <sub>2</sub> Fe <sup>+</sup> Fe(CO) <sub>2</sub> <sup>+</sup> FeNi <sup>+</sup> Ni(CO) <sup>+</sup>	this work
A	3-hexene, hexane	(Cp) <sub>2</sub> Ni <sub>2</sub> Fe <sub>2</sub> (CO) <sub>6</sub> (C <sub>2</sub> Et <sub>2</sub> ) <sup>g</sup> (IR)	this work
A	4-methylbutane,	Fe <sub>2</sub> (CO) <sub>6</sub> (HC <sub>2</sub> R) <sub>2</sub> (IR, MS)	this work
C	4-methylbutane	decomposition	this work
A	4-methylbutane	decomposition	work
A	hydrogenated oligomers ( <i>n</i> = 2, 3) ethylbenzene, ethylcyclohexane, C <sub>8</sub> H <sub>18</sub> (several isomers)	Ru <sub>3</sub> C <sub>2</sub> <sup>+</sup> , Ru <sub>3</sub> C <sub>3</sub> <sup>+</sup> RuPh <sup>+</sup> Ru(C <sub>2</sub> Ph <sub>2</sub> ) <sup>+</sup> Ru(C <sub>2</sub> Ph <sub>2</sub> ) <sup>+</sup>	this work
A	diphenylethane diphenylethylene ( <i>cis</i> + <i>trans</i> )	Ru <sub>3</sub> (CO) <sub>12</sub> (IR) H <sub>4</sub> Ru <sub>4</sub> (CO) <sub>12</sub> (IR)	this work
A	C <sub>3</sub> H <sub>12</sub> , hydrogenated oligomers ( <i>n</i> = 2, 4), octenes <sup>h</sup> , octanes <sup>h</sup> , nonanes <sup>i</sup>	H <sub>4</sub> Ru <sub>4</sub> (CO) <sub>12</sub> (IR) Ru <sub>3</sub> (CO) <sub>12</sub> (IR) (Cp)NiRu <sub>3</sub> (CO) <sub>9</sub> (H) <sub>3</sub> (IR) (Cp)NiRu <sub>3</sub> (CO) <sub>9</sub> (H) <sub>3</sub> (IR) H <sub>4</sub> Ru <sub>4</sub> (CO) <sub>12</sub> (IR)	this work
A	ethylbenzene	Ru <sub>2</sub> (CO) <sup>+</sup>	this work
A	ethylbenzene	RuC <sup>+</sup> RuPh <sup>+</sup>	this work
A	hydrogenated dimer	-	work
E	neohexene, propane	HRu <sub>3</sub> (CO) <sub>9</sub> (C <sub>2</sub> Bu <sup>l</sup> ) (IR) H <sub>2</sub> Ru <sub>3</sub> (CO) <sub>9</sub> (C=CHBu <sup>l</sup> ) (IR, MS) H <sub>3</sub> Ru <sub>3</sub> (CO) <sub>9</sub> (C.CH <sub>2</sub> Bu <sup>l</sup> ) (IR, MS) H <sub>4</sub> Ru <sub>4</sub> (CO) <sub>12</sub> (IR)	this work
B	neohexane butanes	(Cp)NiRu <sub>3</sub> (CO) <sub>9</sub> (H) <sub>3</sub> (IR) (Cp)NiOs <sub>3</sub> (CO) <sub>9</sub> (H) <sub>3</sub> (IR)	this work
B	neohexane, neohexene butanes	(Cp)NiOs <sub>3</sub> (CO) <sub>9</sub> (H) <sub>3</sub> (IR) (Cp)NiOs <sub>3</sub> (CO) <sub>9</sub> (H) <sub>3</sub> (IR)	this work

<sup>a</sup> In parentheses the identification method used for the complex (IR, MS etc.). <sup>b</sup> Reaction conditions: (A) 100 ml vial (see experimental) 4 h at 120°C; (B) 18 h at 120°C; (C) 6 h at 120°C; (D) refluxing octane, hydrogen flow, 2 h; (E) refluxing pentane, 12 h, 1 atm H<sub>2</sub>. <sup>c</sup> The main reaction products are printed in boldface, the high yield products in italics. <sup>d</sup> Hydrogenated vinylcyclopentadienyl and cyclopentadienyl ligands. <sup>e</sup> In all the experiments metal powder was observed. This will not mentioned again. The term "decomposition" is used when no organometallics could be detected. <sup>f</sup> See text. <sup>g</sup> Percentage of unreacted complex. <sup>h</sup> Products of methathesis-hydrogenation of the vinylidene. <sup>i</sup> Products of Cp + vinylidene.

TABLE 3  
 REACTIONS OF  $(Cp)_2Ni_2Fe_2(CO)_6(C_2R_2)$  WITH  $C_2R'_2$  UNDER  $H_2$  AND OTHER REACTIONS OF THE CLUSTER FRAMES

Complex	Other reactant	Reaction conditions <sup>a</sup>	Organic products <sup>b</sup>	Organometallic products	Reference
$(Cp)_2Ni_2Fe_2(CO)_6(C_2Ph_2)$	$C_2Et_2$ (2/1)	B	$C_2Et_2$ , <i>stilbene</i> ( <i>cis</i> + <i>trans</i> ), diphenylethane, <b>diphenylalkyne</b> Not analyzed	$(Cp)_2Ni_2Fe_2(CO)_6(C_2Ph_2)$ (30%), $Fe_2(CO)_6(C_2Ph_2)_2$ (20%), $(Cp)_2Ni_2Fe(CO)_3C_2Ph_2$ (20%)	this work
$(Cp)_2Ni_2Fe_2(CO)_6(C_2Ph_2)$	$C_2Et_2$ (2/1)	D	Not analyzed	$(Cp)_2Ni_2Fe_2(CO)_6(C_2Ph_2)$ (90%), $(Cp)_2Ni_2Fe(CO)_3(C_2Ph_2)$ (3%), $(Cp)_2Fe_2(CO)_4$ (5%)	this work
$(Cp)_2Ni_2Fe_2(CO)_6(C_2Et_2)$	$C_2Ph_2$ (2/1)	B	$C_2Ph_2$ , <i>hexene</i> , <i>hexane</i> , <i>oligomers</i> , $C_2Et_2$	$(Cp)_2Ni_2Fe_2(CO)_6(C_2Et_2)$ (40%), $(Cp)_2NiFe(CO)_3(C_2Et_2)$ (10%)	this work
$H_4Ru_4(CO)_{12}$	$[(Cp)Ni(CO)]_2$	A	—	$H_3Ru_3(CO)_9(CpNi)$ (2%), $[(Cp)Ru(CO)_2]_2$ (10%)	18
$H_4Ru_4(CO)_{12}$	$[(Cp)Ni(CO)]_2$	A	—	$H_3Ru_3(CO)_9(CpNi)$ (2%)	6
$H_3Ru_3(CO)_9CCH_2Bu^t$	—	B	neohexane	$H_3Ru_3(CO)_9(CpNi)$ (1%)	this work
$Ru_3(CO)_{12}$	$(Cp)_2Ni_2[HC_2C(=CH_2)CH_3]$	C	—	$(Cp)NiRu_3(CO)_9(H)(C=CHPr^i)$	11

<sup>a</sup> Reaction conditions were: (A) Refluxing octane 20–30 min, nitrogen atmosphere; (B) Sealed 25 ml vial (2.5 ml of 10 M solution in heptane), 0.9 atm  $H_2$ , 120°C, 4 h; (C) Refluxing octane, 20 min, hydrogen atmosphere; (D) Refluxing heptane, 90 min, hydrogen flow. <sup>b</sup> See footnote c Table 2.

## Results and discussion

It is obviously impossible to unlink the reactivities of the cluster frames and the coordinated ligands, but for simplicity we consider the two separately.

Qualitative results for the hydrogenation of the complexes are reported in Table 2.

Other reactions, mainly involving the cluster frames, were performed with the aim of improving understanding the behaviour of the clusters under hydrogen and these are summarized in Table 3.

### (a) Reactions of the cluster frames

In all the experiments, variable amounts of metal powder, due to reduction in presence of hydrogen, were observed; this was expected, and had been noted in previous experiments [6]. As reported in the Experimental (and in Table 4) (below), the metal powder catalyzes the complete hydrogenation of the triple bond; and this is consistent with previous findings [6]; C–C hydrogenolysis occurs only to a minor extent in the presence of the metallic powder.

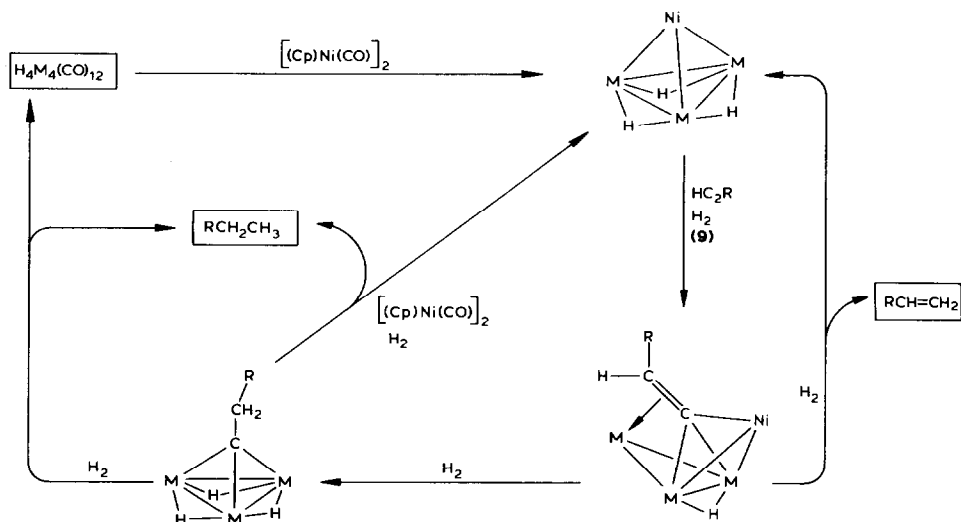
On the other hand, several clusters show good stability, and even after being kept at 120°C under H<sub>2</sub>, were partly recovered unaltered.

The formally unsaturated, 62 electron, square planar complexes (( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Ni<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub>(RC<sub>2</sub>R'), complexes 6) unexpectedly show good stability for short reaction times, whereas for longer times complete metal–metal bond hydrogenolysis occurs; the behaviour of the same clusters in the mass spectrometer (M.I.K.E. experiments [25]) and in solution under N<sub>2</sub> [26] is different, and results in "cluster contraction" [27] and formation of complexes 7. The reactions of complexes 6 with alkynes (Table 3), under H<sub>2</sub> are also noteworthy; neither coordination of further alkyne nor alkyne exchange with the cluster occurs, despite the formal unsaturation. Instead, hydrogenation of the cluster bound alkyne occurs, whereas the free alkyne is unaffected. This shows that, at least for the complexes 6, cluster coordinated alkynes are hydrogenated with greater efficiency.

In some instances, "cluster expansion" [27] reactions are also observed; thus, from ( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Ni<sub>2</sub>Ru(CO)<sub>3</sub>(C<sub>2</sub>Ph<sub>2</sub>) the pentametallic ( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Ni<sub>2</sub>Ru<sub>3</sub>(CO)<sub>8</sub>(C<sub>2</sub>Ph<sub>2</sub>) has been obtained in small yields.

Finally, for some clusters, modification of the metal atom frames, and sometimes "isolobal substitution" occur [28]; these reactions may form part of a full hydrogenation cycle (although with very low efficiency). This is the case, for example, when the vinylidene-substituted butterfly clusters 3 are hydrogenated; these complexes release the fully and partly hydrogenated ligands, and give ( $\eta$ -C<sub>5</sub>H<sub>5</sub>)NiM<sub>3</sub>(CO)<sub>9</sub>(H)<sub>3</sub> and, for M = Ru, also H<sub>4</sub>Ru<sub>4</sub>(CO)<sub>12</sub>. We previously suggested three possible reaction paths leading to clusters 3; in particular, for 3b (M = Os), metal–metal hydrogenolysis of ( $\eta$ -C<sub>5</sub>H<sub>5</sub>)NiOs<sub>3</sub>(CO)<sub>9</sub>(H)<sub>3</sub> in presence of alkynes was considered [10].

We have already reported that ( $\eta$ -C<sub>5</sub>H<sub>5</sub>)NiRu<sub>3</sub>(CO)<sub>9</sub>(H)<sub>3</sub> can be obtained by treating with nickel reactants H<sub>4</sub>Ru<sub>4</sub>(CO)<sub>12</sub> [18]; the latter is an hydrogenation catalyst, and is also frequently found as a final product in the hydrogenation of several clusters, including H<sub>3</sub>Ru<sub>3</sub>(CO)<sub>9</sub>CCH<sub>2</sub>Bu' [6]. In some instances, complexes of type 3 under H<sub>2</sub> release H<sub>3</sub>M<sub>3</sub>(CO)<sub>9</sub>CCH<sub>2</sub>R derivatives. Finally H<sub>3</sub>-Ru<sub>3</sub>(CO)<sub>9</sub>CCH<sub>2</sub>Bu' reacts with ( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Ni<sub>2</sub>(CO)<sub>2</sub> to give small amounts of



SCHEME 1

$(\eta-C_5H_5)NiRu_3(CO)_9(H)_3$  and neohexane (see Table 3).

Scheme 1 accounts for the above results.

Noteworthy are the isolobal substitutions of  $(\eta-C_5H_5)Ni$  for  $Ru(CO)_3$  or  $CCH_2R$  in tetrahedral cluster frames.

Attempts to isolate other intermediates for the formation of the clusters **3**, starting from  $(\eta-C_5H_5)NiOs_3(CO)_9(H)_3$  and  $C_2Ph_2$  (less reactive than the  $HC_2R$  alkynes) under hydrogen, gave only homometallic alkyneosmium substituted clusters; no edge-substituted tetrahedral derivatives comparable with those found by Johnson and Lewis were detected [29].

Treatment of  $(\eta-C_5H_5)_3Ni_3Os_3(CO)_9$  with  $C_2Ph_2$  leads directly to  $(\eta-C_5H_5)NiOs_3(CO)_9(H)_3$  and homometallic substituted products. The hydrogenation of diphenylalkyne observed during these reactions probably occurs "via" homometallic alkyneosmium clusters; this is considered again in sections b and c below.

#### (b) Hydrogenation of the coordinated ligands

The hydrogenation products arising from the multi-site coordinated ligands are shown in Table 2 and (for  $C_2Ph_2$ ) in Table 4. In the latter Table the results of hydrogenations for various times are listed; these involve the same ligand in different coordination environments on homo- and hetero-metallic clusters.

The nature (and yield) of the organic hydrogenation products is probably dependent on the following factors:

- (i) the nature of the metals in the cluster;
- (ii) the structure of the cluster, and thus on the coordination of the alkyne to three or four metal centres with C–C multiple bond "activation" [14];
- (iii) the possible competition within the hydrogenolysis of the M–M, M–M', M–C and C–C (multiple) bonds;
- (iv) the selectivity in the hydrogenation of coordinated and noncoordinated multiple C–C bonds (for isopropenylalkyne);

TABLE 4. HYDROGENATION OF  $C_2Ph_2$  COORDINATED TO DIFFERENT METAL-ATOM CORES

Complex (and alkyne coordination)	Reaction time <sup>a</sup>	"Light products"	Organic products (GC)			Organometallic products
			$C_2Ph_2$	$H_2C_2Ph_2$ <i>cis</i>	$H_4C_2Ph_2$ <i>trans</i> <sup>c</sup>	
$(Cp)_2Ni_2Fe(CO)_3(C_2Ph_2)$ $\mu_3\eta^2$	2 h 15 min	10%	2300	trace	100	$(Cp)_2Ni_2Fe(CO)_3(C_2Ph_2)$ (30%) <sup>d</sup> $(Cp)_2Fe_2(CO)_4$ (10%)
	6 h	20%	121	3.5	100	$(Cp)_2Ni_2Fe(CO)_3(C_2Ph_2)$ (10%) $(Cp)_2Fe_2(CO)_4$ (12%)
$Fe_3(CO)_9(C_2Ph_2)$ $\mu_3\eta^2$	12 h	25%	15	21.0	100	$(Cp)_2Fe_2(CO)_4$ (20%)
	24 h	40%	—	18.3	100	decomposition
	6 h	—	3200	trace	100	decomposition
	9 h 30 min	10%	647.0	13.0	100	decomposition
$Ru_4(CO)_{12}(C_2Ph_2)$ $\mu_4\eta^2$	18 h	15%	30.5	18.6	100	$Ru_4(CO)_{12}(C_2Ph_2)$ (50%)
	3 h	trace	25700	trace	100	$H_4Ru_4(CO)_{12}$ (50%) $Ru_4(CO)_{12}(C_2Ph_2)$ (40%) $H_4Ru_4(CO)_{12}$ (60%)
$(Cp)_2Ni_2Fe_2(CO)_6(C_2Ph_2)$ $\mu_4\eta^2$	6 h	5%	11200	trace	100	850
	12 h	7%	7212	2.0	100	1630
$(Cp)_2Ni_2Fe_2(CO)_6(C_2Ph_2)$ $\mu_4\eta^2$	24 h	10%	1130	6.0	100	3805
	2 h 15 min	trace	33000	1.2	100	—
	6 h	2%	16600	20	100	175
Fe/Ni powder	12 h	12%	6300	18	100	1030
	24 h	15%	1256	25	100	2205
	18 h	10%	—	—	100	1086
Ru/Ni powder	18 h	12%	—	trace	100	1215

<sup>a</sup> Reaction conditions; sealed 25 ml vials (2.5 ml, heptane solution 10 mM/l), 0.9 atm  $H_2$ , 120°C. <sup>b</sup> By "light products" we mean the products from hydrogenolysis of C—C bonds, viz., benzene, toluene, ethylbenzene and ethylbenzene; these are included in the total percentage of the light products and were detected either by GC or GC/MS (see experimental section). <sup>c</sup> The remaining portion of the hydrocarbon products, formed from the diphenylacetylene and its hydrogenation derivatives was analyzed under different chromatographic conditions; the ratio of the products is expressed relative to *trans*-stilbene as 100 (integration of the GC peaks). <sup>d</sup> The percentages of the unreacted products were calculated by comparison with a control test of the starting reaction solution (densitometry on the TLC plates).

(v) the presence of the formed powder, as discussed above.

Two main trends are observed; the coordinated alkynes and vinylidenes undergo either partial or total hydrogenation of the C–C multiple bonds (in more or less selective way); or the ligands can undergo C–C hydrogenolysis. Side reactions are oligomerization-hydrogenation of the alkynes and olefin metathesis of the coordinated vinylidenes [30].

The nature of the metals seems to be of secondary importance. Thus for the  $C_2Ph_2$  ligand (Table 4), similar hydrogenation products in comparable yields are obtained from  $Ru_4(CO)_{12}(C_2Ph_2)$  and  $(\eta-C_5H_5)_2Ni_2Fe_2(CO)_6(C_2Ph_2)$  under identical conditions. The unique feature of these clusters is the  $\mu_4-\eta^2$ -coordination of the alkyne to four metal centres.

The coordination of the alkyne to several metals and the resulting alkyne activation must certainly influence the products but generally tri- and tetra-metallic clusters give similar products, with only minor differences in the yields.

The type of metal–carbon bonds can also be of importance in these reactions; thus from the results, it can be concluded that:

- (i) the “apical” ligands readily and completely give the fully hydrogenated alkanes (see also ref. 6). In these complexes only M–C( $\sigma$ ) bonds are observed;
- (ii) the  $\mu_4-\eta^2$ -vinylidene ligands give either olefins or alkanes. This feature is shown in Scheme 1;
- (iii) the  $\mu_3-\eta^2$  and  $\mu_4-\eta^2$  coordinated alkynes generally give the corresponding alkenes and alkanes, and, in smaller amount, C–C hydrogenolysis products;
- (iv) by contrast, the  $\mu_3-\eta$  and  $\mu_4-\eta^2$  alkynes in the complexes 7 and 4 give considerable amounts of C–C hydrogenolysis products.

Thus the following sequence can be written for the ease of hydrogenation of the coordinated substrates: “apical ligands” > vinylidene ligands > alkynes. Apparently, hydrogenation is easier when a larger number of M–C ( $\sigma$ ) bonds is present, these usually being more reactive than the M–C ( $\pi$ ) bonds.

It can also be concluded that hydrogenation is easier when longer C–C distances are present; indeed, the “apical” ligands show the greatest “activation” of the C–C bonds whereas the  $(Cp)_2Ni_2Fe(CO)_3(C_2Ph_2)$  complexes, which have the shortest C–C distances, give hydrogenation products with significantly greater difficulty. Other factors may influence this behaviour; Muetterties found that a C–C distance above 1.30 Å is sufficient for the activation of the alkyne to give hydrogenation [31]. However, the reactivity towards hydrogen also depends upon the possibility of reaching an “unsaturated transition state” and hence on the activation energy required. Indeed, among the  $\mu_2-\eta^2$ -alkyne substituted bimetallic derivatives  $Cp_2Mo_2(CO)_4(RCR_2')$ ,  $Fe_2(CO)_6(RC_2R')$ ,  $Co_2(CO)_6(RC_2R')$ ,  $Cp_2Ni_2(RC_2R')$ ,  $CpNiCo(CO)_3(RC_2R')$  and  $(COD)_2Ni_2(RC_2R')$ , only the last complex and the iron derivatives react with hydrogen under mild temperatures and pressures [32].

It seems, especially for the coordinated alkynes, that the hydrogenation behaviour is the result of the balance of several effects; among these are (i) the thermal decomposition cluster species which can also act as catalysts, the presence of metal powder, and the competition between M–M, M–M', M–C and C–C hydrogenolysis. The M–M and M–M' hydrogenolysis is responsible for the formation of lower nuclearity products and the metal powder, and hence for the production of saturated hydrocarbons in some instance. The hydrogenolysis of M–C( $\sigma$ ) and M–C( $\pi$ ) bonds was considered above.

Hydrogenolysis of C–C bonds also occurs in the above experiments. As shown by the control tests, this is a minor process when the metal powder is subjected to the reaction conditions. In contrast, clusters such as **7**, which are characterized by short C–C bonds, give high yields of C–C hydrogenolysis products, and this is also the case for cluster **4**. A possible explanation of this behaviour as might be that when formally unsaturated clusters are used, there is initial attack of hydrogen on the cluster metals, and then, by hydrogen transfer and M–C bond cleavage, hydrogenation products are formed; however, when “saturated” clusters, such as structures **7** and **4** (both “closo” complexes) are used, attack of hydrogen occurs directly on the ligand, and C–C hydrogenolysis becomes of primary importance. An alternative explanation might be that on “unsaturated” frames there is the possibility of coordinating hydrogen without M–M cleavage, whereas on “saturated” frames, addition of hydrogen would require M–M cleavage. This latter explanation would also lead to expectation of the formation of *cis*-stilbene (see ref. 33, below), but we usually found the *trans*-isomer.

(c) *The hydrogenation of diphenylacetylene and the behaviour of isopropenylacetylene*

The results of Table 4, for  $C_2Ph_2$ , are consistent with the qualitative results of Table 2. An increase in the yields of hydrogenation products with time is observed; in particular, together with decomposition of the cluster to powder, increasing amounts of saturated hydrocarbons are observed\*. However, for a discussion of the possible selectivity in the hydrogenation of alkynes on clusters the formation of alkenes is much more interesting.

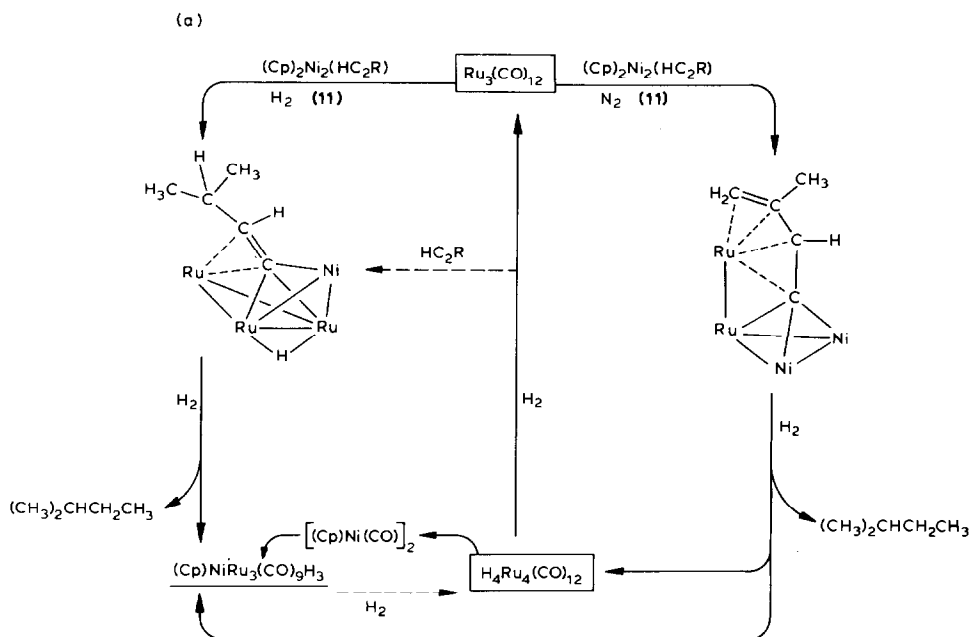
In the hydrogenation products obtained from  $C_2Ph_2$ , *trans*-stilbene is generally observed in considerable yield; smaller amounts of *cis*-stilbene were also detected (usually in almost constant ratio to the *trans*-isomer). Only *trans*-stilbene was observed, when  $C_2Ph_2$  was treated with hydrogen at 100°C in hydrocarbons in the presence of the cluster catalyst  $HRu_3(CO)_{11}^-$  [37].

Muetterties found that when bimetallic products are hydrogenated, only *cis*-olefins are formed, and no saturated hydrocarbons are observed (the only exception being  $Fe_2(CO)_6(C_2Bu^1_2)$ ); this was explained by suggesting that the reaction intermediates (not always precisely defined, but, at least for  $(COD)_2Ni_2(RC_2R')$ , assumed to be a species with weak or no Ni–Ni interaction requires *cis*-addition of hydrogen for stereochemical reasons. The *cis*-olefin is then expelled because of its low coordination ability, so that no isomerization or further hydrogenation to alkane takes place, even though these products are thermodynamically favoured [33].

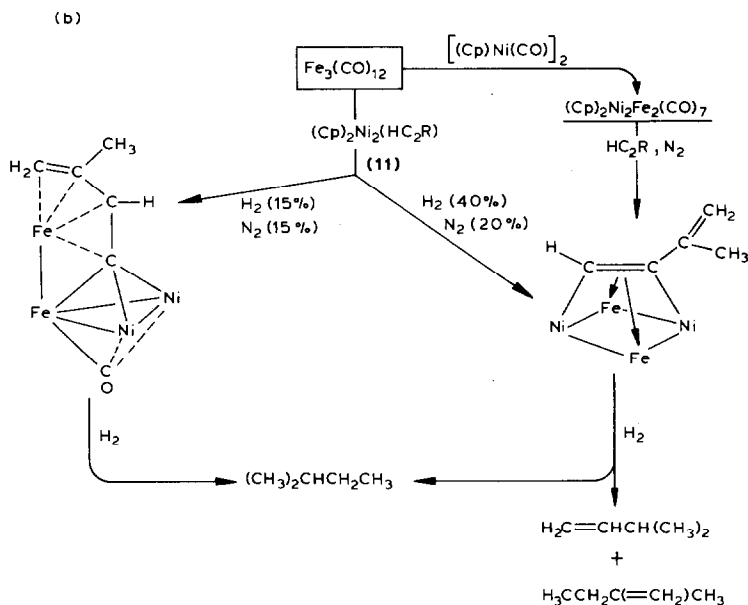
In considering the results obtained with clusters, we must take account of another mechanism for the attack of hydrogen on the substrate. The results indicate that coordination of the alkyne to several metal centres, and its consequent activation, has some influence on the hydrogenation products; thus monometallic intermediates should not be considered for the above reactions. The determining step of the reactions may be either the H–H bond cleavage or the gradual cleavage of M–C bonds, to give intermediates with ethylenic, vinylidenic or alkenylidenic substituents, as well as apical ligands, and hence partly hydrogenated structures before the release of the final organic products. Once the partly hydrogenated intermediates formed,

\* For  $Ru_4(CO)_{12}(C_2Ph_2)$  results consistent with those obtained under reflux [34] have been found.

easier hydrogenation would occur. Indeed, the vinylidene and apical derivatives have been found more prone to hydrogenation; the former gives either olefins or alkanes and the latter mainly alkanes.



SCHEME 2A



SCHEME 2B



The formation of homo-metallic vinylidene and alkenylidene complexes of osmium (with concomitant hydrogenation of  $C_2Ph_2$ ), as well as the synthesis and reactivity of the vinylidene products **3** provide indirect evidence for this hypothesis; hence, the formation of *trans*-ethylenes could occur via partly hydrogenated clusters as discussed by Shapley [24] and Deeming [35]. Thus the selectivity in alkyne hydrogenation on bimetallic or on cluster complexes may depend on the possibility of forming different intermediates.

The isopropenylalkyne ligand is also of interest for discussions of the selectivity of the above reactions. It contains a triple and a double C–C bond in conjugated positions and gives a considerable variety of interactions in homo- [36] and hetero-metallic [12,13] clusters.

As mentioned above (see Introduction) the reaction of  $(\eta-C_5H_5)_2Ni_2$ (isopropenylalkyne) with  $Ru_3(CO)_{12}$  under  $H_2$  leads to the isopropylvinylidene cluster **3c** [11] in which apparently the C=C bond has been hydrogenated; further hydrogenation of **3c** leads to alkane. Noteworthy is the hydrogenation of the double bond before the hydrogenation of the triple bond. The same reaction under  $N_2$  leads preferentially to complex **5b**, in which the triple bond is considerably "activated" and the double bond preserved. Hydrogenation of **5b** also gives the alkane but in this case the triple bond is reduced before the double bond.

These results are shown in Scheme 2 together with those of the hydrogenation of the isopropenylalkyne iron-nickel derivatives.

The behaviour of isopropenylalkyne seems to depend either on the method of preparing the clusters, and on the coordination of the ligand to the metals. These results are fully consistent with the previously discussed hypotheses for the formation of *trans*-olefins.

### Conclusive remarks

The results presented provide evidence that cluster bound alkynes (and derived ligands) can be hydrogenated, sometimes in low efficiency catalytic cycles, and with selectivities depending on the alkynes bound to bimetallic derivatives.

The dependence of the hydrogenation products upon the overall cluster frame and electronic count, and other structural parameters of the cluster bound alkynes, as well as the reactivity of vinylidene and apical clusters, all point to hydrogenation processes occurring on clusters rather than on metal fragments.

The results obtained can not be fully explained in terms of hydrogenation of free alkynes or of mono- or bi-metallic alkyne derivatives. The hydrogenation of cluster bound alkynes in the presence of (unaffected) free alkynes reinforces this observation.

Thus, the alkyne substituted homo- and hetero-metallic clusters may be of importance as intermediates (or catalyst precursors) in the homogeneously catalyzed alkyne hydrogenation.

Further experiments on multi-site coordinated diphenylacetylene are being carried out.

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