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Homogeneous hydrogenation of alkynes and of 1,4-cyclohexadiene in the presence of the clusters $Ru_3(CO)_7(\mu\text{-}PPh_2)_2(C_6H_4)$, $Ru_4(CO)_{11}(\mu_4\text{-}PPh)(C_6H_4)$, $Ru_3(CO)_7(\mu\text{-}PPh_2)_2(HC_2Ph)$ and $Ru_4(CO)_{11}(\mu_4\text{-}PPh)(C_2Ph_2)$

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Abstract

The title complexes, containing phosphido or phosphinidene bridges, catalyze the hydrogenation of alkynes and of 1,4-cyclohexadiene (1,4-CHD). The benzyne-substituted clusters $Ru_3(CO)_7(PPh_2)_2(C_6H_4)$ (**1**) and $Ru_4(CO)_{11}(PPh)(C_6H_4)$ (**2**) show the highest hydrogenation activity yet observed for substituted metal carbonyl clusters towards alkynes; the activity is related to the nature of the alkyne substrate, $C_2Et_2 < EtC_2Ph < C_2Ph_2$.

The alkyne complexes $Ru_3(CO)_7(PPh_2)_2(HC_2Ph)$ (**3**) and $Ru_4(CO)_{11}(PPh)(C_2Ph_2)$ (**4**), structurally closely related to **1** and **2**, have also been examined in comparable reactions; complex **3** shows very high activity, especially towards 1,4-CHD.

Organometallic intermediates could not be isolated but direct and indirect evidence supporting a reaction pathway based on cluster catalysis was obtained; this will require the formation of an active site, dihydrogen activation and insertion of the substrate into M–H bonds. Possible alternative mechanisms are also discussed.

Keywords: Metal carbonyl clusters; Phosphido, phosphinidene bridges; Alkyne, benzyne ligands; Homogeneous catalysis; Hydrogenation

1. Introduction

Homo- and hetero-metallic ruthenium carbonyl clusters catalyze the homogeneous hydrogenation of alkynes [1,2] and of linear and cyclic dienes [3]. We are interested in the structure/reactivity relationships relevant to the behaviour of these complexes. We found, for example, that some clusters with alkynes coordinated in parallel fashion with respect to a cluster edge behave as intermediates in hydrogenation reactions [1,2,4]. It was also established that phosphido- and phosphinidene-bridged ruthenium clusters display catalytic activity and reaction intermediates were characterized [5].

Here we report on the behaviour of the benzyne clusters $Ru_3(CO)_7(\mu\text{-}PPh_2)_2(C_6H_4)$ (**1**) and $Ru_4(CO)_{11}(\mu\text{-}PPh)(C_6H_4)$ (**2**) [6] as homogeneous catalysts for the hydrogenation of C_2Et_2, PhC_2Et, C_2Ph_2 and 1,4-CHD; these clusters are very good hydrogenation catalysts, and the turnover numbers (TON) observed are the highest reported for these types of compound. The recovery of unreacted parent clusters,

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[1] RC_2R'; R = R′ = Ph, Et; R = Ph, R′ = Et.

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the observed ease of hydrogenation of the alkynes ($C_2Et_2 < PhC_2Et < C_2Ph_2$), together with the observed effect of dihydrogen pressure and catalyst concentration, agree with the concept of 'cluster catalysis'.

We have also studied the behaviour of $Ru_3(CO)_7(\mu\text{-}PPh_2)_2(HC_2Ph)$ (**3**) [7] and $Ru_4(CO)_{11}(\mu_4\text{-}PPh)(C_2Ph_2)$ (**4**) [8], bearing an alkyne instead of a benzyne ligand. Cluster **3** is isostructural with complex **1**, and the structures of **4** and **2** are closely related. The structures of complexes **1**–**4** are given in Fig. 1.

2. Experimental

2.1. General experimental details and materials

Clusters **1**, **2** [6], **3** [7] and **4** [8] were obtained by established procedures. The alkynes and 1,4-CHD were commercial products and were used as received after GLC purity tests. High-purity benzene was tested by GLC and GC-MS. Gases (N_2, H_2) were dehydrated and solvents (*n*-octane, toluene, chloroform) were dried before use.

2.2. Catalytic reactions of complexes *1*–*4* and gas-chromatographic identification of the organic products

The reactions were performed, as previously described [1], in 25 ml sealed vials containing 2.0 ml *n*-octane solution of the catalyst and of the substrate under 1 atm pressure of H_2, if not otherwise specified. After warming at 120°C for the required reaction time, the solutions were analyzed with a Carlo Erba 4200 gas chromatograph operated under the following conditions: *n*-octane/Porasil C (100/120 mesh) column, N_2 flow 25 ml min^{-1}, 60°C (6 min) then 3°C min^{-1} up to 135°C for C_2Et_2 and 1,4-CHD; SE 30 5% on Chromosorb WAW (60/80 mesh) column, N_2 flow 46 ml min^{-1}, 60°C (6 min) then 10°C min^{-1} up to 240°C for EtC_2Ph and C_2Ph_2. Column dimensions 2 m × 0.6 mm (i.d.).

2.3. Identification of organic and organometallic products

The reaction solutions were examined by IR spectroscopy (Brucker Equinox 55, KBr cells) and subjected to TLC (Kieselgel PF Merck; eluants: mixtures of light petroleum and diethyl ether in variable v/v proportions according to the nature of the products). The products were analyzed also with a quadrupolar Finnigan Mat TSQ-700 mass spectrometer [9].

2.4. Reactions of cluster *1* with alkynes

Reaction mixtures changed from purple to orange-yellow; the IR spectra of the clear solutions showed the presence of about 80% of unreacted **1**, small amounts of the metallacyclic isomeric complexes $Ru_3(CO)_5(\mu\text{-}PPh_2)_2\{C_6H_4(RC_2R')\}$ (**5a**,**b**) [10] and trace amounts of 1,3-CHD. Complex **1** was reacted with C_2Ph_2 (substrate/cluster ratio = 1840.1) in a sealed 250 ml vial under 1 atm H_2 for 50 min (experiment A); a conversion of 31.7 and a TON of 584.0 were observed. About 90% of the cluster could be recovered and, among the organic products, about 1% of 1,3-CHD was observed. The products from the reactions of 1,4-CHD could not be identified. With benzene, a clear brown solution was obtained containing unreacted **1** and an unidentified product (IR bands at 2045 s, 2029 s, 1957 s, 1810 vs cm^{-1}).

2.5. Reactions of complex *2* with alkynes

No colour changes were observed and clear solutions were always obtained. IR spectra showed the presence of unreacted **2** and of very small amounts of the complexes $Ru_4(CO)_{10}(\mu_4\text{-}PPh)(C_6H_4)(RC_2R')$ (**6**) [10]. In the reaction of **2** with C_2Ph_2 (after 15 min) a whitish precipitate was observed whose ^{1}H-NMR and mass spectra were consistent with a formula $H_xC_2Ph_3$ ($x = 1$, 2; tentative attribution triphenyl-ethene or ethane) [11].

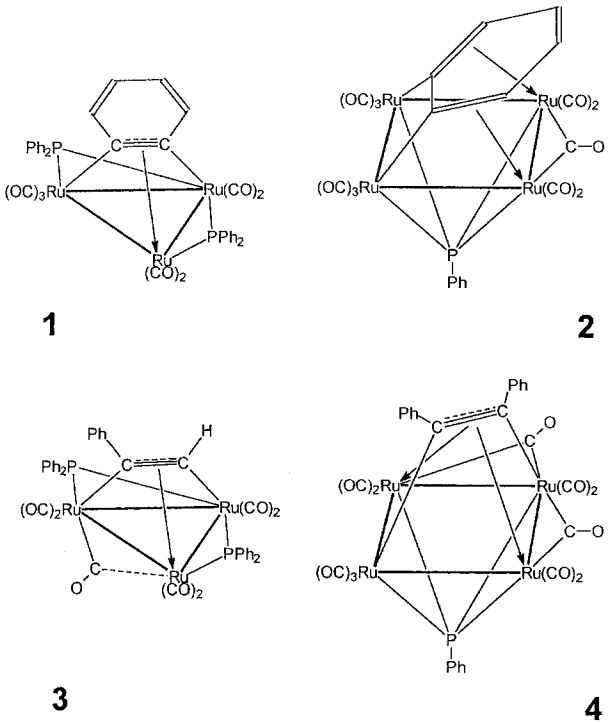

Fig. 1. Structures of complexes **1**–**4** as determined by X-ray diffraction (Refs. [6–8]).

Table 1
Hydrogenation of C_2Et_2, PhC_2Et, C_2Ph_2 in the presence of clusters **1**–**4**[a]

Cluster and experiment	Reaction time (min)	Conversion	TON	Selectivity to		
				$C_2H_4R_2$	*cis*-$C_2H_2R_2$	*trans*-$C_2H_2R_2$
Hex-3-yne(C_2Et_2)						
1 [C]	30	0.2	1.6	17.4	–	82.6
	45	2.1	15.4	2.8	6.5	90.7
	60	4.9	35.3	2.6	6.7	90.7
2 [D]	15	0.3	1.4	–	54.6	45.4
	30	0.3	1.5	–	50.0	50.0
	45	0.6	2.4	–	25.0	75.0
3 [E]	15	0.2	4.1	–	16.7	83.3
	30	0.5	9.4	21.8	3.6	74.5
	45	0.2	4.3	–	12.0	88.0
4 [F]	15	0.2	1.4	–	–	100.0
	30	0.3	2.1	–	–	100.0
	45	0.5	3.5	–	–	100.0
1-Phenyl-1-butyne (EtC_2Ph)						
1 [G]	15	6.1	27.3	–	4.4	95.6
	30	10.6	47.1	–	4.6	95.4
	45	11.7	51.9	–	4.4	95.6
2 [H]	15	0.2	0.8	–	–	100.0
	30	0.8	2.9	–	–	100.0
	45	1.3	4.5	–	–	100.0
3 [I]	15	0.2	2.6	–	42.1	57.9
	30	0.3	3.7	–	33.3	66.7
	45	1.5	20.8	–	4.6	95.4
4 [J]	15	0.2	3.9	–	–	100.0
	30	0.5	8.0	–	–	100.0
	45	1.9	32.1	–	–	100.0
Diphenylacetylene (C_2Ph_2)						
1 [K]	15	4.5	83.0	18.4	11.3	70.3
	35	9.2	169.5	4.1	51.1	44.7
	50	31.7	584.0	1.3	57.3	41.5
2 [L]	15	3.3	74.5	7.5	39.8	52.7
	35	7.2	161.4	3.8	59.9	36.3
	50	10.5	235.2	2.4	59.5	38.1
3 [M]	15	10.3	57.8	30.5	35.4	34.1
	30	16.2	90.6	4.3	49.7	46.0
	45	33.6	188.1	2.0	47.5	50.5
4 [N]	15	5.3	12.7	2.9	12.5	79.6
	30	7.2	17.2	6.4	34.0	59.6
	45	13.0	30.9	2.5	57.5	40.0

[a] Always $t = 120°C$, $H_2 = 1$ atm. Substrate/cluster (S/C): [C] = 715.4; [D] = 430.3; [E] = 1708.7; [F] = 755.4; [G] = 444.8; [H] = 344.7; [I] = 1368.9; [J] = 1696.7; [R] = 1840.1; [L] = 2244.5; [M] = 559.2; [N] = 238.2.

Complex **2** was reacted with C_2Ph_2 in a sealed 250 ml vial as previously described for **1** (experiment B); about 90% of the cluster was recovered, but no 1,3-CHD could be detected. With 1,4-CHD a clear orange solution was obtained, shown by IR to contain **2** and additional bands at 1926 m–w, 1893 m and 1872 m cm^{-1}. With benzene IR bands at 1957 vs and 1811 vs cm^{-1} were observed.

2.6. Reactions of complex *3* with alkynes

Solutions turned from deep red to pale yellow. No organometallic products could be detected.

2.7. Reactions of complex *4* with alkynes

Solutions turned from clear orange to pink or red suspensions containing mostly decomposition. TLC analysis of the solutions from the reactions with C_2Ph_2 showed the presence of some unreacted **4** and of alkynic oligomers (mass spectrometry). With 1,4-CHD no change in colour was observed and only unreacted **4** was recovered.

2.8. Hydrogenation reactions with clusters *5* and *6*

The diphenylacetylene clusters **5** and **6** were prepared

Table 2
Effect of CO, of dihydrogen pressure and of substrate/cluster ratios on the hydrogenation of diphenylacetylene[a]

Cluster and experiment	S/C	Conversion	TON	Selectivity to		
				$C_2Ph_2H_4$	*cis*-SB	*trans*-SB
1 [O]	197.2[b]	10.1	20.0	–	37.8	62.2
		4.6	9.1	–	40.4	59.6
		2.6	5.1	–	61.2	38.8
2 [P]	179.7[b]	7.1	12.7	–	27.4	72.6
		3.4	6.1	–	23.1	76.8
		1.8	3.3	–	70.8	29.2
1 [Q]	340.9[e,f]	7.3	24.8	52.8	29.8	17.3
		5.2	17.6	33.3	31.6	35.1
		8.7	29.7	36.0	20.7	43.3
3 [R]	344.8[e,f]	9.0	30.9	27.9	17.4	54.7
		5.2	18.1	24.8	18.7	56.5
		5.9	20.5	51.1	25.2	23.7
1 [S]	177.0[c]	5.6	10.0	22.2	25.2	52.6
	265.9	3.5	9.4	17.9	34.1	48.0
	529.2	1.9	10.0	26.6	23.4	50.0
1 [T]	132.6[d]	9.7	12.8	41.0	32.9	26.1
	66.2	7.8	5.1	38.4	24.7	36.9
	33.1	17.9	5.9	79.0	21.0	–
2 [U]	169.2[c]	6.2	10.6	47.6	30.4	21.9
	254.3	9.2	23.3	35.1	34.9	30.0
	501.0	14.7	73.7	30.2	34.6	35.1
2 [V]	254.3[d]	3.7	9.5	15.0	16.4	68.5
	125.6	5.9	7.4	28.6	28.1	43.3
	70.4	18.7	13.2	27.0	32.4	40.6

[a] Always $t = 120$°C and 30 min reaction time.
[b] Decreasing H_2 pressure: 1.0, 0.50, 0.25 atm.
[c] Decreasing amount of cluster, keeping constant alkyne concentration, $H_2 = 1$ atm.
[d] Decreasing amount of alkyne, keeping constant cluster concentration, $H_2 = 1$ atm.
[e] Using 1 atm of a H_2/CO mixture (0.5/0.5 atm).
[f] Increasing reaction times (15, 30, 45 min).

following established methods [10] and were reacted with C_2Ph_2 under H_2 as reported above for clusters **1**–**4**. After the reactions only unreacted clusters **5** or **6** could be recovered.

3. Results and discussion

3.1. Hydrogenation of C_2Ph_2, PhC_2Et and C_2Et_2

The results of these experiments are given in Table 1. Table 2 shows the effects of CO, of dihydrogen pressure and of the substrate/cluster ratio on the hydrogenation of C_2Ph_2.

Clusters **1** and **2** show modest hydrogenation activity towards C_2Et_2 (TON 35.3 and 2.4, respectively), medium activity towards PhC_2Et (TON 51.9 and 4.5) and high activity towards C_2Ph_2 (TON 584.0 and 235.2) (Table 1). The selectivity towards monoenes is higher for **2** than for **1**. Cluster **3** is less active than **1** and **2** but the trend observed for the three alkynes is the same. Finally, cluster **4** shows a modest activity (TON = 3.5, 4.5 and 30.9, respectively). The lower activity of **4** is predictable when considering its synthetic route and its role as by-product in the alkyne hydrogenation reactions with $Ru_4(CO)_{13}(\mu$-PPh) [8]. For all the clusters the selectivity towards *trans*-derivatives is higher (and increases with time) for C_2Et_2 and PhC_2Et; in contrast, C_2Ph_2 gives higher selectivity for the *cis*-isomer, which again increases with time.

When the dihydrogen pressure is decreased, the hydrogenation activity of clusters **1** and **2** drops sharply (Table 2). This indicates that the reactions are dependent on dihydrogen. One should bear in mind that, when $Ru_3(CO)_9(PPh_3)_3$ was used as a hydrogenation catalyst for cyclic olefins [12], the hydrido-carbonyls $H_4Ru_4(CO)_{12-x}(PPh_3)_x$ were formed in the reaction mix-

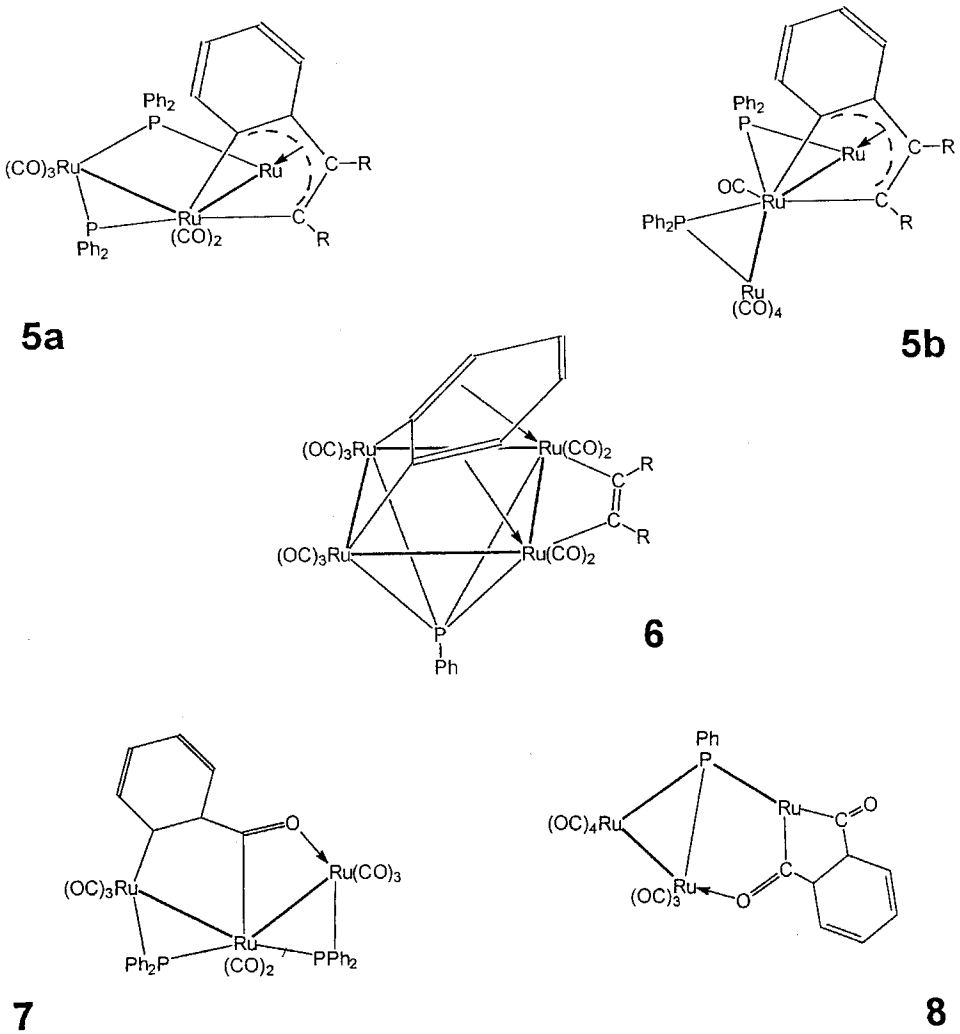

Fig. 2. Structures of complexes **5** (isomers), **6**, **7** and **8** as determined by X-ray diffraction (Refs. [10,14,19]).

tures; increasing the dihydrogen pressure had no effect on the yields of hydrogenated products, but led to the preferential formation of $H_4Ru_4(CO)_8(PPh_3)_4$. By rising the temperature complex **1** was obtained [13]; it was considered a catalytic hydrogenation intermediate. Finally, pyrolysis of $Ru_3(CO)_9(PPh_3)_3$ yielded the binuclear $Ru_2(CO)_5(PPh_3)(\mu\text{-}PPh_2)(\mu\text{-}O{=}CPh)$; this complex acted as a catalyst precursor.

The hydrogenation of C_2Ph_2 with clusters **1** and **3** using a mixture of H_2/CO (0.5/0.5 atm) was also attempted (experiments Q, R; Table 2); the presence of CO lowers the TON. Worthy of note is the high amount of fully hydrogenated products obtained in these reactions; it is also interesting to observe that the selectivities to fully and partially hydrogenated products shown by **1** and **3** follow different trends. This behaviour can be explained by considering that cluster **1** reacts with CO under mild conditions forming complex **7** with a CO inserted into a Ru-benzyne bond and that cluster **2** also reacts with CO, albeit under more drastic conditions, to give complex **8** (Fig. 2, below) [14]. The formation of these kind of complexes could hence modify the hydrogenation activity, as observed for **1**. The formation of these complexes under CO, and of complexes **5** and **6** with alkynes, shows once more the role of phosphido and phosphinidene bridges in keeping together metal fragments.

In order to evaluate the effect of the cluster and substrate concentration the following procedure was adopted: for each cluster two experiments were performed, one in which the cluster concentration was held constant and that of the substrate C_2Ph_2 was varied (experiments T, V), and one in which the cluster concentration was varied and that of the substrate held constant (experiments S, U). With cluster **1**, decreasing the cluster concentration, and therefore increasing the substrate/cluster ratio from 177 to 529, results in nearly constant TON values and formation of a considerable amount of fully hydrogenated products. However, when the cluster concentration was held constant (with the consequent decrease of the substrate/cluster ratio from 133 to 33), the TON decreased and the amount of

Table 3
Hydrogenation of diphenylacetylene on clusters **5** and **6**[a]

Cluster and experiment	Reaction time (min)	Conversion	TON	Selectivity to		
				$C_2H_4R_2$	*cis*-SB	*trans*-SB
5 [X]	15	13.8	1.1	36.7	28.3	35.0
	30	25.9	2.1	11.0	52.5	36.4
	45	47.4	3.8	6.8	51.2	42.0
6 [Y]	15	6.6	1.8	23.7	38.3	38.0
	30	7.9	2.2	36.9	32.5	30.6
	45	4.5	1.3	33.3	16.3	50.4

[a] Always $t = 120°C$, $H_2 = 1$ atm. [X] S/C = 8.1; [Y] S/C = 28.1.

fully hydrogenated product increased with time. With cluster **2** decrease of cluster concentration (substrate/cluster ratio increasing from 169 to 501) results in an increase of the TON and a decrease of fully hydrogenated products during time; a decrease of the substrate concentration (substrate/cluster from 254 to 70) results in nearly constant TON values. These results indicate that the reaction rate is dependent on the substrate concentration rather than on that of the cluster.

Finally, the data collected in Table 3 indicate that clusters **5** and **6** (which were found in small amounts in the reaction mixtures of **1** and **2**) show only very modest hydrogenation activity and therefore should be considered inactive by-products and not intermediates in these reactions.

Complexes **5** and **6** are obtained upon reaction of **1** or **2**, respectively, with alkynes under stoichiometric conditions [10]. The isomeric complexes **5** contain a metallacyclic ring formed by the linking of C_2Ph_2 with the coordinated benzyne on **1**, while complexes **6** contain a C_2R_2 ligand coordinated in independent fashion. The structures of **5** and **6**, and those of **7** and **8** are given in Fig. 2.

3.2. Hydrogenation-isomerization of 1,4-CHD and attempted hydrogenation of benzene

The results of these experiments are compiled in Table 4 [15].

Clusters **1** and **4** are very active in the hydrogenation of 1,4-CHD; however, the selectivity towards cyclohexene is only 50–60%. Cluster **3** shows very high activity but, once again, the selectivity towards cyclohexene is relatively low. Cluster **2** shows low activity but better selectivity for cyclohexene. The considerable amounts of 1,3-CHD formed indicate that isomerization occurs in competition with (or prior to) hydrogenation. It is noteworthy that the alkyne clusters **3** and **4** are more active than the benzyne clusters **1** and **2** in these reactions, opposite to the behaviour observed for the hydrogenation of alkynes.

*3.3. Comments on the catalytic activity of the benzyne complexes **1** and **2***

A comparison of the catalytic activities of complexes **1**–**4** with those of other ruthenium clusters (electronically unsaturated, or bearing parallel alkynes) is given in Table 5. The activity of complexes **1** and **2** is remarkable; to our knowledge it is the highest reported for ruthenium clusters.

While studying the homogeneous hydrogenation of 1,4- and 1,3-CHD using $Ru_3(CO)_{12}$, $H_4Ru_4(CO)_{12}$, $H_2Ru_4(CO)_{13}$ and related compounds [2] we isolated from the reaction mixtures complexes **9**–**12**, substituted with facial benzene or 'parallel' cyclohexadiene ligands, shown in Fig. 3.

Complexes **9**–**12** were inactive in the hydrogenation of 1,4-CHD. This was explained by considering that these derivatives were presumably formed, in an early reaction step, by oxidative addition of 1,3- or 1,4-CHD to the catalysts and that in the presence of external H_2 they could further react to release the parent substrate.

Clusters **1** and **2**, formed upon oxidative addition and P–C bond cleavage of PPh_3 on $Ru_3(CO)_{12}$ [16], have been considered as models for the dissociative chemisorption of benzene on metal surfaces [6]. They contain 'parallel' benzyne ligands, which can be readily compared with 'parallel' alkyne ligands [1,4,17]. It was previously observed that clusters with parallel alkynes can act as active intermediates in the homogeneous hydrogenation of alkynes [1,4].

3.4. Possible reaction pathways

The results obtained indicate that clusters **1** and **2** are active catalysts. From the reactions of **1** and **2** with alkynes under dihydrogen large amounts of unreacted parent clusters were recovered and very small yields of complexes **5** or **6** isolated, respectively. However, no organometallic intermediates or by-products could be isolated, which were helpful for establishing unequivocally a reaction pathway.

Table 4
Hydrogenation of 1,4-CHD on clusters **1**–**4**[a]

Cluster and experiment	Reaction time (min)	Conversion	TON	Selectivity to	
				cis-hexene	1,3-CHD
1 [W]	15	0.4	3.3	60.5	39.5
	30	1.7	15.1	61.5	38.5
	45	7.2	62.1	50.2	49.8
2 [Z]	15	0.6	8.0	34.9	65.1
	30	0.7	9.2	34.7	65.3
	45	0.4	4.6	27.8	72.2
3 [ZA]	15	2.3	71.1	41.3	53.5[b]
	30	4.7	146.2	28.1	71.9
	45	23.9	742.0	36.6	63.4
4 [ZB]	15	0.3	7.7	50.0	50.0
	30	0.6	15.1	35.6	64.4
	45	3.7	95.9	39.0	61.0

[a] Always $t = 120$°C, $H_2 = 1$ atm. [W] S/C = 865.8; [Z] S/C = 1275.4; [ZA] S/C = 3091.4; [ZB] S/C = 2563.2.
[b] Selectivity to cyclohexane 5.2%.

Clusters **5** and **6** show very modest hydrogenation activity (Table 3). This indicates that a mechanism involving addition or substitution of the alkynes in complexes **1** and **2** as the first reaction step, followed by uptake of hydrogen, should be disregarded. However, we hypothesize that cluster catalysis occurs on the basis of the following direct or indirect pieces of evidence. It is important to note that phosphido or phosphinidene bridges such as those found in clusters **1**–**4** are thought to prevent the fragmentation of clusters under CO or H_2, thus favouring cluster catalysis. These bridges would also allow reversible M–M bond cleavage [18] and hence formation of active vacant sites. Alternatively these could be generated by release of a coordinated carbonyl. However, the reaction of CO with cluster **1**, discussed above, leads to complex **7** which, in the presence of dihydrogen, forms the known $H_2Ru_3(CO)_8(PPh_2)_2$ and releases benzaldehyde [19]. This could explain the lower TON observed in the presence of CO.

The occurrence of cluster catalysis is also supported by the recovery of very large amounts of clusters **1** and **2** after the hydrogenation experiments. The observed dependence of the catalytic activity on the cluster and substrate concentration also suggests that cluster catalysis occurs [20].

The dependence of the catalytic activity on dihydrogen pressure indicates that uptake and activation of dihydrogen is one of the rate-determining steps, perhaps the first reaction step. Addition of dihydrogen would also result in the transformation of the coordinated ligand (benzyne, alkyne) into a vinyl [2,21]; the ease of this process would depend on the number of M–C bonds existing between the ligand and the cluster. This could explain why **1** and **3** (three M–C bonds) are usually more active than **2** and **4** (four bonds). Finally, the observed (preferential) formation of *cis*-stilbene when C_2Ph_2 is hydrogenated on clusters **1**–**4** is also consistent with cluster catalysis [2].

Another interesting aspect of the above reactions is the behaviour of the different alkyne substrates. It can be seen that, for all of the clusters **1**–**4**, the ease of hydrogenation of the alkynes is:

$$C_2Et_2 < PhC_2Et < C_2Ph_2$$

This could indicate that a further step of the reaction is the coordination of the alkyne and its insertion into an M–H bond; hydrogenation would therefore occur faster if the entering alkyne coordinated easily onto the cluster. In previous work we have observed that C_2Ph_2 is hydrogenated faster than C_2Et_2 ([4]b, [22]) and this was explained by the better coordinating properties of the former. On the other hand, experiments A and B indicate that there is no alkyne–benzyne exchange on **1** (or **2**) during hydrogenation.

It is also worth noting that the ease of hydrogenation of 1,4-CHD on clusters **1** and **2** is: $C_2Et_2 < PhC_2Et <$ 1,4-CHD $< C_2Ph_2$, whereas on clusters **3** and **4** the order becomes $C_2Et_2 < PhC_2Et < C_2Ph_2 <$ 1,4-CHD (Table 4). Thus, the alkyne clusters are more active in these reactions; the reverse behaviour is observed in the hydrogenation of C_2Ph_2, where **1** and **2** are the most active. Once again this can be explained by considering the relative ease of coordination of 1,4-CHD, compared with C_2Ph_2 on the benzyne or alkyne clusters.

Benzene is not hydrogenated under the conditions employed, presumably because of its lower coordinating ability.

Finally a non-negligible aspect of these reactions is the release of small amounts of 1,3-CHD when cluster **1** is reacted with alkynes and the formation of triphenyl-ethene (or ethane) from cluster **2** when reacted with C_2Ph_2. This is consistent with the proposed mechanism; the formation and release of 1,3-CHD could occur at the expense of the coordinated benzyne after uptake of dihydrogen and in competition with the hydrogenation of the alkynes. Triphenyl-ethene (or ethane) could be formed by coupling of the coordinated benzyne with the incoming C_2Ph_2 in the presence of dihydrogen; alternatively it could be formed by coupling of a coordinated vinyl with C_2Ph_2.

Table 5
Comparison of the activity of clusters **1**–**4** with that of selected ruthenium-containing clusters

Cluster	S/C ratio[a]	TOF[b]	Selectivity to monoenes	Ref.
Hydrogenation of diphenylacetylene				
$Ru_3(CO)_{12}$	49.4	97.4	100	[1]
$H_4Ru_4(CO)_{12}$	60.3	117.3	100	[1]
$Cp_2Ru_3(CO)_5(C_2Ph_2)$	94.3	121.0	98.5	[4]b
$HRu_3(CO)_7(PPh_2)_3$	108.0	90.1	100	[5]b
$HRu_3(CO)_9(PPh_2)$	100.0	99.1	99.3	[5]b
$Ru_4(CO)_{13}(PPh)$	24.8	131.8	100	[5]c
Cluster **1**	194.6	700.8	98.7	t.w.
Cluster **2**	274.5	282.3	97.6	t.w.
Cluster **3**	559.2	250.8	81.1	t.w.
Cluster **4**	238.2	41.2	97.5	t.w.
Hydrogenation of 1-phenyl-1-butyne				
Cluster **1**	444.8	69.1	100	t.w.
Cluster **2**	344.7	6.0	100	t.w.
Cluster **3**	1369.0	27.7	100	t.w.
Cluster **4**	169.7	42.8	100	t.w.
Hydrogenation of hex-3-yne				
$Ru_3(CO)_{12}$	241.1	58.1	100	[21]
$Cp_2Ru_3(CO)_5(C_2Ph_2)$	198.4	9.2	100	[4]b
$HRu_3(CO)_9(PPh_2)$	230.0	22.4	95.3	[5]b
$HRu_3(CO)_7(PPh_2)_3$	342.0	4.1	80.1	[5]b
Cluster **1**	71S.4	35.3	97.2	t.w.
Cluster **2**	430.3	3.2	100	t.w.
Cluster **3**	559.2	18.8	78.2	t.w.
Cluster **4**	755.4	4.6	100	t.w.
Hydrogenation of 1,4-CHD				
$Ru_3(CO)_{12}$	429.4	123.5	32.6	[3]
$H_4Ru_4(CO)_{12}$	366.0	48.9	41.3	[3]
$Cp_2Ru_3(CO)_5(C_2Ph_2)$	480.8	229.5	83.7	[21]
Cluster **1**	865.8	82.8	50.2	t.w.
Cluster **2**	127.5	6.1	27.8	t.w.
Cluster **3**	309.1	989.3	36.6	t.w.
Cluster **4**	256.3	128.8	100	t.w.

[a] S/C = substrate/cluster.
[b] Maximum TOF observed.

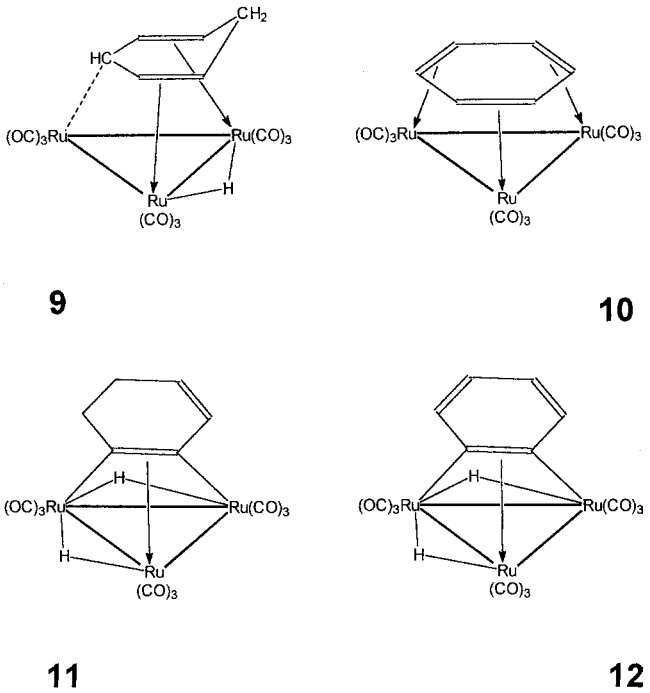

Fig. 3. Structures of complexes **9**–**12** (see Ref. [3]).

Although fragment catalysis cannot be completely ruled out, the above evidence points to a 'classic' reaction pathway based on cluster catalysis requiring formation of an active site, dihydrogen activation and insertion of the substrate into a metal–hydrogen bond [23]; this is tentatively shown in Scheme 1 for trinuclear cluster percursors.

An alternative mechanism involving cluster catalysis could also be envisaged; this would be represented by the insertion of alkynes into M–P bonds ([4]b, [18]) as the rate determining step, followed by uptake of dihydrogen and release of the hydrogenated products through 'vinylphosphinic' intermediates [24]. However, there is no evidence for this, more unlikely, mechanism.

The reactions reported in this paper represent a small but interesting step in the development of structure/reactivity relationships applied to homogeneous catalysis. The high activity and the comparable behaviour observed for the isostructural clusters **1** and **3** are indeed a good example of a structure/reactivity relationship.

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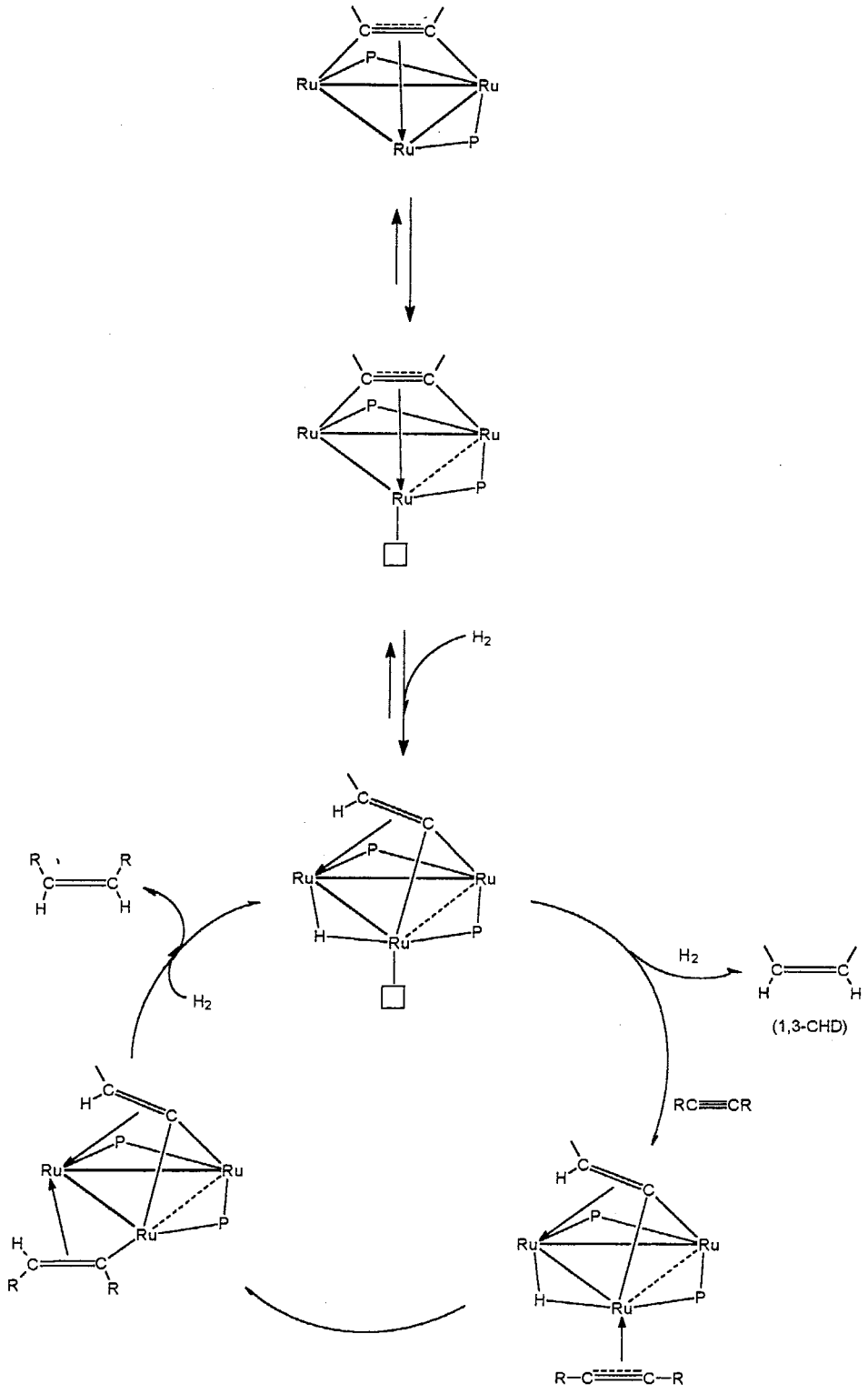

Scheme 1.

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