Journal of Organometallic Chemistry, 369 (1989) 419–431
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 09898

Phosphine-substituted and phosphido-bridged metal clusters in homogeneous catalysis

IV *. Selective hydrogenation of diphenylacetylene and isomerization of *cis*-stilbene in the presence of $Ru_3(CO)_{12-n}(PPh_2H)_n$ ($n = 2, 3$), $HRu_3(CO)_{10}(\mu\text{-}PPh_2)$, $HRu_3(CO)_9(\mu\text{-}PPh_2)$ and $HRu_3(CO)_7(\mu\text{-}PPh_2)_3$

Mario Castiglioni

Dipartimento di Chimica Generale ed Organica Applicata, Università di Torino, Corso Massimo d'Azeglio 48, 10125 Torino (Italy)

Roberto Giordano and Enrico Sappa *

Dipartimento di Chimica Inorganica, Chimica Fisica e Chimica dei Materiali, Università di Torino, Via Pietro Giuria 7, 10125 Torino (Italy)

(Received January 3rd, 1989)

Abstract

The clusters $Ru_3(CO)_{12-n}(PPh_2H)_n$ ($n = 2, 3$), $HRu_3(CO)_{10}(\mu\text{-}PPh_2)$, $HRu_3(CO)_9(\mu\text{-}PPh_2)$ and $HRu_3(CO)_7(\mu\text{-}PPh_2)_3$ show considerable activity in the selective hydrogenation of diphenylacetylene to stilbenes; the phosphine-substituted derivatives are also very efficient in the isomerization of *cis*-stilbene to *trans*-stilbene. The latter product is often found as a precipitate in the vials after the hydrogenation or isomerization experiments. Different *cis*/*trans*-stilbene ratios in the hydrogenation solutions have been found for the phosphine-substituted and the phosphido-bridged clusters; this points to different reaction patterns and/or intermediates. A comparison of the behaviour of C_2Ph_2, C_2Et_2 and HC_2Bu^t under the same conditions and in the presence of the same phosphido-bridged cluster has been made; the nature of the alkyne has an important influence on the hydrogenation rate and the formation of reaction intermediates.

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* Parts I, II, III, see ref. 6, 7.

0022-328X/89/$03.50

Introduction

The catalytic properties of metal carbonyl clusters under various conditions are the subject of much study [1]. A serious limitation to their use in homogeneous catalysis is the tendency of the metal–metal bonds to undergo cleavage in the presence of small molecules, such as CO, H_2, alkynes. A widely used method of improving the stability of the cluster involves the use of bridging or capping of the metal frames [2] with suitable ligands such as the phosphido- [3] or phosphinidene-bridges [4].

In previous studies we found that homo- and hetero-metallic phosphine-substituted clusters are more active than their parent derivatives, in homogeneous hydrogenation reactions [5], and that when $Ru_3(CO)_{12-n}(PPh_2H)_n$ complexes are used, phosphido-bridged derivatives, still catalytically active, are formed [6].

We thus decided to study the behaviour of the phosphido-bridged derivatives obtainable from $Ru_3(CO)_{12-n}(PPh_2H)_n$ ($n = 1$–3). In the first part of our study we examined the behaviour of $HRu_3(CO)_{10}(\mu\text{-}PPh_2)$ (**1**), $HRu_3(CO)_9(\mu\text{-}PPh_2)$ (**2**), $H_2Ru_3(CO)_8(\mu\text{-}PPh_2)_2$ (**3**), $HRu_3(CO)_7(\mu\text{-}PPh_2)_3$ (**4**), $Ru_2(CO)_6(\mu\text{-}PPh_2)_2$ (**5**) and $Ru_3(CO)_{12-n}(PPh_2H)_n$ ($n = 2$, 3) (complexes **6**, **7** respectively) in the hydrogenation of t-butylacetylene [7]. We found that clusters **1**–**7** behave as selective homogeneous catalysts, giving mainly t-butylethylene; comparable turnovers were found for all the clusters, and this suggested the intermediacy of a common (cluster) catalytic species. From the reaction mixtures the clusters $Ru_3(CO)_6(\mu\text{-}PPh_2)(HC_2Bu^t)(Ph_2PC(H)C(Bu^t))$ (**8**) and $Ru_3(CO)_4(\mu\text{-}PPh_2)(Ph_2PC(H)C(Bu^t))(Ph_2PC{\equiv}CBu^t)$ (**9**), which were considered reaction intermediates, were isolated.

We report here on the behaviour of C_2Ph_2 (and to a lesser extent C_2Et_2) in the presence of clusters **1**, **2**, **4**, **6** and **7**. The reasons for the choice of C_2Ph_2 were: (i) it offers the possibility of evaluating the selectivity of the reactions towards *cis*- or *trans*-ethylenic products and (ii) comparison can be made between its behaviour and that of HC_2Bu^t and C_2Et_2.

The three alkynes show well known, and different, reactivity patterns with $Ru_3(CO)_{12}$ as catalyst, [8*,9*,10*], and are hence expected to behave differently in the hydrogenations. We have found that selective hydrogenation to ethylenic products always occurs, but very different reaction rates are observed, and the reaction intermediates are probably different.

Experimental

General experimental details. Materials and analysis of the organometallic products

Complexes **1**, **2**, **4**, **6** and **7** were prepared by published methods [6,7,11]; C_2Ph_2 and C_2Et_2 were commercial products (Farchan), used as received after GLC purity checks.

The organometallic products obtained in the catalytic reactions were purified on TLC preparative plates (Kieselgel P.F. Merck, eluants mixtures of light petroleum and diethyl ether). The organic products obtained in the reactions described below were analyzed by GLC (see below). The elemental analyses of the organometallic products were performed with a F & M C,H,N Analyzer. The IR spectra were

* Reference numbers with asterisks indicate notes in the list of references.

recorded on a Perkin–Elmer 580 B spectrometer and the NMR spectra on a JEOL JNM GX 270 FT instrument.

Hydrogenation and isomerization experiments

Gas-chromatographic analyses of the reaction solutions. Unless otherwise specified, the hydrogenations were performed in sealed glass vials (volume 25 ml), each containing 2 ml of a n-octane solution of the cluster and of alkyne; the vials were filled with 0.9 atm of H_2 by standard vacuum techniques, and then kept at 120 °C in a thermostatted oven for the relevant time. The isomerizations for *cis*-stilbene were also carried out in sealed vials; no hydrogen was introduced in this case before sealing. Details of the concentrations of clusters and substrates are given in Table 1.

In the hydrogenation experiments the concentration of the substrate was maintained constant as far as possible; the substrate/cluster ratios are different, depending on the cluster solubility. A large excess of diphenylacetylene was generally used, but complete solubility was always observed. Only after the hydrogenations was a whitish crystalline material observed in the vials.

The organic products in the solutions after the hydrogenation (or isomerization) experiments were analyzed with a Carlo Erba 4200 FID gas-liquid chromatograph equipped with 2 m × 0.6 mm i.d. columns used under the following conditions; hex-3-yne, n-octane/Porasyl C (80/100 mesh), 25 ml/min N_2 flow, 70 °C for 6

Table 1

Cluster and substrate concentrations, and substrate/cluster molar ratios in hydrogenation and isomerization

Experiment [a]	Cluster	Cluster (mol/l)	Substrate (mol/l)	Substrate/cluster molar ratio
Hydrogenation of hex-3-yne				
(A)	$HRu_3(CO)_9(PPh_2)$	7.65×10^{-6}	1.76×10^{-3}	230
(B)	$HRu_3(CO)_7(PPh_2)_3$	5.15×10^{-6}	1.76×10^{-3}	342
(C)	$HRu_3(CO)_7(PPh_2)_3$ [b]	5.15×10^{-6}	1.76×10^{-3}	342
Hydrogenation of diphenylacetylene				
(D)	$HRu_3(CO)_{10}(PPh_2)$	7.15×10^{-6}	6.0×10^{-4}	84
(E)	$HRu_3(CO)_9(PPh_2)$	7.42×10^{-6}	7.46×10^{-4}	100
(F)	$HRu_3(CO)_9(PPh_2)$ [c]	7.86×10^{-6}	7.46×10^{-4}	95
(G)	$HRu_3(CO)_7(PPh_2)_3$	6.0×10^{-6}	2.81×10^{-4}	47
(H)	$HRu_3(CO)_7(PPh_2)_3$	4.90×10^{-6}	7.46×10^{-4}	152
(I)	$HRu_3(CO)_7(PPh_2)_3$ [b]	5.92×10^{-6}	6.4×10^{-4}	108
(K)	$Ru_3(CO)_{10}(PPh_2H)_2$	6.28×10^{-6}	5.84×10^{-4}	93
(L)	$Ru_3(CO)_9(PPh_2H)_3$	4.19×10^{-6}	4.78×10^{-4}	138
Isomerization of cis-stilbene [d]				
(M)	$HRu_3(CO)_{10}(PPh_2)$	7.15×10^{-6}	1.12×10^{-3}	157
(N)	$HRu_3(CO)_9(PPh_2)$	7.42×10^{-6}	1.12×10^{-3}	151
(O)	$HRu_3(CO)_7(PPh_2)_3$	5.21×10^{-6}	1.12×10^{-3}	215
(P)	$Ru_3(CO)_{10}(PPh_2H)_2$	5.23×10^{-6}	1.12×10^{-3}	214
(Q)	$Ru_3(CO)_9(PPh_2H)_3$	4.49×10^{-6}	1.12×10^{-3}	249

[a] The letters indicating the experiments are the same in all the Tables. [b] Under decreasing hydrogen pressure. [c] For short reaction times. [d] Without hydrogen.

Table 2

Organometallic products, cluster decomposition and formation of *trans*-stilbene in hydrogenation and isomerization

Experiment [a]	Catalyst	Changes in colour	Cluster decomposition [b] (%)	Yields of *trans*-stilbene [c] (%)	Organometallic products observed [d]
Hydrogenation of hex-3-yne					
(A)	$(HRu_3(CO)_9(PPh_2)$	Immediate reaction with the alkyne; greenish colour turning gradually to yellow	95	–	**3** (1%), **5** (5%), yellow unidentified (trace)
(B)	$HRu_3(CO)_7(PPh_2)_3$	No change	20	–	parent (40%), **5** (40%)
(C)	$HRu_3(CO)_7(PPh_2)_3$	No change	15	–	as above
Hydrogenation of diphenyl-acetylene					
(D)	$HRu_3(CO)_{10}(PPh_2)$	No change	20	44–77	**3** (1%), **4** (40%), **5** (20%)
(E)	$HRu_3(CO)_9(PPh_2)$	No change until 75 min purple at 90 min	85	31–42	**4** (5%), **10** (trace), **11** (trace)
(F)	$HRu_3(CO)_9(PPh_2)$	As above	80	40–49	as above
(G)	$HRu_3(CO)_7(PPh_2)_3$	Gradual darkening to purple	25	45–50	**4** (50%), **5** (20%), **11** (1%)
(H)	$HRu_3(CO)_7(PPh_2)_3$	As above	35	40–50	as above
(I)	$HRu_3(CO)_7(PPh_2)_3$	As above	30	see text	as above
(X)	$HRu_3(CO)_7(PPh_2)_3$	As above	35	49.5	as above
(K)	$Ru_3(CO)_{10}(PPh_2H)$	No change	20	59–80	**3** (2%), **4** (30%), **5** (30%) parent (10%)
(Y)	$Ru_3(CO)_{10}(PPh_2H)_2$	No change	20	55.8	As above
(L)	$Ru_3(CO)_9(PPh_2H)_3$	No change	20	64–78	**3** (1%), **4** (25%), **5** (20%), parent (15%)
Isomerization of cis-stilbene					
(M)	$HRu_3(CO)_{10}(PPh_2)$	No change	20	–	**4** (20%), **5** (20%), **11** (trace)
(N)	$HRu_3(CO)_9(PPh_2)$	Gradual darkening	70	–	**5** (20%), **11** (trace)
(O)	$HRu_3(CO)_7(PPh_2)_3$	No change	20	–	As for G–I
(P)	$Ru_3(CO)_{10}(PPh_2H)_2$	No change	10	50.4	As for K–Y
(Q)	$Ru_3(CO)_9(PPh_2H)_3$	No change	15	51	As for L

[a] See Table 1. [b] Maximum degree of decomposition after the longer reaction time. [c] Minimum and maximum yield observed. [d] Approximate yields.

min, then 4°C/min till 155°C: diphenylacetylene (and stilbene), SE 30 on 5% Chromosorb WAW (60/80 mesh) with 46 ml/min N_2 flow, 60°C for 6 min, then 10°C/min till 240°C.

Tentative identification of the organometallic products in the reaction solutions

Identification of the solid organic product. The solutions after the hydrogenation or isomerization experiments were subjected to preparative TLC to check for decomposition of the catalysts and to identify the organometallic products. Unambiguous identification of the products was, however, difficult because of the very small amounts available. The identities of the products detected, the degree of decomposition of the clusters, and the amount of solid organic product deposited, are shown in Table 2.

After several hydrogenation or isomerization runs, when the vials were cooled deposition of a whitish crystalline residual was observed; the crystals were filtered off and dissolved in acetone [12*], and the solution allowed to give crystals by slow evaporation in the air. The crystals were examined with a Carlo Erba 4200 FID-Kratos MS-50 linked GLC/MS, operated either with EI (70 eV) or chemical ionization. The molecular weight was confirmed by osmometry.

Further evidence for identification of the solid as *trans*-stilbene was obtained by a comparison of the melting point of the reaction products with that of a pure specimen, and by comparison of the IR and ^1H NMR spectra.

Results and discussion

Hydrogenation of hex-3-yne. The results obtained are shown in Table 3.

The conversions observed were very low: only cluster **2** showed activity, probably because of the ease of its reaction with the alkyne (Table 2). Initially *cis*-3-hexene is formed, as expected, but after long reaction times *trans*-3-hexene is the main

Table 3

Hydrogenation of hex-3-yne in the presence of clusters **2**, **4**

Experiment [a]	Cluster	Reaction time (min)	Turnover	Conversion (%)	Selectivity (%) towards			
					hexane	1-hexene	*cis*-3-hexene	*trans*-3-hexene
(A)	$HRu_3(CO)_9(PPh_2)$ [b]	15	2.5	1.1	–	–	46.4	54.6
		30	7.4	3.2	–	12.5	6.3	78.2
		45	16.8	7.3	–	8.2	1.4	90.4
(B)	$HRu_3(CO)_7(PPh_2)_3$	15	0.3	0.1	trace	–	–	–
		30	1.0	0.3	trace	trace	–	trace
		45	3.4	1.0	10.0	40.0	–	50.0
		60	4.1	1.2	8.3	33.4	–	58.3
		75	5.5	1.6	12.5	31.2	–	56.3
		90	6.5	1.9	15.8	26.3	–	57.9
(C)	$HRu_3(CO)_7(PPh_2)_3$ [c]	45	4.4	1.3	7.7	38.5	–	53.8
		45	2.7	0.8	trace	37.5	–	62.5
		45	0.7	0.2	trace	trace	–	> 90.0

[a] See Table 1. [b] Cluster **2** reacts immediately with the alkyne (see Table 2). [c] Under a decreasing pressure of H_2; in the order 1, 0.75 and 0.50 atm.

product, *cis-trans* isomerization probably occurring, as observed for C_2Ph_2. Cluster **4** shows a very poor catalytic activity and 1-hexene and *trans*-3-hexene are the main products, the proportion of the latter decreasing with time. Finally, the formation of 1-hexene and of hexane is favoured by the presence of hydrogen, as shown by the decrease in the yields of these products when the pressure of H_2 is lowered.

Hydrogenation of diphenylacetylene. Before a discussion of the hydrogenation results, some comments on the nature and yield of the solid organic product observed are necessary. This was unequivocally identified as *trans*-stilbene from its mass spectra, molecular weight as determined by osmometry, and melting point, and by comparison of its IR and NMR spectra with those of an authentic specimen. The possibility of formation of oligomers containing *trans*-stilbene and diphenylacetylene was ruled out; the chemical ionization experiments did not show any ion with *m/e* above 182.

The presence of hexaphenylbenzene was ruled out on the basis of the melting points of the products isolated. Moreover, in the isomerization experiments of *cis*-stilbene, the formation of hexaphenylbenzene would require dehydrogenation of the substrate. This compound is generally observed in the reactions involving C_2Ph_2 and $M_3(CO)_{12}$ (M = Ru, Os) carbonyls in the absence of hydrogen [13].

The presence of (sometimes) large amounts of *trans*-stilbene complicates the interpretation of the GLC results for the reaction solutions; thus the observed selectivities towards *trans*-stilbene are lower and the *cis/trans* ratios are higher than those shown in Table 4, and should be corrected for the presence of the solid. However, in most of the experiments, the amount of *trans*-stilbene deposited was nearly constant (see Table 2) and so the data reported in the subsequent tables have not been corrected [14*].

The results from the hydrogenation of diphenylacetylene are shown in Table 4.

Considerable catalytic activity is observed for all the complexes, and the final conversion values are between 70 and 100; the reaction pattern is somewhat similar in all cases, with a very high initial rate, followed by a lower one, probably because of cluster modification or formation of stable intermediates or side products. This can be seen from Fig. 1, where the conversions obtained in the experiments with various clusters are shown. (The drawing are in the same scale).

For t-butylacetylene we showed previously that the phosphido-bridged and the phosphine-substituted clusters behave differently in the initial reaction step the former showing greater activity, until they were transformed into the (suggested) common, catalytically active, cluster species [7]. The final results were, however, comparable for all the clusters.

For diphenylacetylene we have found a similar pattern of reaction and comparable substrate conversions for all the clusters, with some notable exceptions when the substrate/cluster ratios are low (experiments G, H, in the presence of **4**). This suggests that a common (cluster) catalytic species is also formed in this case but the *cis/trans*-stilbene ratios observed in the hydrogenation solutions are not in accord with this hypothesis.

Two different trends are observed for the phosphido-bridged and the phosphine-substituted clusters (Table 4 and Table 5, below); the former give *cis/trans*-ratios varying from 2.10 and 1.05 (initial values), and the latter ratios between 0.7 and 0.2. This reflects the tendency of the phosphido-bridged clusters to give rise to formation of larger amounts of *cis*-stilbene in the initial reaction steps

Table 4

Hydrogenation of diphenylacetylene in the presence of clusters **1**, **2**, **4**, **6**, **7**

Experiment [a]	Cluster	Reaction time (min)	Turnover	Conversion (%)	Selectivity (%) towards		*cis*/*trans* ratio
					cis-stilbene	*trans*-stilbene	
(D)	$HRu_3(CO)_{10}(PPh_2)$	15 *[b]	54.0	64.4	56.2	43.8	1.28
		30 *	59.7	71.1	48.9	51.1	0.96
		45 *	62.2	74.1	40.6	59.4	0.68
		60 *	64.5	76.9	31.6	68.4	0.46
		75 *	66.5	79.2	27.9	72.1	0.39
		90 *	67.2	80.1	23.0	77.0	0.30
(E)	$HRu_3(CO)_9(PPh_2)$	15 *	47.2	46.9	67.2	31.5 [c]	2.13
		30 *	59.1	58.8	55.6	44.0 [c]	1.26
		45 *	61.4	61.1	54.0	45.8	1.18
		60 *	66.2	65.8	54.4	45.4	1.20
		75 *	69.6	69.2	55.3	44.5	1.24
		90 *	75.3	74.9	57.7	42.3	1.36
(F)	$HRu_3(CO)_9(PPh_2)$ [d]	3 *	40.0	42.2	59.2	40.5	1.46
		6 *	46.4	48.9	58.3	41.5	1.40
		9 *	50.2	52.9	56.5	43.5	1.30
		12 *	51.5	54.3	55.8	44.0	1.27
		15 *	56.2	59.2	53.9	45.9	1.17
		18 *	62.0	63.2	51.4	48.6	1.06
(G)	$HRu_3(CO)_7(PPh_2)_3$	10	11.5	24.6	51.2	48.8	1.05
		30 *	31.0	65.7	38.5	61.5	0.63
		45 *	46.0	98.5	28.2	71.8	0.39
(H)	$HRu_3(CO)_7(PPh_2)_3$	15 *	51.0	33.5	55.2	44.8	1.23
		30 *	72.9	47.9	50.7	49.3	1.03
		45 *	75.5	49.6	51.2	48.8	1.05
		60 *	90.1	59.2	49.3	50.7	0.97
		75 *	91.0	59.8	49.7	50.3	0.99
		90 *	95.6	62.8	50.3	49.7	1.01
(I)	$HRu_3(CO)_7(PPh_2)_3$ [e]	60 *	65.0	60.1	54.9	45.1	1.22
		60 *	54.3	50.2	51.8	48.2	1.07
		60 *	48.6	45.0	50.4	49.6	1.02
		60	21.3	19.7	56.3	43.7	1.29
(K)	$Ru_3(CO)_{10}(PPh_2H)_2$	15 *	59.0	63.4	40.7	59.3	0.69
		30 *	63.5	68.3	34.7	55.3	0.53
		45 *	66.7	71.7	26.9	73.1	0.37
		60 *	68.4	73.5	21.9	78.1	0.28
		75 *	69.5	74.7	20.6	79.4	0.26
		90 *	69.7	74.9	19.8	90.2	0.25
(L)	$Ru_3(CO)_9(PPh_2H)_3$	15	39.7	28.8	35.8	64.2	0.56
		30 *	80.3	58.2	33.3	66.7	0.50
		45 *	81.4	59.0	32.2	67.8	0.47
		60 *	83.0	60.2	29.1	70.9	0.41
		75 *	90.4	65.5	26.4	73.6	0.36
		90 *	100.1	72.6	22.0	78.0	0.28
(Z) [f]	Complex **11**	3		67.3	45.0	55.0	0.82
		6		66.5	44.1	55.9	0.79
		9		64.9	45.3	56.5	0.77
		12		65.7	44.7	55.3	0.81
		15		66.6	44.7	55.3	0.81
		18		67.4	45.8	54.2	0.85

[a] See Table 1. [b] The experiments where *trans*-stilbene was found as a solid in the vials are indicated with the asterisk. [c] In some instances the sum of the values is lower than 100; the deficit is attributable to diphenyl-ethane. [d] Short reaction time. [e] Decreasing H_2 pressure: in the order 1 atm, 0.75, 0.50, 0.25 atm. [f] Experiment not reported in Table 1.

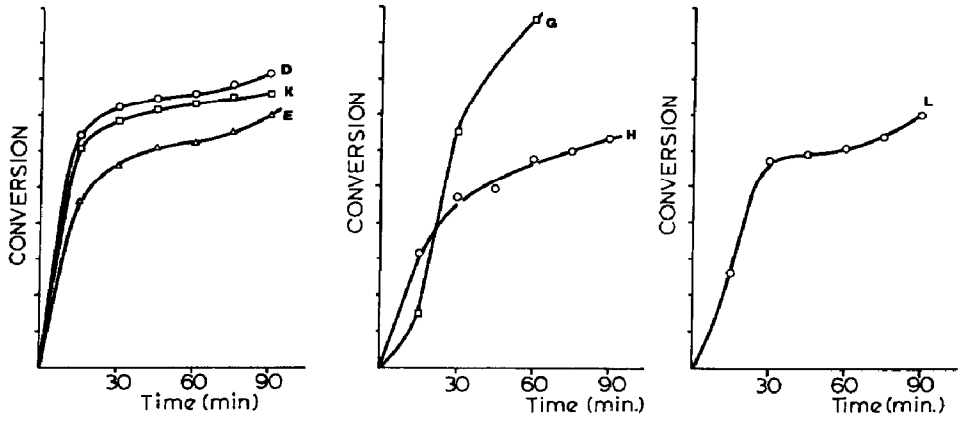

Fig. 1. Conversions observed in different hydrogenation experiments of diphenylacetylene (for the letters indicating the experiments, see Tables 2 and 4).

and this undergoes isomerization to *trans*-stilbene upon prolonged reaction. In contrast, clusters **6**, **7** give higher yields of *trans*-stilbene even in the initial reaction steps; this behaviour may be associated with the existence of different reactions paths (involving different intermediates) for the two kinds of derivatives, or with the observed different isomerizing abilities of the clusters, as shown in Table 5.

Table 5 shows that there is a relationship between the *cis*/*trans*-stilbene ratios observed in the hydrogenation experiments and the conversions observed in the isomerization runs (see Table 6); experiments E, F, G, H, I, in which phosphido clusters were involved, also showed that under comparable conditions the *cis*/*trans*-stilbene ratios depend on the amount of substrate and on the pressure of hydrogen. High concentrations of the substrate and low pressures of hydrogen favour the formation of the *cis*-isomer. This suggests cluster decomposition, but the small extent of decomposition observed for several clusters in the hydrogenations and isomerizations (Table 2) favours the view that there is "cluster catalysis", at least in the initial reaction steps. Moreover, complex **11** can be regarded as a cluster

Table 5

Relationship between the *cis*/*trans*-stilbene ratios observed in the hydrogenation experiments and the isomerizing ability of the clusters

Cluster	Hydrogenations			Isomerizations		
	Experiment [a]	Substrate/cluster ratio	*cis*/*trans* [b] ratio	Experiment [a]	Substrate/cluster ratio	Conversions [c] (%)
$HRu_3(CO)_{10}(PPh_2)$	D	84	1.28–0.30	M	151	10–32
$HRu_3(CO)_9(PPh_2)$	E	100	2.13–1.36	N	151	14–29
$HRu_3(CO)_9(PPh_2)$	F	95	1.46–1.06			
$HRu_3(CO)_7(PPh_2)_3$	G	47	1.05–0.39	O	215	6–17
$HRu_3(CO)_7(PPh_2)_3$	H	152	1.23–1.01			
$Ru_3(CO)_{10}(PPh_2H)_2$	K	93	0.69–0.25	P	214	21–46
$Ru_3(CO)_9(PPh_2H)_3$	L	138	0.56–0.28	Q	214	62–90

[a] See Table 1. [b] Initial and final ratio. [c] Minimum and maximum value.

Table 6

Isomerization of *cis*-stilbene in the presence of clusters **1, 2, 4, 6, 7**

Experiment [a]	Cluster	Reaction time (min)	Turnover	Conversion (%)	Selectivity towards *trans*-stilbene (%)
(M)	$HRu_3(CO)_{10}(PPh_2)$	5	15.9	10.1	100
		15	51.0	32.4	100
(N)	$HRu_3(CO)_9(PPh_2)$	5	22.0	14.5	100
		15	43.7	28.8	100
(O)	$HRu_3(CO)_7(PPh_2)_3$	5	13.4	6.2	100
		15	36.7	17.0	100
(P)	$Ru_3(CO)_{10}(PPh_2H)_2$	15 *[b]	44.5	20.7	100
		30 *	74.5	34.6	100
		45 *	96.8	45.0	100
		60 *	98.8	45.9 [c]	88.2 [c]
(Q)	$Ru_3(CO)_9(PPh_2H)_3$	5 *[b]	155.7	62.1	100
		15 *	168.7	67.3	100
		30 *	190.5	75.9	100
		60 *	224.8	89.7	100

[a] See Table 1. [b] The experiments in which a solid residue was observed are marked with an asterisk. [c] Some diphenylethane was observed (selectivity 11.8%).

intermediate; even in short reaction times it gives a *cis*/*trans*-stilbene ratio intermediate between those observed for the phosphido-bridged and the phosphine-substituted clusters (Table 4).

Isomerization of cis-stilbene. The isomerization of *cis*-stilbene in the presence of clusters **1, 2, 4, 6, 7** and in the absence of hydrogen has also been studied; the results are in Table 6.

The phosphido-bridged clusters give relatively low conversions when compared with **6** and **7**, which also give large amounts of solid *trans*-stilbene. Apparently there is increased conversion when fewer phosphido-bridges are present in the clusters, whereas for the phosphine-substituted complexes an increase in the number of ligands raises the activity. This behaviour also indicates that the isomerization and hydrogenations could involve different intermediates.

Some comments on the possible reaction intermediates. In the previously reported hydrogenation of t-butylacetylene [7] we were able to isolate two presumed reaction intermediates, complexes **8** and **9**, sometimes in considerable yields. The results discussed above indicate that C_2Ph_2, an internal and more sterically demanding alkyne, gives different intermediates when it reacts with phosphido-bridged clusters. It has in fact been shown that the reactions of this alkyne with complexes **1** [15], **2** [11] give the open complex **10**, and that those of **4** give complex **11** [16]. It is thus probable that similar complexes are among the reaction intermediates. It has been shown that complex **2** gives high yields of products even after a few minutes (experiment F), when **10** is probably present, and small amounts of **11** have been found in the reaction solutions formed from **4**.

The proposed structures of clusters **8, 9**, characterized spectroscopically, and these of clusters **10, 11**, determined by X-ray diffractometry [11,16] are shown in Fig. 2, below.

The presence of similar intermediates readily accounts for the observed formation of *cis*-stilbene in the initial steps of the reactions.

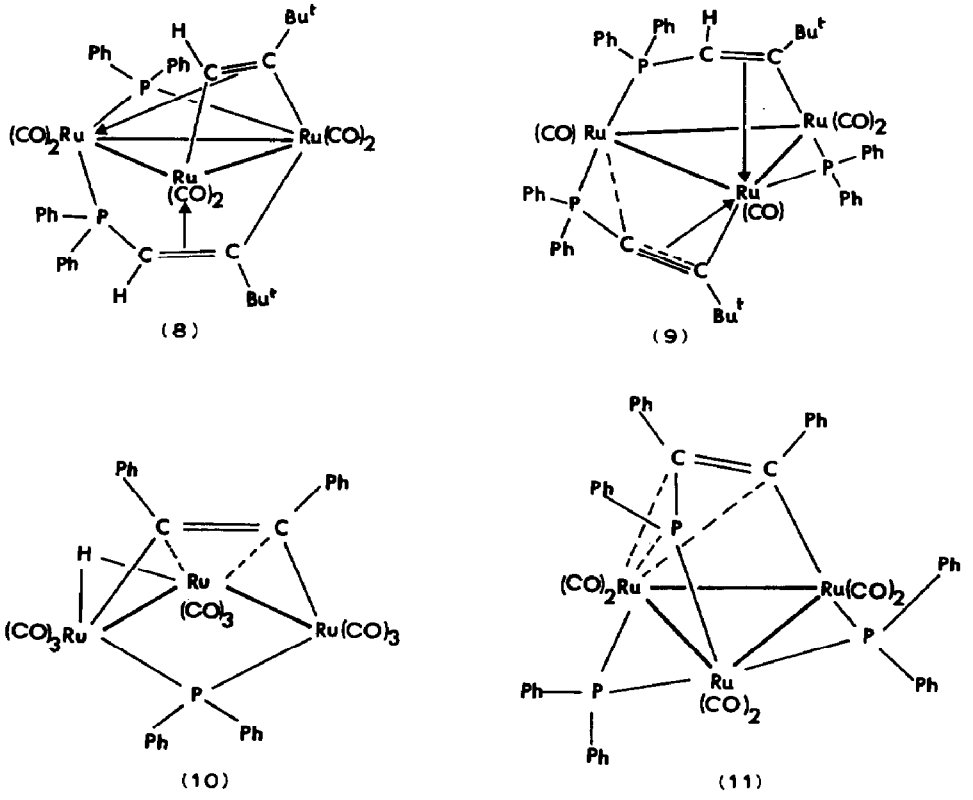

Fig. 2. Proposed structure for complexes **8**, **9** (see ref. 7) and structures of complexes **10**, **11**.

In the case of the phosphine-substituted clusters we could not identify the reaction intermediates unequivocally. After reaction of **7** with C_2Ph_2 we isolated a purple solid, showing a complex ^{31}P NMR spectrum [17*] (complex **12**), which gave crystals unsuitable for X-ray analysis. Several suggestions can be made to account for the behaviour of these complexes; the coordination of the substrate to a single metal centre is improbable, especially for complex **7**. A multi-centre coordination could occur (and would be favoured by electronic effects due to the phosphines) on the metal centres. Recent studies have shown that the phosphines are always in equatorial positions and do not exert major effects on the cluster, except for some tendency to force some CO's from terminal to semi-bridging positions [18]. The well documented stability of these phosphine-substituted derivatives rules out the possibility of "fragment catalysis"; we have observed that the clusters **6**, **7** show little tendency to undergo decomposition, even after 90 min (Table 2). If the suggestion of a multi-site coordination of the alkyne is correct, it should be noted that in $Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}\perp\text{-}C_2Et_2)$ the ethyl groups are slightly rotated in *trans* position to one another [19].

Another attractive possibility relates the recently described [20] insertion of the alkyne into the P–H bond of the coordinated PPh_2H ligands. This would account for both the catalytic activity of the complexes in hydrogenation and their efficiency in *cis-trans* isomerization. Complexes with a $RuPh_2PC(Ph)=C(H)(Ph)$ ligand could be formed either from clusters **6** and **7** (with statistically increased probability on

Table 7

Comparison of the behaviour of HC_2Bu^t, C_2Et_2 and C_2Ph_2 in hydrogenations in the presence of cluster $HRu_3(CO)_7(PPh_2)_3$

Alkyne [a]	Reaction time (min)	Turnover	Conversion (%)	Selectivity (%) towards			
				alkane	1-alkene	*cis*-alkene [b]	*trans*-alkene [b]
HC_2Bu^t	15	65.0 [c]	18.8	3.20	96.8	–	–
(344)	45	91.0	26.4	2.6	97.4	–	–
	60	99.0	28.7	2.8	97.2	–	–
	90	111.0	32.2	2.8	97.2	–	–
C_2Et_2	15	0.3	0.1	trace	–	–	–
(342)	45	3.4	1.0	10.0	40.0	–	50.0
	60	4.1	1.2	8.3	33.4	–	58.3
	90	6.5	1.9	15.8	26.3	–	57.9
C_2Ph_2	15	51.0	33.5	–	–	44.8	55.2
(152)	45	75.5	49.6	–	–	51.2	48.8
	60	90.1	59.2	–	–	49.3	50.7
	90	95.6	62.8	–	–	50.3	49.7

[a] The figures in parentheses refer to the substrate/cluster ratio. [b] Internal alkenes. [c] From ref. 7.

going from **6** to **7**) and from the phosphido-substituted complexes for **1–4** via insertion of alkyne into M–P bonds and partial hydrogenation; the latter process would require longer reaction times.

This process would account for all the observed results, namely: (i) the high *cis*/*trans*-stilbene ratio observed initially with the phosphido-bridged clusters: (ii) the tendency for isomerization on prolonged reaction, so that the final results are comparable for all the clusters observed: (iii) the great tendency of the phosphine-substituted derivatives to induce *cis-trans* isomerization.

Some comments on the behaviour of different alkynes in the presence of cluster **4**. The degrees of conversion of the substrate and the observed selectivities towards ethylenes vary considerably for HC_2Bu^t, C_2Et_2 and C_2Ph_2, as shown in Table 7.

The observed order of activity is the following: $C_2Et_2 \ll HC_2Bu^t < C_2Ph_2$. This probably reflects the influence of the alkyne substituents on the coordination of the alkynes to the metals or in their insertion into M–P or P–H bonds; as discussed above [8*,9*,10*], the alkynes react differently with $Ru_3(CO)_{12}$. Intermediates with different structures have been found or suggested for HC_2Bu^t and C_2Ph_2; unfortunately we could not isolate complexes with C_2Et_2 from the reactions of cluster **4**. The insertion reactions of alkynes into M–P bonds have been studied in detail only for diphenylacetylene [21].

Concluding remarks

We have found that C_2Ph_2 is readily hydrogenated to *cis*- and *trans*-stilbene in the presence of all the clusters with comparable efficiencies. Some clusters, in particular those with PPh_2H, are also active in the isomerization of *cis*- to *trans*-stilbene. In many experiments, solid *trans*-stilbene was found in considerable amounts in the products.

The reactions described here and in earlier papers confirm that phosphido-bridged and phosphine-substituted clusters are active hydrogenation catalysts; there is

evidence for "cluster catalysis" in all the reactions studied, at least during short reaction times. The isomerizing ability of the phosphine-substituted derivatives is noteworthy.

The results depend on various factors, including: (i) the nature of the alkyne (ii) the type of reaction intermediates formed, and (iii) the molar ratios of the substrate, hydrogen, and cluster, which can influence the competition between hydrogenation and isomerization.

Acknowledgements

Financial support to this work was provided by CNR (Rome). We thank Drs. Giovanni Predieri and Lorenza Operti for the recording the mass and NMR spectra and discussing the results. Johnson–Matthey is thanked for a loan of $RuCl_3$ (to E.S.).

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(acetone) were eluted together or between the hydrogenation products. The gain in precision due to the solubilization of *trans*-stilbene would have been lost, because of the imprecision of the gas-chromatographic data.

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