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Phosphorus-bridged metal clusters in homogeneous catalysis

V *. Selective hydrogenation of diphenylacetylene and isomerization of *cis*-stilbene in the presence of μ_3-phosphinidene-bridged iron and ruthenium clusters **

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Abstract

The behaviour of the iron clusters $Fe_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}PR)$ (R = ^iPr, $PNEt_2$), $(\mu\text{-}H)Fe_3(CO)_9(\mu_3\text{-}P\text{-}p\text{-}C_6H_4OMe)$, $Fe_3(CO)_9(\mu_3\text{-}P^tBu)_2$ and that of the 62 electron $Ru_4(CO)_{13}(\mu_3\text{-}PPh)$ complex in the homogeneous hydrogenation of diphenylacetylene and isomerization of *cis*-stilbene have been examined. The iron derivatives show only a moderate activity in hydrogenation and isomerization. The ruthenium cluster shows considerable activity in both processes, but the outcome depends markedly on the reaction time and temperature. The variations are explained in terms of the reactivity of the cluster frame.

Introduction

Investigation of the homogeneously catalyzed hydrogenation of alkynes, alkenes and dienes in the presence of homo- and hetero-metallic clusters [1] led us to discover that phosphine-substituted derivatives are generally more active than the parent compounds [2]. When the clusters $Ru_3(CO)_{12-n}(PPh_2H)_n$ ($n = 1\text{–}3$) were used, hydrido-phosphido-bridged derivatives were found to be formed during the catalytic processes [2b] and these derivatives were themselves shown to be catalytically active. Recently, alkyne hydrogenation catalysis via an unsaturated phosphido-bridged hydride complex of rhenium was observed [3].

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* For Parts I–IV see refs. 2, 4, 8.

** Dedicated to the memory of Professor Mario Valle (8.12.1931–21.11.1989), a friend and colleague.

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We decided to study in detail the activity of phosphido-bridged clusters in the hydrogenation and isomerization of alkynes [3,4]; very few studies have been made on the homogeneous catalytic behaviour of this type of complex, and they dealt with hydroformylation [5] or hydrogenation [6] of ethylenes or with electron-transfer catalysis [7].

We found that several structurally and chemically related triruthenium hydridophosphido derivatives show considerable activity in hydrogenation and isomerization, and all of them show comparable activities, presumably because a common catalytically active cluster species is formed from the various starting complexes in the early stages of the reaction [4].

It is noteworthy that in all our catalytic studies involving acetylenes and phosphido-bridged clusters we could find trimetallic derivatives showing that alkynes or acetylides had inserted into metal-phosphorus bonds; in some cases we obtained evidence that these derivatives were intermediates in the hydrogenation processes [4,8].

Close synthetic and structural relationships have been observed between phosphido- and phosphinidene-bridged clusters [9]; the latter usually readily undergo insertion of alkynes into metal–phosphorus bonds, whereas only a few phosphido-bridged derivatives undergo this reaction, which sometimes follows a complex course and may lead to products formally derived from phosphinidene precursors. For example, the reaction of $(\mu\text{-H})Ru_3(CO)_7(\mu\text{-PPh}_2)_3$ with C_2Ph_2 gives $Ru_3(CO)_6(\mu\text{-PPh}_2)_2[PhP \cdot CPh \cdot CPh]$ through alkyne insertion and reductive elimination of benzene [10].

We have now extended our studies to the activity of some μ_3-phosphinidene-bridged iron and ruthenium clusters in the homogeneous hydrogenation of diphenylacetylene and the isomerization of *cis*-stilbene. The activities of the complexes

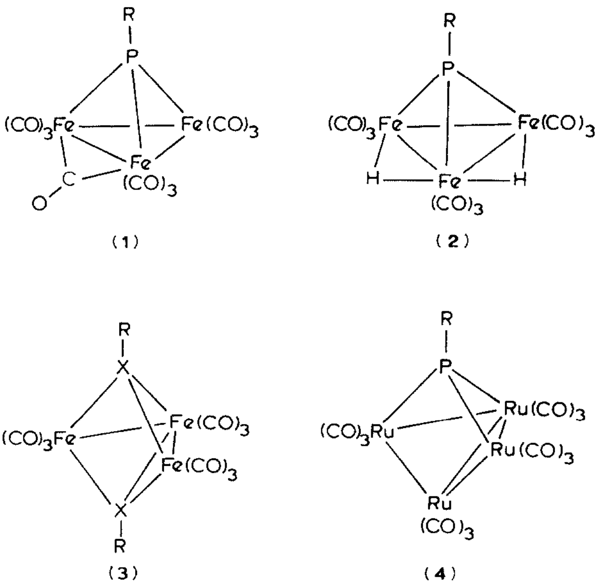

Fig. 1. Structures of complexes **1**–**4**.

$Fe_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}P^iPr)$ (complex **1**), $Fe_3(CO)_9(\mu\text{-}CO)[\mu_3\text{-}P(NEt_2)]$ (complex **1a**) $(\mu\text{-}H)_2Fe_3(CO)_9[\mu_3\text{-}P(p\text{-}C_6H_4OMe)]$ (complex **2**), $Fe_3(CO)_9(\mu_3\text{-}P^tBu)_2$ (complex **3**), [11] and $Ru_4(CO)_{13}(\mu_3\text{-}PPh)$ (complex **4**), [12] have been examined. Some results for the nitrene derivative $Fe_3(CO)_9(\mu_3\text{-}NEt)_2$ (**3a**) [13] relevant to the discussion are also given. The structures of the complexes are shown schematically in Fig. 1.

Complex **1** contains a bridging carbonyl, **2** has two bridging hydrides, and **3** has two μ_3-phosphinidene (or nitrene, **3a**) ligands capping an open frame. Complex **4** has a tetraruthenium butterfly arrangement. A common feature of these derivatives is the presence of μ_3-phosphinidene bridges. Another interesting common property is their ready reaction with alkynes involving insertion of the acetylene molecules into metal–phosphorus bonds [14,15]; in successive steps or under different reaction conditions (e.g. thermal or photochemical), *nido*- or *closo*-pentagonal bipyramidal structures are formed. The role of these reactions in determining the outcome of catalytic reactions is discussed.

We have found that the iron derivatives are only moderately active in either the hydrogenation of diphenylacetylene or the isomerization of *cis*-stilbene; the ruthenium derivative is considerably more active in both processes, but the outcome depends markedly on the reaction time and temperature. The variations in the products are probably related to the nature of the cluster metal and to the overall electron count for the heteronuclear cluster frame. The formation (and rupture) of complexes with inserted alkynes may account for the behaviour of the clusters.

Experimental

General experimental details. Materials and analysis of the products

Complexes **1**–**4** were obtained by published methods [11,12]. Diphenylacetylene and *cis*-stilbene were commercial products (Farchan, Fluka), and were used as received, after confirmation of their purity by GLC.

The organometallic products formed in the catalytic reactions were identified by IR spectroscopy (Perkin Elmer 580 B) on the reaction solutions; in some instances, the solutions were separated by preparative TLC. The organic products obtained in the catalytic reactions were analyzed by gas chromatography, as discussed below.

Hydrogenation and isomerization experiments. Gas chromatographic analysis of the reaction solutions

Unless otherwise specified the hydrogenations were performed in sealed glass vials (25 ml volume) each containing 2 ml of a n-octane solution of the cluster and the alkyne; the vials were then filled with 0.9 atm of hydrogen, sealed by standard vacuum techniques, and kept in a thermostatted oven for the chosen time. The isomerization of *cis*-stilbene was also performed in sealed vials but in the absence of hydrogen.

Details of the concentrations of clusters and substrates are given in Table 1.

In the hydrogenation experiments an excess of diphenylacetylene was generally used and its concentration was kept constant as far as possible; complete solubility was always observed and clear solutions were obtained. However, when the vials were cooled after some hydrogenation experiments, in the presence of **4**, whitish

Table 1

Cluster and substrate concentration and substrate/cluster molar ratios in hydrogenation and isomerization experiments

Experiments [a]	Cluster	Cluster (mol/l)	Substrate (mol/l)	Substrate/cluster molar ratio
Hydrogenation of diphenyl-acetylene				
A	$Fe_3(CO)_{10}(P^iPr)$ (**1**) [b]	1.05×10^{-5}	5.69×10^{-4}	54.2
B	$Fe_3(CO)_{10}[P(NEt_2)]$ (**1a**)	1.04×10^{-5}	6.98×10^{-4}	67.1
C	$H_2Fe_3(CO)_9(P$-*p*-tolyl) (**2**) [a]	9.24×10^{-6}	5.61×10^{-4}	60.7
D	$H_2Fe_3(CO)_9(P$-*p*-tolyl) [b]	1.01×10^{-5}	5.65×10^{-4}	55.9
E	$Fe_3(CO)_9(P^tBu)_2$ (**3**)	9.78×10^{-6}	5.61×10^{-4}	57.4
F	$Fe_3(CO)_9(NEt)_2$ (**3a**)	1.19×10^{-5}	5.69×10^{-4}	47.8
G	$Ru_4(CO)_{13}(PPh)$ (**4**) [d]	2.28×10^{-6}	5.65×10^{-4}	24.8
H	$Ru_4(CO)_{13}(PPh)$	7.42×10^{-6}	5.61×10^{-4}	75.6
K	$Ru_4(CO)_{13}(PPh)$	7.22×10^{-6}	5.85×10^{-4}	81.0
J	$Ru_4(CO)_{13}(PPh)$ [e]	2.28×10^{-6}	5.64×10^{-4}	247.0
Isomerization of cis*-stilbene*				
I	$Fe_3(CO)_{10}(P^iPr)$ (**1**)	1.00×10^{-5}	1.12×10^{-3}	112.0
L	$Fe_3(CO)_{10}(P^iPr)$	1.05×10^{-5}	1.12×10^{-3}	107.0
M	$H_2Fe_3(CO)_9(P$-*p*-tolyl) (**2**)	1.12×10^{-5}	1.12×10^{-3}	100.0
N	$Ru_4(CO)_{13}(PPh)$ (**4**)	7.42×10^{-6}	1.12×10^{-3}	151.0
O	$Ru_4(CO)_{13}(PPh)$	2.28×10^{-6}	1.12×10^{-3}	491.0

[a] The letters indicating the experiments are the same in all tables and text. [b] At 120 °C. [c] At 80 °C. [d] at 100 °C. [e] At 120 °C under reduced H_2 pressure.

crystals were observed, and were identified as *trans*-stilbene in the light of previous experience [8] and by comparison with standard samples. As previously noted [8], we made no corrections to the data in the Tables 2–4 to allow for the presence of solid *trans*-stilbene.

The soluble organic products in the hydrogenation and isomerization solutions were analyzed 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 N_2 flow, 60 °C for 6 min then 10 °C/min up to 240 °C.

Identification of the organometallic products in the reaction solutions

The hydrogenation and isomerization solutions were also examined by IR or by TLC, as outlined above, to reveal decomposition of the catalysts and to identify organometallic intermediates or by-products.

Results and discussion

Diphenylacetylene was chosen as a substrate since it allows the possibility of evaluating the selectivity towards *cis*- or *trans*-ethylenic products [8]; the reactions of this alkyne with clusters **1**–**4** have been extensively studied [14,15].

Hydrogenation of diphenylacetylene

The results obtained for the iron complexes are listed in Table 2.

With complexes **1**–**3** low turnover values (between 4 and 13) are observed; this is probably due, at least in part, to the low hydrogenating efficiency of iron compared

Table 2

Hydrogenation of diphenylacetylene in the presence of clusters **1**–**3**

Cluster and exp.	Temp. (° C)	Time (min)	Turnover	Conversion	Selectivity to		*cis*/*trans* ratio
					cis-stilbene	*trans*-stilbene	
1 (A)	120	15	6.1	11.2	27.7	72.3	0.38
		30	7.8	14.4	38.2	61.8	0.62
		45	8.7	16.6	35.4	64.6	0.55
		60	9.5	17.5	34.9	65.1	0.54
		75	9.6	17.7	33.9	66.1	0.51
		90	10.5	19.4	21.1	78.9	0.27
1a (B)	120	15	3.1	4.6	10.9	89.1	0.12
		30	6.2	9.2	28.3	71.7	0.39
		45	4.4	6.6	19.7	80.3	0.24
		90	3.8	5.7	17.5	82.5	0.21
2 (C)	80	15	6.5	10.7	20.6	79.4	0.25
		30	5.6	9.2	22.8	77.2	0.29
		45	6.4	10.5	25.7	74.3	0.35
		60	7.2	11.9	26.1	73.9	0.35
		75	5.8	9.5	20.0	80.0	0.25
		90	6.1	10.0	21.0	79.0	0.26
2 (D)	120	15	12.6	22.6	31.9	68.1	0.47
		30	9.6	17.2	26.2	73.8	0.35
		45	9.6	17.1	26.9	73.1	0.37
		60	9.7	17.4	27.6	72.4	0.38
		75	12.5	22.4	31.2	68.8	0.45
		90	9.9	17.7	28.2	71.8	0.39
3 (E)	120	15	5.2	9.1	44.8	55.2	0.81
		30	5.9	10.3	45.0	55.0	0.82
		45	4.3	7.5	28.9	71.1	0.41
		60	4.9	8.6	41.4	58.6	0.71
		75	5.8	10.1	17.1	82.9	0.21
		90	4.3	7.5	22.2	77.8	0.29
3a (F)	120	15	5.7	12.0	11.7	88.3	0.13
		45	2.9	6.0	16.7	83.3	0.20
		90	3.4	7.2	18.1	81.9	0.22

with that of ruthenium and other Group VIII metals [16*]. On the other hand, the formation of stable intermediate species (see below) could also account for the low catalytic efficiency. The features of the turnover numbers and the *cis*/*trans*-stilbene ratios are of some interest.

With complex **1** the turnover numbers slightly increase with time. Complex **1a**, containing the μ_3-PNEt$_2$ ligand, is less efficient, and gives a maximum turnover after 30 min, the values then decreasing. *trans*-Stilbene is the main product, but interestingly, for both complexes the amount of *cis*-stilbene formed reaches a maximum after 30 min and then decreases.

Complex **2**, containing a bridging hydride, is slightly more efficient even at 80 ° C, whereas complex **3**, containing two phosphinidene ligands, is less efficient; for both complexes two maximum values are generally found for the turnover

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* A reference number with an asteriks indicates a note in the list of references.

Table 3

Hydrogenation of diphenylacetylene in the presence of cluster **4**

Experiment	Temp. (°C)	Time (min)	Turnover	Conversion	Selectivity to		*cis/trans* ratio
					cis-stilbene	*trans*-stilbene	
(G)	100	15	135.6	54.7	55.9	44.1	1.27
		30	143.0	57.7	52.3	47.7	1.10
		45	161.8	65.3	44.6	55.4	0.80
		60	173.0	69.8	40.7	59.3	0.69
		75	179.9	72.6	29.5	70.5	0.42
		90	183.9	74.2	27.2	72.8	0.37
(H)	120	3	12.9	17.0	72.9	26.5	0.36
		6	13.8	18.3	73.8	26.2	0.35
		9	22.7	30.0	67.7	32.3	0.48
		12	35.0	46.3	67.2	32.8	0.49
(K)	120	15	130.2	80.3	27.5	72.5	0.38
		30	138.8	85.6	44.5	55.5	0.80
		45	137.6	84.9	50.1	49.9	1.00
		60	131.8	81.3	53.8	46.2	1.28
		75	128.0	79.0	58.0	42.0	1.38
		90	129.4	79.8	60.5	39.5	1.53
(J)	120	30	169.2	68.4	59.2	40.8	1.45
		30	129.1	52.2	70.1	29.9	2.35
		30	109.3	44.2	71.3	28.7	2.48
		30	53.9	21.8	71.6	28.4	2.52

values, one at 15–30 min and the second at 75–90 min; similar behaviour (or alternatively rise to a maximum and then a fall) is observed for the *cis/trans*-stilbene ratios. The yield of the *trans*- is in all cases greater than that of the *cis*-product. This could indicate that after a certain time a species that catalyses *cis–trans* isomerization is formed, or that various reaction intermediates are present in the solutions, as discussed below. The presence of organometallic species in solution is also discussed below.

The assumption that formation of stable intermediates lowers or modifies the catalytic ability is supported by the results with the nitrene complex **3a**, which is known to react with phenylacetylene under conditions similar to those adopted in our experiments, to give dinitrogen- and dialkyne-metallacyclic isomers [17]. In consequence **3a** shows a very poor catalytic activity, and furthermore this decreases with time.

The results obtained in the presence of complex **4** are shown in Table 3.

Complex **4** shows considerable catalytic activity (turnover numbers up to 180), varying with the temperature and the hydrogen pressure. The trends in the turnover values and the *cis/trans*-stilbene ratios are generally different from those observed for iron. In addition, very large changes in the *cis/trans* ratios are observed as the experimental conditions are changed, as can be seen from Fig. 2a.

At 100 °C increasing turnover values (larger than those at 120 °C) are observed; a maximum in the amount of *cis*-stilbene is observed after 15 min followed by a decrease; a gradual increase in the amount of *trans*-stilbene and a progressive decrease in the *cis/trans*-stilbene ratio are then found.

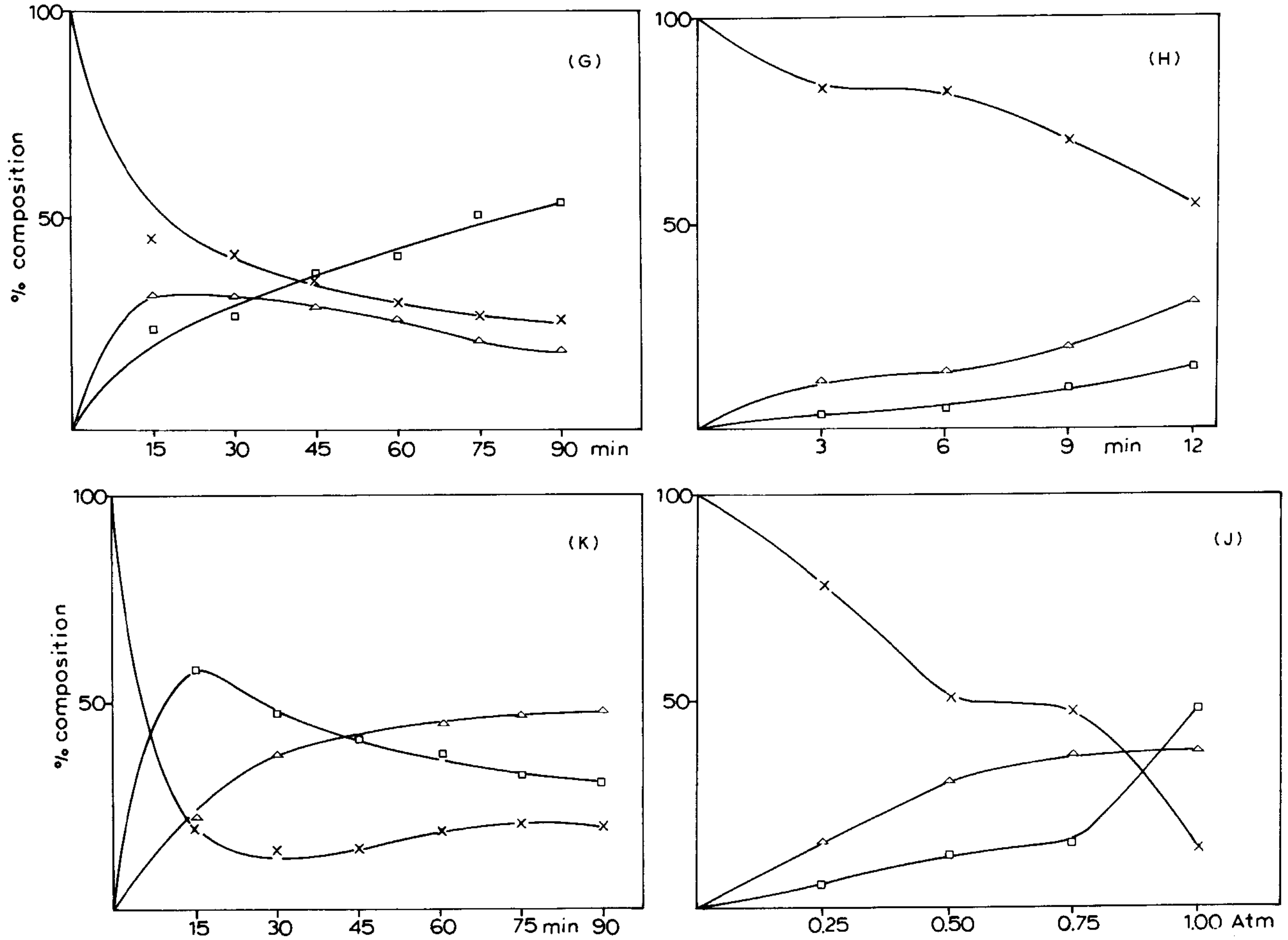

Fig. 2a. Hydrogenation of diphenylacetylene in the presence of complex **4** at 100° and 120°C and under reduced pressure of hydrogen. The letters refer to the experiments listed in Table 1. × = C_2Ph_2; □ = *trans*-stilbene; △ = *cis*-stilbene.

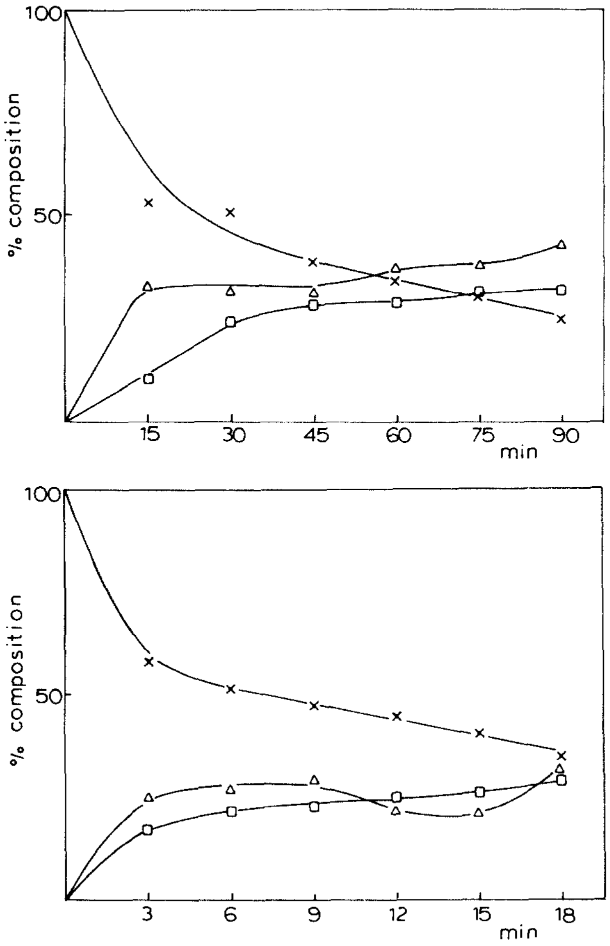

Fig. 2b. Hydrogenation of diphenylacetylene at 120 °C in the presence of $HRu_3(CO)_9(\mu\text{-}PPh_2)$; from Ref. 8.

At 120 °C over a short period the turnover increases and there is a progressive increase in the amount of both *cis*- and *trans*-stilbene. This indicates that under these conditions efficient hydrogenation and *cis*–*trans* isomerization occur. At this temperature after reaction times comparable with those at 100 °C there is remarkable inversion: thus there is a maximum in the amount of *trans*-stilbene after 15 min and this is followed by a progressive decrease, with parallel increase of *cis*-stilbene so that finally this becomes the major product. The observed behaviour clearly indicates the presence of two different catalytic or intermediate species after various reaction temperatures and times. It is noteworthy that, when pressure is lowered, larger amounts of *cis*-stilbene are formed.

Possible reasons for the observed behaviour could be the following:

(i) Reaction of complex **4** with hydrogen occurs to give $H_2Ru_4(CO)_{12}(\mu\text{-}PPh)$. This complex is formed in 100% yields under photochemical conditions under 1 atm of H_2 at room temperature and could be the catalytic species in the initial step;

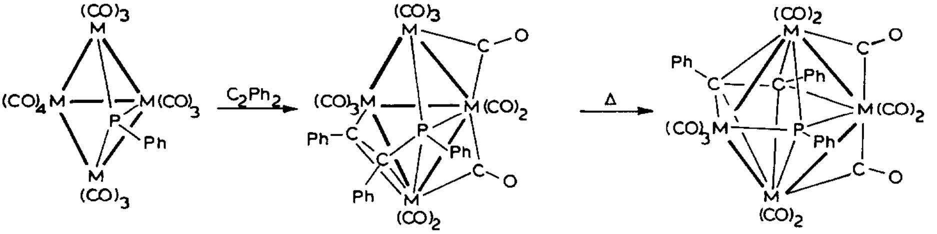

Fig. 3. Reactions of complex **4** with diphenylacetylene (see Ref. 15). Formation of *nido* and *closo* species.

however, the dihydride is unstable even at room temperature and upon decomposition gives the known unsaturated species (μ-H)$Ru_3(CO)_9$(μ-PPh_2) [18]. The latter derivative has been found active in hydrogenation of C_2Ph_2; the variation in the turnover trend and *cis*/*trans* ratios at 120 °C are in accord with those found for **4** at 100 °C and at 120 °C in an initial short period, as shown in the diagrams in Fig. 2b (based on data from ref. 8). These reactions could involve insertion of the substrates into M–H(hydride) bonds, and this would account for the inhibiting effect observed at higher hydrogen pressures.

(ii) However, the isomerization results (in the absence of hydrogen) and the behaviour at 120 °C over longer periods cannot be explained in terms of the above hypothesis. It should be kept in mind that derivatives of cluster **4** in which alkynes have inserted into Ru–P bonds are formed thermally [15] in a process which is certainly competitive with the proposed formation of the dihydride. The reactions of **4** to give C_2Ph_2 are shown in Fig. 3.

It could thus be assumed that at 100 °C the *nido* pentagonal bipyramidal species, which could release *cis*-stilbene and perhaps promote *cis*–*trans* isomerization (see discussion below) predominates, thus accounting for the increase in the turnovers and the maximum in the amount of *cis*-stilbene; over time isomerization to *trans*-stilbene occurs slowly.

The trends observed over longer reaction times at 120 °C could be due to two competing processes; for example the formation of the "short living" *nido* species that readily releases *cis*-stilbene in competition with the gradual insertion of the alkyne to form the *closo* species (Fig. 3), which will release stilbenes with greater difficulty. Isomerization to *trans*-stilbene and/or formation of $HRu_3(CO)_9$(μ-PPh_2) with modification of the catalytic activity could occur as competing processes.

(iii) A third and alternative hypothesis involves the fragmentation of the cluster under hydrogen to give mono-nuclear hydridic ruthenium phosphine derivatives; these species have been found to be active catalysts in transfer hydrogenation of ketones [19] and in the hydrogenation of alkynes [20]. In this case, however, fully hydrogenated products would be expected, and these were not observed; furthermore the catalytic activity should increase with time.

Support for the above suggestion of the role of complexes with alkynes inserted into metal–phosphorus bonds comes from the known reactivity of complexes **1–4**. In thermal reactions the iron clusters undergo insertion of diphenylacetylene into the Fe–P bonds and in the photochemical reaction the alkyne is inserted into the Fe–Fe bonds [14]. The complexes with the alkyne inserted into Fe–P bonds are apparently intermediates in the formation of more stable complexes with the alkyne inserted into Fe–Fe bonds; in the former a P–C=C bridge is formed in which the two phenyl groups are necessarily in a *cis*-disposition. The same reaction scheme, leading to a pentagonal bipyramidal structure like that of the final product, has been observed for the ruthenium complex **4** [15] (Fig. 3).

Infrared monitoring and TLC separation of some reaction mixtures showed that complex **1** and more especially **1a** gave *nido* products $Fe_3(CO)_{10}[P(R)CPh \cdot CPh]$ [14c]; formation of *nido* structures [14d] was also observed for complex **3**. However, complexes **2** and **3** also gave *closo* structures of the type $Fe_3(CO)_8(\mu\text{-PR})(CPhCPh)$ [14c,d]. Finally, complex **4**, at 120 °C after "long" reaction times gave mainly the *closo* complex shown in Fig. 3. Other unidentified complexes, presumably involving alkyne ligands, were also present in the solutions, as shown by the complex patterns of signals.

Thus, one possible explanation of the catalytic data discussed in this paper involves the competition between the formation of the *closo* pentagonal bipiramidal products from the *nido* structure and the release of the alkyne from the latter to give hydrogenated products, as well as the competition between these processes and those mentioned under (i).

Homogeneous catalytic cycles involving clusters and cluster-frame modifications are known; for example $Rh_4(CO)_{12}$ catalyses hydroformylation of cyclohexene under low pressure, presumably via a *nido–arachno* modification and formation of $H_2Rh_4(CO)_{12}$ [21]. Furthermore the phosphinidine complex $Fe_2Co_2(CO)_{11}(\mu_4\text{-PPh})_2$ catalyses 1-pentene hydroformylation by a process involving Co–Co bond-opening, and modification of the cluster frame from *closo* to *nido* [22].

Isomerization of cis-*stilbene*

The results obtained for complexes **1**–**4** are shown in Table 4.

For the iron derivatives low turnovers (albeit larger than those in the hydrogenations) are observed; complex **1** gives a maximum turnover after 15 min, followed by a steady decrease; however, the IR spectra of the reaction solution show that complex **1** is still present.

In contrast, for **2** there is a progressive increase; one explanation for this behaviour could be the presence of bridging hydrogens in **2**, allowing ready insertion of the substrate.

Complex **3** is almost inactive; this and the above results indicate that the presence of phosphinidene-bridges is not necessary for the isomerization, and that this reaction probably occurs without insertion into metal–phosphorus bonds; this accords with previous findings [5].

In the case of complex **4**, low and increasing turnover values are observed over short reaction times; over longer time very high turnover values (about 450) are reached, and then there is a progressive decrease.

As previously found [4,8], and as discussed above for the iron derivatives, hydrogenation and isomerization processes generally occur under different conditions or in the presence of different catalytic species. Probably this is true also for the reactions described here.

Since these experiments were performed in the absence of hydrogen, formation of hydrido-bridged catalytic species must be ruled out. It is noteworthy that among the iron derivatives complex **2** (characterized by a bridging hydride) is moderately active.

Table 4

Isomerization of *cis*-stilbene

Cluster and experiment	Temperature (°C)	Time (min)	Turnover	Conversion [a]
1 (L)	120	3	7.1	6.6
		6	3.4	3.2
		9	3.9	3.6
		12	3.2	3.0
1 (T)	120	15	22.7	20.4
		30	10.4	9.3
		45	6.6	5.1
		60	5.3	4.8
2 (M)	120	15	16.1	16.0
		30	15.3	15.2
		45	25.8	25.6
		60	25.8	25.7
4 (N)	120	3	8.6	5.7
		6	8.5	5.6
		9	9.1	6.0
		12	13.8	9.1
	120	15	451.2	91.4
		30	440.8	89.3
		45	422.5	85.6
		60	372.7	75.5

[a] Selectivity to *trans*-stilbene = 100% in all the experiments.

Another possibility, discussed previously [8], could be the formation of $PPhH_2$ phosphine-substituted derivatives from the phosphido- or phosphinidene bridged ones. Once again their formation would require the presence of hydrogen.

Nevertheless it is noteworthy that the high *trans*-stilbene concentrations found for the hydrogenation experiments of C_2Ph_2 in the presence of **4** at 120°C and after 15 min (see Fig. 2) can be related to the high isomerization activity observed; the decrease in the amount of *trans*-stilbene with time could be attributed partly to the observed isomerization and partly to deposition of solid *trans*-stilbene (see Experimental section).

To explain the isomerization results it is necessary to invoke the *nido–closo* transformations discussed above; examples in favour of our hypothesis have been recently reported. Thus $HC\equiv C\cdot COOMe$ inserts in a *cis* fashion into either the Co–Co bond of $(Cp)_2Co_2(\mu\text{-}PMe_2)_2$ or into a metal–phosphorus bond as discussed for complexes **1**–**4**. Upon protonation, the species with the alkyne inserted into the Co–Co bond gives a complex with a *trans*-vinylidene formally inserted into a Co–P bond; the same product could be obtained from the derivative with the alkyne inserted into the Co–P bond [23]. Insertion of alkynes into Ru–H bonds in mononuclear derivatives to give vinyls can occur in either a *cis*- or a *trans*-fashion depending on the alkyne substituents [24].

Concluding remarks

Some general remarks can be made about the behaviour of phosphine-substituted and phosphido- or phosphinidene-bridged clusters in hydrogenation and isomerization reactions described here and in previous papers.

The nature of the cluster metals is apparently important for the activity as well as for the selectivity; thus the iron clusters show low activity regardless of the presence of bridging hydrides or other features [16].

The electron count of the clusters is seemingly irrelevant; indeed good catalytic activity was observed for phosphine and phosphinidene-substituted 48 electron species, and comparable results were obtained for the 46 electron $HRu_3(CO)_9(PPh_2)$, whereas the 48 e^- iron derivatives studied here show low activity. By contrast the unsaturated 62 e^- complex **4** is much more active. However, interconversions occur readily for all the above ruthenium clusters, as discussed below.

The nature of the phosphorus ligands is important; the phosphines are thought to increase both the activity and the selectivity through electronic effects. In particular, the phosphine-substituted derivatives are much more active in isomerization than the phosphido-bridged complexes [8]. The presence of phosphido- or of phosphinidene-bridges should stabilize the cluster frames, and this has been observed; however, by keeping together the metal fragments, the bridges allow further rearrangements of the structures, so that change of one into another can occur readily. This leads to the formation of common catalytic or intermediate species, and prevents evaluation of the effect of the number and type of phosphorus bridges, as well as of the role of bridging hydrides. Moreover the substrates could compete for insertion into M–H or M–P bonds.

In general complexes with alkynes inserted into M–P bonds play an important role in the above reactions. For this reason further studies on the reactivity of the metal phosphorus bonds towards unsaturated organic substrates under mild conditions are much needed.

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