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Heterometallic clusters in homogeneous catalysis. Hydrogenation of diphenylacetylene and isomerization of *cis*-stilbene in the presence of $[Fe_2Ru(CO)_{12}]$, $[FeRu_2(CO)_{12}]$, $[H_2FeRu_3(CO)_{13}]$, $[H_2Ru_4(CO)_{13}]$, and related compounds. Identification of organometallic complexes and a discussion of their role

Roberto Giordano and Enrico Sappa

Dipartimento di Chimica Inorganica, Chimica Fisica e Chimica dei Materiali, Universita' di Torino. Via Pietro Giuria 7, I-10125 Torino (Italy)

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Abstract

The clusters $[M_3(CO)_{12}]$ (M = Ru or Fe), $[Fe_2Ru(CO)_{12}]$, $[FeRu_2(CO)_{12}]$, $[H_4Ru_4(CO)_{12}]$ and $[H_2M'M_3(CO)_{13}]$ (M = Ru, M' = Fe or Ru) have been tested as homogeneous catalysts for the hydrogenation of C_2Ph_2 and isomerization of *cis*-stilbene. The effect of the cluster stoichiometry, of dihydrogen and of the substrate/cluster ratio have been evaluated. There is evidence of competition between dihydrogen, which favours the formation of catalytically active hydrides or "metal fragments", and C_2Ph_2, which favours metal-fragment condensation to give alkyne-substituted clusters; with the exception of $[H_2Ru_3(CO)_9C_2Ph_2]$, these derivatives are stable by-products and react slowly with dihydrogen, giving only small amounts of hydrogenation products. The alkyne-substituted derivatives found in the hydrogenation solutions are the reported products of the reactions of iron, ruthenium or iron–ruthenium carbonyl clusters with C_2Ph_2 under dinitrogen; however, there are differences in the yields. Moreover, in the reactions of $[H_2Ru_4(CO)_{13}]$ or $[H_2FeRu_3(CO)_{13}]$, a new derivative was obtained; this was characterized spectroscopically as a third isomer of $[Ru_3(CO)_8(C_2Ph_2)_2]$.

1. Introduction

Considerable interest has been devoted to heterometallic clusters in recent years; the development of rational synthetic methods [1] has allowed studies on their reactivity [2]. The heteropolymetallic aggregates are potential precursors of heterogeneous catalysts [3] as well as soluble models for interactions between small substrate molecules and metal surfaces [4]. New coordination-activation patterns of different metallic centres may occur and, in some instances, chiral syntheses are achievable [5].

We are interested in the role of heterometallic clusters as homogeneous catalysts in hydrogenation and isomerization of alkynes and dienes. We found that, in some instances, "cluster catalysis" occurs [6] and that the activity is related to electronic effects of

substituents [7]. However, hydrogenation experiments with phosphine- or phosphido-bridged clusters as catalysts showed that the activity is dependent neither on the presence of hydrido- or phosphido-bridges nor on their number [8]. This was ascribed to the formation and rearrangement of metal fragments. Starting from different but chemically related clusters, we obtained indeed similar activities, probably because of the formation of common reactive intermediates [8a]; with phosphinidene-bridged clusters we observed that the type of metal in the cluster core is of the utmost importance for catalytic activity, and we also hypothesized that the hydrogenating activity is related to the stability of the alkyne-substituted species formed during the reactions [8c].

Thus, apparently the factors influencing the homogeneous catalytic activity of heterometallic clusters are (i) the nature of the metals and (ii) the organometallic species formed during the reactions. However, understanding of these specific factors is far from being

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Correspondence to: Professor E. Sappa.

Fig. 1. Structures of clusters 1–7.

2. Experimental details

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

[Fe(CO)$_5$], [Fe$_3$(CO)$_{12}$], and [Ru$_3$(CO)$_{12}$] (Strem Chemicals), diphenylacetylene (Fluka) and cis-stilbene (Aldrich) were commercial products, used as received after checking purity; dihydrogen and dinitrogen were dried prior to use.

The syntheses of the catalysts and of alkyne-substituted complexes under dinitrogen were performed in conventional glassware consisting of three-necked flasks equipped with a dinitrogen inlet, condenser, mercury pressure release valve and magnetic stirring; hydrocarbon solvents (heptane, octane, toluene) were dried over sodium. The reaction mixtures were taken to small volume under reduced pressure and purified by TLC (Kieselgel PF Merck, mixtures of diethyl ether and light petroleum as eluants); when possible the complexes were crystallized from suitable solvents prior to use. Some syntheses were performed under dihydrogen in sealed glass vials.

Compounds were analyzed with an F&M CHN. Analyzer and a Perkin-Elmer AAS; some elemental analyses were performed by F. Pascher (Remagen, Germany). The complexes were characterized by IR (Perkin-Elmer 580), and ^{1}H and ^{13}C NMR (JEOL EX-400 FT) spectroscopy and mass spectrometry (Kratos MS 80; EI, 70 eV).

2.2. Synthesis of complexes 2, 3, 5, 6, 7

These were obtained through a modification of the procedure reported by Stone [9*]. [Ru$_3$(CO)$_{12}$] (0.80 g, 1.26 mmol), Fe(CO)$_5$ (2 ml, ca. 10 mmol) and H$_2$O (2 ml) were heated in refluxing heptane for 90 min; the dark solution was filtered. The residue was extracted twice with CHCl$_3$ and the extracts combined with the filtrate. The combined volume was reduced under reduced pressure and purified by TLC (eluant light petroleum, 40–70°C), giving [H$_4$Ru$_4$(CO)$_{12}$] (25% based on ruthenium), [H$_2$Ru$_4$(CO)$_{13}$] (25%), [FeRu$_2$(CO)$_{12}$] (15%), [H$_2$FeRu$_3$(CO)$_{13}$] (20%), [Ru$_2$Fe(CO)$_{12}$] (5%), and some decomposition products.

2.3. Hydrogenation of diphenylacetylene and isomerization of cis-stilbene

The hydrogenation and isomerization reactions were performed in sealed vials (25 ml volume) as described earlier [6–8]. The soluble organic products in the reac-

satisfactory. In an attempt to illuminate them, we studied the hydrogenation of diphenylacetylene and isomerization of cis-stilbene in the presence of [Fe$_3$(CO)$_{12}$] (1), [Fe$_2$Ru(CO)$_{12}$] (2), [Ru$_2$Fe(CO)$_{12}$] (3), [Ru$_3$(CO)$_{12}$] (4), [H$_2$FeRu$_3$(CO)$_{13}$] (5), [H$_2$Ru$_4$(CO)$_{13}$] (6), and [H$_4$Ru$_4$(CO)$_{12}$] (7). The structures of the complexes are shown in Fig. 1.

The chemistry of complexes 1–7 towards diphenylacetylene under dinitrogen has been extensively studied. This will be discussed in the context of our work, in which we identified the organometallic products formed during the catalytic reactions. The products obtained under dihydrogen are the same as those already obtained under dinitrogen, albeit with different yields. The reactions of [H$_2$Ru$_4$(CO)$_{13}$] and [H$_2$FeRu$_3$(CO)$_{13}$] with C$_2$Ph$_2$ under dihydrogen or dinitrogen also gave a new product, characterized as the "red isomer" of [Ru$_3$(CO)$_8$(C$_2$Ph$_2$)$_2$]. The alkyne-substituted derivatives are probably formed as a consequence of "metal fragment condensation" [1a] favoured by the ligand; hydrogenation experiments have shown that most of these clusters are stable by-products, which slowly release hydrogenated products in low yields. Competition with the formation of metal fragments induced by dihydrogen is probably responsible for the results observed.

tion solutions were analysed with a Carlo Erba FID 4200 gas-liquid chromatograph equipped with 2 m × 0.6 mm columns used as follows: SE 30 on 5% Chromosorb WAW (60/80 mesh) with 46 ml/min dinitrogen flow, 60°C for 6 min, then 10°C/min up to 240°C. In some instances considerable amounts of solid *trans*-stilbene were observed in the vials: this is discussed below.

2.4. Identification of organometallic products in the hydrogenation and isomerization solutions

The hydrogenation solutions, after GLC, were purified on TLC plates and the fractions analysed by spectroscopy and/or by elemental analyses. The identification of the complexes was confirmed by independent syntheses, as described below. The products are listed in Tables 2 and 4.

2.5. Reactions of complexes 4, 6, 7 with diphenylacetylene under dinitrogen or under dihydrogen

2.5.1. Reactions of [Ru₃(CO)₁₂]

The reaction of [Ru$_3$(CO)$_{12}$] with C$_2$Ph$_2$ [10,11] was repeated with modified conditions; [Ru$_3$(CO)$_{12}$] (1.0 g, 1.56 mmol) with C$_2$Ph$_2$ (0.5 g, 2.80 mmol) was heated under reflux in heptane under dinitrogen for 5 min. The brown suspension was filtered, reduced to small volume under vacuum and purified by TLC; five main products were obtained, brown [Ru$_4$(CO)$_{12}$C$_2$Ph$_2$] (5%) (complex **A**) [11b], red-purple [Ru$_3$(CO)$_8$(C$_2$-Ph$_2$)$_2$] (15%) (complex **B**), yellow-orange [Ru$_3$(CO)$_6$-(μ-CO)$_2$(C$_2$Ph$_2$)$_2$] (15%) (complex **C**), yellow [Ru$_2$(CO)$_6$(C$_2$Ph$_2$)$_2$] (10%) and dark yellow [Ru$_4$-(CO)$_{11}$(C$_2$Ph$_2$)$_2$] (5%) (complex **D**) [12].

2.5.2. Reactions of [H₄Ru₄(CO)₁₂]

Complex **7** was allowed to react with C$_2$Ph$_2$ in heptane under dinitrogen; a considerable excess of C$_2$Ph$_2$ was used, as under catalytic conditions. After 4 min reflux, a dark-brown clear solution was obtained; upon cooling, about 30% of **7** was deposited. The solution was filtered and reduced to small volume. TLC purification (eluant light petroleum 40–70°C and diethyl ether, 10% in vol.) showed the presence of [H$_4$Ru$_4$(CO)$_{12}$] (about 10%), [Ru$_4$(CO)$_{12}$C$_2$Ph$_2$] (**A**) (50%) and a mixture of products which was further separated by TLC (eluant light petroleum). Purple [Ru$_3$(CO)$_8$(C$_2$Ph$_2$)$_2$] (**B**) and dark yellow [Ru$_4$-(CO)$_{11}$(C$_2$Ph$_2$)$_2$] (**D**) were identified in small amounts.

2.5.3. Reactions of [H₂Ru₄(CO)₁₃]

Complex **6** was allowed to react with a 2.5–1 molar excess of C$_2$Ph$_2$ in heptane, under dinitrogen; at reflux the red solution turned brown-red. After 4 min a

red-yellow colour was observed and the reaction was stopped; TLC purification afforded about 25% of [Ru$_3$(CO)$_{12}$], 30% of a mixture of [Ru$_4$(CO)$_{12}$(C$_2$Ph$_2$)] (**A**) and [H$_2$Ru$_3$(CO)$_9$(C$_2$Ph$_2$)] (complex **E**) [13], 35% of an impure bright red derivative (complex **F**, see below) and some decomposition product. During purification of **F**, purple and yellow bands were observed during chromatography; these were tentatively identified as **B** and **C**.

Attempts to recrystallize complex **F** from heptane or from heptane/chloroform mixtures gave mother liquors containing a yellow product (the red crystals were also contaminated by small amounts of yellow crystals [14*]. The same happened with CDCl$_3$ solutions after overnight ^{13}C NMR runs. This indicates some disproportionation.

2.5.4. Reactions of 5, 6, 7 under dihydrogen in sealed vials

In some instances the organometallic complexes in the hydrogenation vials (2.5 ml volume) were too scarce to allow any analyses other than IR spectroscopy. Hence, we performed the reactions of complexes **5, 6, 7** with C$_2$Ph$_2$ under 1 atm of dihydrogen in 250 ml vials. The products and yields obtained were generally the same (see Table 2). In some instances, and in particular for [H$_2$Ru$_4$(CO)$_{13}$], the relative yields of [Ru$_4$(CO)$_{12}$C$_2$Ph$_2$], [Ru$_3$(CO)$_8$(C$_2$Ph$_2$)$_2$] (purple isomer) and of **F** were dependent on the cluster/alkyne ratio. The yields of **F** increased with reduced dihydrogen pressure and decreased with an excess of C$_2$Ph$_2$.

Complex **F**: Found: C, 48.5; H, 2.68; Ru, 33.8. C$_{22}$H$_{10}$Ru$_3$O$_8$ calc.: C, 48.8; H, 2.28; Ru, 34.4%. Molecular weight (osmometry): 832. IR (ν(CO), heptane): 2067s, 2026vs(sh), 2016vs, 1975s, 1878m, 1858m, cm^{-1}. ^{1}H NMR (CDCl$_3$, room temperature): 7.41 (d); 7.20 (t); 7.12 (t); 6.88 (m); 6.24 (d, Ph). ^{13}C NMR (CDCl$_3$, room temperature, TMS): 118.0 (s); 121.8 (s); 126.9 (m, Ph); 132.9 (s); 135.0 (s); 144.0 (s); 190.0 (s); 195.3 (s); 206.6 (b, 6CO); 240.0 (b, 2CO, bridging). Mass spectrum: P$^+$= 828 m/e, isotopic pattern consistent with Ru$_3$.

2.6. Hydrogenation of alkyne-substituted clusters

Some diphenylacetylene derivatives, prepared under dinitrogen or dihydrogen in sealed 250 ml vials as described above, were treated with 1 atm of dihydrogen in 25 ml vials sealed in the absence of diphenylacetylene. The results obtained are collected in Tables 5 and 6 (see Discussion).

2.7. Reactions of clusters 5 and 6 with dihydrogen

[H$_2$FeRu$_3$(CO)$_{12}$] and [H$_2$Ru$_4$(CO)$_{12}$] were sealed in 25 ml vials under 1 atm of dihydrogen and heated at

TABLE 1. Hydrogenation of C_2Ph_2 in the presence of clusters 1–7

Cluster and experiment [a]	Reaction time (min)	Conversion	Turnover	Selectivity to		c/t ratio
				c-SB [b]	t-SB	
Trinuclear complexes						
$[Ru_3(CO)_{12}]$	15	90.81	44.85	47.78	52.22	0.91
A	30	98.63	48.71	11.36	88.64	0.13
	45	71.70	35.41	54.39	45.61	1.19
$[FeRu_2(CO)_{12}]$	15	28.83	20.67	64.97	35.03	1.85
B	30	13.33	9.56	81.47	18.53	4.40
	45	27.98	20.06	76.09	23.91	3.18
$[Fe_2Ru(CO)_{12}]$	15	9.59	11.25	82.06	17.94	4.58
C	30	10.76	12.63	77.88	22.12	3.52
	45	16.83	19.75	80.15	19.85	4.04
$[Fe_2Ru(CO)_{12}]$	30	10.79	29.28	66.26	33.74	1.96
D	30	14.79	22.57	69.78	30.22	2.31
	30	28.77	20.40	70.66	29.34	2.41
$[Fe_2Ru(CO)_{12}]$	30	9.89	26.56	27.40	72.60	0.38
E	30	8.06	21.64	14.39	85.61	1.17
	30	5.78	15.52	51.90	48.10	1.08
$[Fe_3(CO)_{12}]$	15	95.00	6.71	9.06	90.94	0.10
F	30	98.73	6.97	9.66	90.34	0.11
	45	100.0	7.06	12.60	87.40	0.14
$[Fe_3(CO)_{12}]$	15	9.29	5.29	32.19	43.70 [c]	0.74
G	30	6.36	3.62	30.82	66.04	0.47
	45	7.98	4.54	41.98	55.76	0.75
Tetranuclear complexes						
$[H_4Ru_4(CO)_{12}]$	15	8.34	5.03	25.30	74.70	0.34
H	30	97.23	58.65	5.72	94.27	0.06
	45	61.96	37.37	59.04	40.96	1.44
$[H_4Ru_4(CO)_{12}]$	30	48.74	41.92	60.85	24.54	2.48
I	30	36.85	31.70	62.33	34.95	1.78
	30	15.50	13.33	69.94	23.67	2.95
$[H_2Ru_4(CO)_{13}]$	15	15.80	14.63	64.56	35.44	1.82
J	30	28.62	26.49	69.57	30.43	2.29
	45	44.90	41.57	63.47	36.53	1.74
$[H_2FeRu_3(CO)_{13}]$	15	25.80	12.43	73.41	26.59	2.76
K	30	50.66	24.40	55.92	44.08	1.27
	45	65.60	31.60	56.05	43.95	1.28
$[H_2FeRu_3(CO)_{13}]$	30	37.90	49.13	70.77	29.23	2.42
L	30	71.34	54.09	22.36	77.64	0.29
	30	89.48	26.32	3.24	96.76	0.03
$[H_2FeRu_3(CO)_{13}]$	30	61.33	39.97	49.47	50.53	0.98
M	30	16.92	11.03	48.76	51.24	0.95
	30	28.06	18.29	68.21	31.79	2.15

[a] Experiments: A, In this, and in the following experiments the conditions (represented by four figures) were: cluster 1.15×10^{-5} mol, substrate 5.68×10^{-4} mol, substrate/cluster = 49.39, $H_2 = 1$ atm. B, 3.92×10^{-6} mol, 2.81×10^{-4} mol; 71.7; $H_2 = 1$ atm. C, 2.42×10^{-6} mol, 2.84×10^{-4} mol; 117.4; $H_2 = 1$ atm. D, 2.13×10^{-6} mol, $5.78/3.25/1.51 \times 10^{-4}$ mol; 271.4/152.6/70.9; $H_2 = 1$ atm. E, 2.13×10^{-6} mol, 5.72×10^{-4} mol; 268.5; $H_2 = 1, 0.5, 0.25$ atm. F, 8.07×10^{-5} mol, 5.70×10^{-4} mol; 7.1; $H_2 = 1$ atm. G, 9.93×10^{-6} mol, 5.65×10^{-4} mol; 56.9; $H_2 = 1$ atm. H, 9.40×10^{-6} mol, 5.67×10^{-4} mol; 60.3; $H_2 = 1$ atm. I, 6.72×10^{-6} mol, 5.78×10^{-4} mol; 86.0; $H_2 = 1, 0.5, 0.25$ atm. J, 6.06×10^{-6} mol, 5.61×10^{-4} mol; 92.6; $H_2 = 1$ atm. K, 1.20×10^{-5} mol, 5.78×10^{-4} mol; 48.2; $H_2 = 1$ atm. L, 4.59×10^{-6} mol, $5.95/3.48/1.35 \times 10^{-4}$ mol; 129.6/75.8/29.4; $H_2 = 1$ atm. M, 8.73×10^{-6} mol, 5.69×10^{-4} mol; 65.2; $H_2 = 1, 0.5, 0.25$ atm. [b] c-SB, *cis*-stilbene; *t*-SB, *trans*-stilbene; c/t ratio, *cis*-/*trans*-stilbene ratio. [c] The deficit from 100% is accounted for by diphenylethane in 24.11, 3.14, and 2.26%, respectively.

TABLE 2. Organometallic products and yields in the hydrogenation solutions

Parent cluster	Colour change	Organometallic complexes and yields [a]	Decomposition [a] (%)
$[Fe_3(CO)_{12}]$	Dark green to brown [b] or green-brown [c]	$[Fe_3(CO)_{12}]$ (12% [b], 5% [c]), $[Fe_3(CO)_9C_2Ph_2]$ (15% [b], 5% [c]), $[Fe_3(CO)_8(C_2Ph_2)_2]$ violet (-% [b], 10% [c]), $[Fe_3(CO)_8(C_2Ph_2)_2]$ green (20% [b], 50% [c]), $[Fe_2(CO)_6(C_2Ph_2)_2]$ (5% [b], 5% [c])	20
$[Fe_2Ru(CO)_{12}]$	Purple to green	$[Fe_3(CO)_{12}]$ (5%), $[Fe_2Ru(CO)_9C_2Ph_2]$ (40%) two unidentified (tr) [d]	15
$[FeRu_2(CO)_{12}]$	No change	$[FeRu_2(CO)_{12}]$ (30%), $[H_2Ru_3(CO)_9C_2Ph_2]$ (5%) $[H_4Ru_4(CO)_{12}]$ (tr), $[Ru_2(CO)_6(C_2Ph_2)_2]$ (20%)	15
$[Ru_3(CO)_{12}]$	No change	$[Ru_3(CO)_{12}]$ (5%), $[H_4Ru_4(CO)_{12}]$ (10%), $[H_2Ru_3(CO)_9(C_2Ph_2)_2]$ (20%), $[Ru_3(CO)_8(C_2Ph_2)_2]$ orange (tr)	15
$[H_2FeRu_3(CO)_{13}]$	Red to purple-brown	$[FeRu_3(CO)_{12}C_2Ph_2]$ (50%) [e], Complex F (15%)	35
$[H_2Ru_4(CO)_{13}]$	Red to orange-brown	$[H_2Ru_3(CO)_9C_2Ph_2]$ (10%), $[Ru_4(CO)_{12}C_2Ph_2]$ (10%), $[Ru_3(CO)_8(C_2Ph_2)_2]$ purple (5%), $[Ru_3(CO)_8(C_2Ph_2)_2]$ orange (tr), $[H_4Ru_4(CO)_{12}]$ (2%), $[Ru_4(CO)_{11}(C_2Ph_2)_2]$ (2%), Unidentified green (tr)	40
$[H_4Ru_4(CO)_{12}]$	Yellow to brown	$[H_4Ru_4(CO)_{12}]$ (30%), $[H_2Ru_3(CO)_9C_2Ph_2]$ (10%), $[Ru_4(CO)_{12}C_2Ph_2]$ (20%), $[Ru_3(CO)_8(C_2Ph_2)_2]$ purple (3%)	20

[a] See [15]. [b] Low substrate/cluster ratio (experiment F, Table 1). [c] High substrate/cluster ratio (experiment G, Table 1). [d] tr, trace amounts. [e] Two isomers; Fe on wingtip 30%, Fe in hinge 20%.

TABLE 3. Isomerization of cis-stilbene in the presence of clusters 2, 5, 6, 7

Cluster and experiment [a]	Reaction time (min)	Conversion	Turnover	Selectivity to	
				t-SB	DPE
$[Fe_2Ru(CO)_{12}]$	15	48.97	69.51	100.0	–
O	30	18.69	26.53	100.0	–
	45	42.80	60.76	100.0	–
$[H_4Ru_4(CO)_{12}]$	15	17.74	15.90	99.38	0.62
P	30	31.99	28.66	99.62	0.38
	45	35.80	32.08	99.66	0.34
$[H_2Ru_4(CO)_{13}]$ [b]	15	60.43	97.96	97.30	2.70
Q	30	76.81	124.51	94.65	5.35
	45	86.17	139.69	94.78	5.22
$[H_2FeRu_3(CO)_{13}]$ [c]	15	36.78	59.88	95.02	4.98
R	30	49.64	80.82	95.97	4.03
	45	64.62	105.21	97.22	2.78
$[H_2FeRu_3(CO)_{13}]$ [d]	30	89.63	182.08	99.44	0.56
S	30	53.66	54.67	99.57	0.43
	30	57.86	29.45	99.86	0.14

[a] Experiments: the conditions were as follows: O, cluster 7.89×10^{-6} mol, substrate 1.12×10^{-3} mol; substrate/cluster = 141.9. P, 1.25×10^{-5} mol, 1.12×10^{-3} mol; 89.6. Q, 6.92×10^{-6} mol, 1.12×10^{-3} mol; 161.8. R, 6.89×10^{-6} mol, 1.12×10^{-3} mol; 162.5. S, 8.27×10^{-6} mol, 1.68×10^{-3}, 8.41, 4.21 $\times 10^{-4}$ mol; 0.67; 1.33; 2.66. In some vials, a large amount of a whitish precipitate was observed after heating. This was collected, dried and weighed. [b] A total of 498 mg was collected from the three vials. [c] 163 mg from three vials. [d] 366 mg from three vials.

120°C for 15–45 min; the solutions were analysed by IR spectroscopy and by TLC. The vials containing $H_2FeRu_3(CO)_{13}$ gave, after 15 min, a mixture of $[H_4Ru_4(CO)_{12}]$ (10%), $[H_2Ru_4(CO)_{13}]$ (5%) and the parent cluster; this remained unaltered and only slight decomposition occurred. In the vials containing $[H_2Ru_4(CO)_{13}]$ the amounts of $[H_4Ru_4(CO)_{12}]$ increased with time (15% after 45'), and very slight decomposition was noted.

3. Results and discussion

3.1. Hydrogenation of diphenylacetylene

The results of the hydrogenation experiments are collected in Table 1. The organometallic complexes identified in the reaction solutions [15*] are collected in Table 2.

Earlier studies showed that regiospecific substitution of phosphines and phosphites occurs easily at the ruthenium in $[H_2FeRu_3(CO)_{13}]$ [16]; substitutions on $[FeRu_2(CO)_{12}]$ and $[Fe_2Ru(CO)_{12}]$ occur first at ruthenium and then at iron, with a first order reaction in which CO dissociation is the rate determining-step. The ruthenium centres are more reactive than the iron centres [17]. However, for $[FeRu_2\text{-}(CO)_{12}]$, $[Fe_2Ru\text{-}(CO)_{12}]$, $[H_2FeRu_3(CO)_{13}]$ and their phosphorus derivatives, iron enhances the water–gas shift activity [18]. Complexes 1–4 were also tested in the hydrogenation of 1- and 2-pentyne and of dienes under mild homogeneous conditions or anchored on γ-alumina. In toluene solution, activity decreased with the number of iron atoms. The main products were 2-pentenes, the *trans* isomer being far more abundant than the *cis* [19].

We have now found that the activity decreases in the series $[Ru_3(CO)_{12}]$, $[Ru_2Fe(CO)_{12}]$, $[Fe_2Ru\text{-}(CO)_{12}]$, $[Fe_3(CO)_{12}]$, that is, with increasing iron. For the tetranuclear clusters, the activity apparently decreases in the series $[H_4Ru_4(CO)_{12}] > [H_2Ru_4(CO)_{13}] > [H_2FeRu_3(CO)_{13}]$.

$[Ru_3(CO)_{12}]$ and $[H_4Ru_4(CO)_{12}]$ show similar activity and *cis*-/*trans*-stilbene ratio (approaching 1:1), attributed to the fact that $[H_4Ru_4(CO)_{12}]$ is formed from

$[Ru_3(CO)_{12}]$ under hydrogen. Other tri- and tetra-nuclear carbonyls generally afford more *trans*- than *cis*-stilbene. This behaviour may be related to the isomerization ability of the clusters (see Table 3).

A decrease in the hydrogen pressure results in lower activity and in an increase of *cis*-stilbene, in accord with the hypothesis that catalysis occurs on metal fragments or on hydrides, as discussed below; an increase of the substrate/cluster ratio results in the expected increase in turnover and in a strong decrease of *cis*-stilbene for $[H_2FeRu_3(CO)_{13}]$.

3.2. Isomerization of cis-stilbene

The results of the isomerization experiments are collected in Table 3. The organometallic products in the reaction solutions [15*] are collected in Table 4.

The complexes tested are more active in isomerization than in hydrogenation, except $[H_4Ru_4(CO)_{12}]$. Note that the turnovers in Table 3 are underestimated, as considerable amounts of solid *trans*-stilbene were collected when cooling the vials; the weight of the solid product is given as a footnote in Table 3.

These results indicate that isomerization also occurs on metal fragments, which are given easily by clusters 2, 5 and 6; indeed, 5 and 6 give disproportionation in different conditions (and under dihydrogen only, see Experimental section), the final product being $[H_4Ru_4(CO)_{12}]$. In contrast, stilbenes are less efficient than C_2Ph_2 in promoting metal-fragment condensation.

Some diphenylethane is obtained even in the absence of dihydrogen. This indicates that hydrogen is transferred from the cluster to the substrate, as in the protonation of tri- and tetra-nuclear ruthenium acetylide or alkyne derivatives [20,21]. Moreover, ethylene is hydrogenated stoichiometrically by $[H_4Ru_4\text{-}(CO)_{12}]$. The complex is also a powerful hydrogenation catalyst and deuteration experiments indicate that it adds hydrogen which is then transferred on the substrate [22]. Very recently it was reported that $[(\mu\text{-}H)Ru_3(CO)_9(\mu_3\text{-}Hampy)]$ {Hampy = 2-amino-6-methylpyridine} is a catalyst precursor for hydrogenation of

TABLE 4. Complexes found in the *cis*-stilbene isomerization experiments

Parent cluster	Colour change	Complexes and yields	Decomposition (%)
$[Fe_2Ru(CO)_{12}]$	No change	$[Fe_2Ru(CO)_{12}]$ (65%), $[Ru_3(CO)_{12}]$ (tr)	25
$[H_4Ru_4(CO)_{12}]$	No change	$[H_4Ru_4(CO)_{12}]$ (90%)	10
$[H_2Ru_4(CO)_{13}]$	Red to orange	$[H_2Ru_4(CO)_{13}]$ (80%), $[H_4Ru_4(CO)_{12}]$ (5%)	10
$[H_2FeRu_3(CO)_{13}]$	Red to orange	$[H_2FeRu_3(CO)_{13}]$ (50–75%), $[H_2Ru_4(CO)_{13}]$ (5%) $[H_4Ru_4(CO)_{12}]$ (15–40%)	5

C_2Ph_2 under 1 atm of dihydrogen; the catalytic species is formed upon insertion of C_2Ph_2 into a Ru–H bond. In this instance cluster catalysis occurs, presumably because the capping ligand prevents fragmentation; the activity is comparable to that we observed [23].

3.3. A comparison of the reactivity of clusters 1–7 with diphenylacetylene under dinitrogen or dihydrogen. The role of the organometallic products in homogeneous catalysis

The reactions of clusters 1–7 with diphenylacetylene under dinitrogen have been the subject of several literature reports, quoted below. The results reported here for the hydrogenation and isomerization reactions, and the reactions of clusters 1–7 with C_2Ph_2 under dinitrogen or dihydrogen indicate competition between formation of catalytically active metal fragments (favoured by dihydrogen) and condensation of metal fragments to give stable products (induced by C_2Ph_2). The overall results depend on the extent to which each process occurs.

3.3.1. Formation of metal fragments

$[Fe_2Ru(CO)_{12}]$ and $[H_2FeRu_3(CO)_{13}]$ are broken up when supported on Al_2O_3 or SiO_2 [24]. However on hydroxylated magnesia, formation of $[HFeRu_3(CO)_{13}]^-$ was observed [25].

In the isomerization experiments, we found that $[H_2Ru_4(CO)_{13}]$ and $[H_2FeRu_3(CO)_{13}]$ form $[H_4Ru_4-(CO)_{12}]$ in amounts depending on the starting cluster and reaction conditions; this indicates the formation and recombination of metal fragments. Finally, the reactions of the same clusters under dihydrogen only show some disproportionation, the final product always being $[H_4Ru_4(CO)_{12}]$.

Thus, we have evidence for the formation of metal fragments under the hydrogenation and isomerization conditions; these fragments are probably responsible for the catalysis. However, the possibility that hydridic clusters act as catalysts cannot be excluded (see [22,23]).

3.3.2. Metal fragment condensation

The chemistry of $[Fe_3(CO)_{12}]$ [26], $[Ru_3(CO)_{12}]$ [10,11,27,28], $[Fe_2Ru(CO)_{12}]$ [29], and of $[H_2FeRu_3-(CO)_{13}]$ [30] towards C_2Ph_2 under an inert atmosphere has been extensively studied. The structures of some complexes obtained in the reactions shown are in Fig. 2.

$[Fe_3(CO)_{12}]$ and $[FeRu_2(CO)_{12}]$ give first $[Fe_2M-(CO)_9(\mu_3-\eta^2-C_2Ph_2)]$ (M = Fe, complex G [26,31]; M = Ru, complex H [29]). With an excess of C_2Ph_2 and upon heating, G gives the violet and green isomers $[Fe_3(CO)_8(C_2Ph_2)_2]$ (complexes I, J, respectively [32]). Under dihydrogen we observed a comparable reactivity
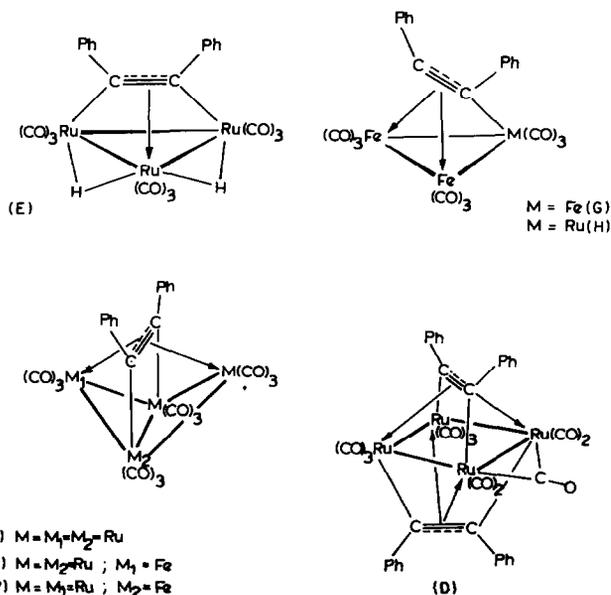
Fig. 2. Structures of some acetylene-substituted clusters as reported in the literature. Top to bottom, and left to right; complex E, complexes G, H, complex A and isomeric complexes O, P, complex D.

trend; the yields of G decrease and those of J strongly increase with an excess of alkyne (Table 2). This indicates that the alkyne favours condensation of metal fragments (Scheme 1).

The butterfly complex $[Ru_4(CO)_{12}C_2Ph_2]$ (A) and $[H_2Ru_3(CO)_9C_2Ph]$ (E) are key products in the reactions of $Ru_3(CO)_{12}$. Upon heating with an excess of alkyne, both give complex B and the pentagonal bipyramidal orange isomer $[Ru_3(CO)_6(\mu-CO)_2-(C_2Ph_2)_2]$ (C) [10] as the final products. Hydrogenation of B and C (see Table 5 below) showed that these are stable side-products. By contrast, hydrogenation of complex A gives $[H_2Ru_3(CO)_9(\mu_3-\eta^2-C_2Ph_2)]$ (E), which is also obtained from $[Ru_3(CO)_{12}]$ and C_2Ph_2 in alkaline solution [13]. Complex E in the presence of dihydrogen releases hydrogenation products and is

$$[H_xMRu_3(CO)_y]$$

$$\downarrow \begin{array}{c} H_2 \\ C_2Ph_2 \end{array}$$

$$[MRu_3(CO)_{12}C_2Ph_2]$$

$$\begin{array}{c} H_2 \swarrow \quad \searrow C_2Ph_2 \end{array}$$

$$[H_2Ru_3(CO)_9C_2Ph_2] \xrightarrow{\quad C_2Ph_2 \quad} [Ru_3(CO)_8(C_2Ph_2)_2]$$

$$\downarrow H_2 \qquad\qquad\qquad \text{isomers}$$

hydrogenated product
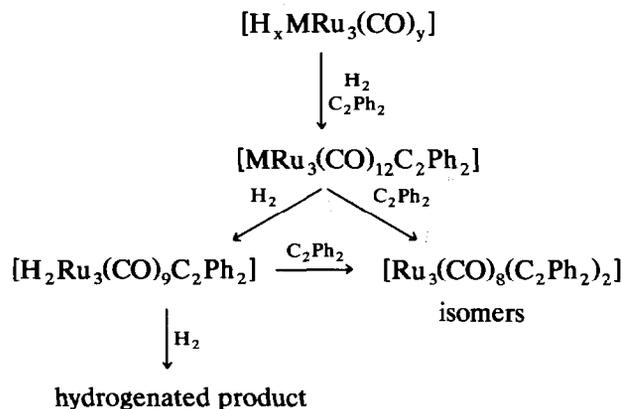
Scheme 1.

TABLE 5. Hydrogenation reactions of alkyne-substituted complexes

Cluster	Reaction time (min)	Selectivity to			
		c-SB	t-SB	DPE	DPA
$[H_2Ru_3(CO)_9C_2Ph_2]$	15	11.53	78.57	9.21	0.69
	30	12.43	76.67	7.51	3.39
$[Ru_4(CO)_{12}C_2Ph_2]$	15	10.64	18.07	–	71.29
	30	3.81	5.57	–	90.62
	45	7.46	12.49	–	80.05
$[FeRu_3(CO)_{12}C_2Ph_2]$ brown	15	6.68	24.84	–	68.48
	30	10.61	14.72	–	74.67
	45	11.39	21.49	–	67.12
$[FeRu_3(CO)_{12}C_2Ph_2]$ red	15	7.88	21.50	–	70.62
	30	15.53	32.18	–	52.29
$[Ru_3(CO)_8(C_2Ph_2)_2]$ purple	15	58.37	41.62	–	tr
	30	tr	tr	–	tr
	45	39.62	60.38	–	tr
$[Ru_3(CO)_8(C_2Ph_2)_2]$ orange	15–45	tr	tr	–	tr

DPE, diphenylethane; DPA, diphenylacetylene.

hence an intermediate or a catalyst (see [23]). This indicates that catalysis results depend on the stability of the alkyne-substituted products, and presumably on the presence of hydrides. Indeed [(Cp)$_2$Ni$_2$-Fe(CO)$_3$(μ_3-η^2-C$_2$Ph$_2$)] [33] containing C$_2$Ph$_2$ coordinated in similar fashion, is obtained in quantitative yields from [(Cp)$_2$Ni$_2$Fe(μ_3-CO)$_2$(CO)$_3$] [34] and C$_2$Ph$_2$ under dihydrogen; however, no hydrogenation products could be obtained in this reaction even under forcing conditions [35].

In the reactions of complexes 5, 6, 7 with C$_2$Ph$_2$, the first products are again the butterfly derivatives [Ru$_3$M(CO)$_{12}$(C$_2$Ph$_2$)] (M = Ru, A; M = Fe, isomeric, complexes O, P) with the iron atom either in a wing tip or a hinge position [30]. Complex 7 gives A under dinitrogen, with substitution of the hydrides and Ru–Ru bond cleavage. The presence of extra hydrogen would therefore lower the yields of A. Complex 6 also gives considerable yields of A, via substitution of hydrides and one CO, and comparable reactivity patterns. Complex 5 gives the heterometallic isomers O and P. The new complex F is obtained only from complexes 5 and 6. This is not a hydrogenation intermediate, as shown by the fact that its yields increase at low dihydrogen pressure or under dinitrogen.

Complex F shows the presence of two bridging carbonyl bands in an IR spectrum, comparable with the orange isomer [Ru$_3$(CO)$_6$(μ-CO)$_2$(C$_2$Ph$_2$)$_2$] (C). However, F is bright red, and the two complexes can be easily separated on TLC plates. The ^{1}H NMR spectrum in the phenyl region of F is comparable with that of C, which is very distinctive [36]. Finally a comparison

of the ^{13}C NMR spectra of F and C shows considerable similarities in the organic carbon resonances. These spectra also confirm the terminal and bridging COs in both complexes, although those of F exchange at room temperature.
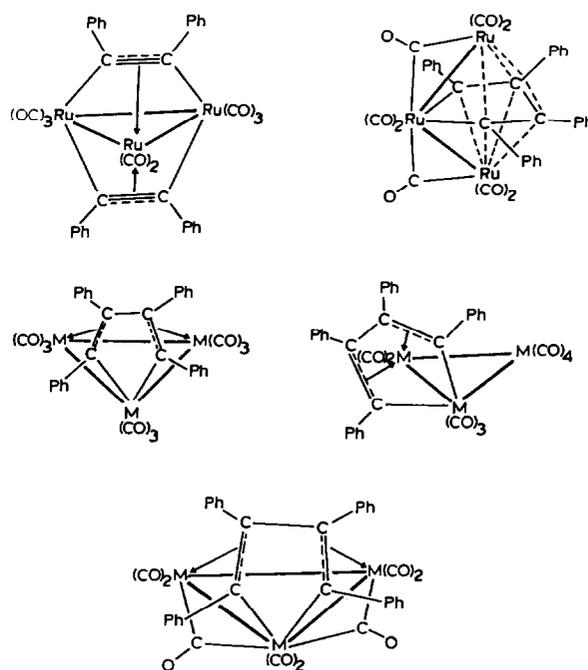
Fig. 3. Possible structures for isomeric complexes [Ru$_3$(CO)$_8$(C$_2$-Ph$_2$)$_2$]. Top: structures of the purple isomer B and of the orange isomer C. Centre and bottom: possible structures for complex F.

TABLE 6. Hydrogenation of alkyne-substituted products

Complex	Colour change	Organometallic products	Decomposition (%)
$[H_2Ru_3(CO)_9C_2Ph_2]$	No change	$[H_2Ru_3(CO)_9C_2Ph_2]$ (70%), $[H_4Ru_4(CO)_{12}]$ (tr)	20
$[Ru_3(CO)_8(C_2Ph_2)_2]$ Purple	Purple to brown-yellow	$[H_4Ru_4(CO)_{12}]$ (tr), $[H_2Ru_3(CO)_9C_2Ph_2]$ (10%), $[Ru_4(CO)_{12}C_2Ph_2]$ (10%), $[Ru_3(CO)_8(C_2Ph_2)_2]$ orange (35%), $[Ru_2(CO)_6(C_2Ph_2)_2]$ (20%)	10
$[Ru_3(CO)_8(C_2Ph_2)_2]$ Orange	No change	$[Ru_3(CO)_8(C_2Ph_2)_2]$ orange (60%), $[H_4Ru_4(CO)_{12}]$ (tr), $[Ru_2(CO)_6(C_2Ph_2)_2]$ (20%)	25
$[Ru_4(CO)_{12}C_2Ph_2]$	Brown to dark-yellow	$[H_4Ru_4(CO)_{12}]$ (5%), $[H_2Ru_3(CO)_9C_2Ph_2]$ (25%), $[Ru_4(CO)_{12}C_2Ph_2]$ (35%), $[Ru_3(CO)_8(C_2Ph_2)_2]$ orange (5%)	15
$[FeRu_3(CO)_{12}]$ Wing tip	No change	$[H_2Ru_3(CO)_9C_2Ph_2]$ (10%), $[Ru_3(CO)_8(C_2Ph_2)_2]$ orange (tr)	30
$[FeRu_3(CO)_{12}]$ Hinge	Red-brown to brown	$[H_2Ru_3(CO)_9C_2Ph_2]$ (15%), $[Ru_3(CO)_8(C_2Ph_2)_2]$ orange (tr)	35

The spectroscopic data, mass spectrum, molecular weight, and elemental analyses, would indicate for **F** a formulation $[Ru_3(CO)_6(\mu\text{-}CO)_2(C_2Ph_2)_2]$ with the two alkynes forming a metallacycle comparable with that of **C**. The two structures proposed are shown in Fig. 3.

Such structures were originally discussed for osmium derivatives [37]. A metallacycle on one cluster edge was found in osmium [38] and iron [39] complexes. A metallacycle symmetrical with respect to the cluster, has not yet been proved. Such a structure would contain a $Ru_3(CO)_6(\mu\text{-}CO)_2$ unit with a characteristic $\nu(CO)$ pattern in a range of derivatives [40]. We propose this type of symmetrical structure with bridging COs for **F**.

3.3.3. Hydrogenation of alkyne-substituted clusters

Hydrogenation products are given in Table 5 and the organometallic products in Table 6.

As previously observed, all the derivatives except **E** give low amounts of hydrogenated products, although C_2Ph_2 is sometimes released rather than stilbenes. This constitutes sound evidence for these being the stable products of metal fragment condensation induced by the alkyne and not reaction intermediates. Moreover, the anomalous trends observed in several experiments (after 30 min) can be explained assuming that initially catalytic metal fragments are formed. Condensation and isomerization then modify the reaction course [41*].

From all these results, we propose for the tetrahedral complexes, the reactivity trend shown in the Scheme 1.

Our hypotheses [8] on the catalytic behaviour of clusters in hydrogenation of alkynes are substantially correct. We have now gained understanding of the

effects of the cluster metals, of the reactants, and of the type and stability of substituted complexes formed. The clusters studied are moderate hydrogenation catalysts for alkynes, and good isomerization catalysts for alkenes.

Acknowledgements

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