

Phosphine-substituted and phosphido-bridged clusters in homogeneous catalysis

III *. Selective hydrogenation of t-butylacetylene in the presence of $\text{Ru}_3(\text{CO})_{12-n}(\text{PPh}_2\text{H})_n$ ($n = 2, 3$), $\text{HRu}_3(\text{CO})_{10}(\mu\text{-PPh}_2)$, $\text{HRu}_3(\text{CO})_9(\mu\text{-PPh}_2)$, $\text{H}_2\text{Ru}_3(\text{CO})_8(\mu\text{-PPh}_2)_2$ and $\text{HRu}_3(\text{CO})_7(\mu\text{-PPh}_2)_3$. Spectroscopic identification of common alkyne-substituted cluster intermediates

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Introduction

Homo- and hetero-metallic clusters are potentially useful as homogeneous catalysts, but one of the major limitations on their use is their tendency to undergo fragmentation in solution in the presence of donor ligands [1]. One of the features of interest in the chemistry of the phosphido-bridged clusters is that such ligands tend to inhibit the fragmentation of polynuclear derivatives [2*], and therefore allow better evaluation of polymetallic reactivity effects. Furthermore, reversible metal-metal bond cleavage can occur [3] and this is of relevance for homogeneous catalytic processes. There are close relationships between phosphine-substituted and phosphido-bridged clusters; the latter were initially obtained by thermal transformation of phosphine substituted derivatives [4*]. The reverse reaction may also occur, and insertion of H_2 or of small molecules into the M-P bonds of phosphido-bridged clusters may lead to phosphine-substituted derivatives [5].

When we began an investigation of the homogeneous catalytic properties of the clusters $\text{Ru}_3(\text{CO})_{12-n}(\text{PPh}_2\text{H})_n$ ($n = 1-3$) [6] we found good catalytic activity, but

* Parts I, II, see refs 6, 7.

* Reference number with asterisk indicates a note in the list of references.

also observed that during some reactions the clusters were modified, to give as the main products $\text{HRu}_3(\text{CO})_7(\mu\text{-PPh}_2)_3$ and $\text{Ru}_2(\text{CO})_6(\mu\text{-PPh}_2)_2$. Preliminary experiments showed that the latter complexes were also active catalysts for the selective hydrogenation of dienes [7]. We therefore decided to investigate a series of phosphido-bridged derivatives which directly or indirectly originate from $\text{Ru}_3(\text{CO})_{12-n}(\text{PPh}_2\text{H})_n$ ($n = 1-3$); these are $\text{HRu}_3(\text{CO})_{10}(\mu\text{-PPh}_2)$ (**1**) [8], $\text{HRu}_3(\text{CO})_9(\mu\text{-PPh}_2)$ (**2**) [9], $\text{H}_2\text{Ru}_3(\text{CO})_8(\mu\text{-PPh}_2)_2$ (**3**) [10], $\text{HRu}_3(\text{CO})_7(\mu\text{-PPh}_2)_3$ (**4**) [11] and $\text{Ru}_2(\text{CO})_6(\mu\text{-PPh}_2)_2$ (**5**) [11,12]. In this study, the activity of complexes **1-5** has been compared with that of the complexes $\text{Ru}_3(\text{CO})_{12-n}(\text{PPh}_2\text{H})_n$ ($n = 2$, complex **6**; $n = 3$, complex **7**). As a substrate we used *t*-butylacetylene, which is known to add oxidatively to $\text{Ru}_3(\text{CO})_{12}$ [13] and which had previously been tested under homogeneous conditions in the presence of heterometallic clusters [14].

We have found that HC_2Bu^t is selectively hydrogenated to give $\text{H}_2\text{C}=\text{CHBu}^t$; very similar final patterns of products are obtained in the presence of all the complexes **1-7**, even though the reaction rates are slightly different. The rather similar activities and selectivities observed for these complexes indicate that a common catalytic species is probably formed in solution; in most of the reaction solutions we observed two alkyne-substituted cluster derivatives, which in the presence of hydrogen gave $\text{H}_2\text{C}=\text{CHBu}^t$ or $\text{CH}_3\text{CH}_2\text{Bu}^t$. These complexes, thought to be reaction intermediates, have been spectroscopically characterized.

Experimental

Complexes **1-5** were supplied by Prof. A.J. Carty (University of Waterloo, Ontario, Canada); complexes **6-7** were prepared as previously described [6]. *t*-Butylacetylene was a commercial product (Fluka) and was used as received after GLC confirmation of its purity.

The organometallic products obtained in the catalytic experiments were purified on preparative TLC plates (Kieselgel P.F. Merck, eluants mixtures of light petroleum and diethyl ether); when possible, these derivatives were crystallized before analysis. The gaseous products obtained in the hydrogenation experiments were analyzed by gas-chromatography as described below.

The analyses of the organometallic products were carried out with a C,H,N 185 F&M analyzer and a Perkin-Elmer 303 atomic absorption spectrometer. Those for the alkyne-substituted intermediates were determined by the Pascher Laboratories (Remagen W. Germany). The FAB mass spectra of the derivatives were recorded at MacMaster University (Hamilton, Ontario, Canada). The IR spectra were recorded on a Perkin-Elmer 580B instrument and the ^1H , ^{31}P and ^{13}C spectra on a JEOL JNM 270 FT instrument.

Hydrogenation experiments. Unless otherwise specified, hydrogenations were performed in sealed glass vials (volume 25 ml), each containing an *n*-octane solution of the cluster and the alkyne. The vials were filled with 0.9 atm of H_2 by standard vacuum techniques. Details of the concentrations of clusters and substrate are given in Table 1. The vials were heated at 120°C in a thermostatted oven for the time shown.

Gas-chromatographic analyses of the reaction solutions. The organic products in the solutions from the hydrogenation experiments were analyzed with a Carlo Erba 4200 FID gas-liquid chromatograph equipped with $2\text{ m} \times 0.6\text{ mm}$ i.d. columns, with

Table 1

Cluster concentrations and substrate/cluster molar ratios in the hydrogenation experiments

Complex	Concentration (mol/l)	Substrate/cluster molar ratio ^a
$\text{Ru}_3(\text{CO})_{10}(\text{PPh}_2\text{H})_2$	5.23×10^{-6}	312
$\text{Ru}_3(\text{CO})_9(\text{PPh}_2\text{H})_3$	5.54×10^{-6}	294
$\text{HRu}_3(\text{CO})_{10}(\mu\text{-PPh}_2)$	7.37×10^{-6}	221
$\text{HRu}_3(\text{CO})_9(\mu\text{-PPh}_2)$	6.74×10^{-6}	242
$\text{H}_2\text{Ru}_3(\text{CO})_8(\mu\text{-PPh}_2)_2$	5.56×10^{-6}	293
$\text{HRu}_3(\text{CO})_7(\mu\text{-PPh}_2)_3$	6.84×10^{-6}	235
	4.74×10^{-6}	344
$\text{Ru}_2(\text{CO})_6(\mu\text{-PPh}_2)_2$	1.58×10^{-5}	103
	5.17×10^{-6}	315

^a t-Butylacetylene, always 0.200 ml (1.63×10^{-3} mol/l).

N_2 (25 ml/min) as carrier gas: n-octane/Porasyll C (100/120 mesh), 60 °C for 5 min, then 5 °C/min till 155 °C.

Tentative identification of organometallic products in the reaction solutions. The reaction solutions were also examined by TLC preparative plates to reveal decomposition of the catalysts and to identify organometallic intermediate or side products; the characterization of some of the by-products was difficult because of the very small amounts formed. In nearly all the solutions, however, two products could be observed; these showed a bright green and a deep red colour (complexes 8 and 9, respectively), and we attempted to make them independently as described below.

The organometallic products detected in the hydrogenation solutions, and the degree of decomposition of the clusters, are shown in Table 2.

Alternative synthetic routes to complexes 8, 9. (a) From clusters 6, 7. These reactions were performed in 400 ml glass vials, filled with 100 ml of octane/toluene solution (90/10 in volume) of the complex; addition of toluene was necessary to bring the clusters into solution. The vials were filled with 1 atm of H_2 by standard vacuum techniques, then sealed. They were kept at 120 °C until an intense green colour indicated the formation of complex 8.

Treatment of 2.0 g of $\text{Ru}_3(\text{CO})_{11}(\text{PPh}_2\text{H})$ (2.51 mmol) with 2.0 ml of alkyne for 90 min gave a clear brown-yellow solution; evaporation to small volume and TLC purification yielded about 15% each of complexes 4 and 5 and trace amounts of 3, together with about 10% of 8, traces of 9, and about 25% of decomposition products.

Treatment of 6 (2.0 g, 2.10 mmol) with 2.0 ml of alkyne (16.3 mmol) for 45 min gave a green solution, which was purified as described above. Seven products were observed, including 4, 5 and 9 (each in ca. 5% yield), together with 8 (ca. 50%), and some decomposition.

Treatment of 7 (2.0 g, 1.80 mmol) with 2.0 ml of alkyne for 30 min gave a deep green solution containing 4, 5 (5% each), 8 (ca. 50%), 9 (ca. 10%), and some decomposition products.

(b) From phosphido-bridged clusters 2–5. The solutions from the hydrogenation experiments in the presence of clusters 1, 3 and 5 turned green after about 15 min reaction, and were shown to contain considerable amounts of 8 (see Table 2).

Table 2

Organometallic products detected in the hydrogenation solutions and the degree of cluster decomposition

Catalyst	Changes in colour	Cluster decomposition ^a	Organometallic products observed ^b
$\text{Ru}_3(\text{CO})_{10}(\text{PPh}_2\text{H})_2$	Dark yellow to pale yellow	20%	see text
$\text{Ru}_3(\text{CO})_9(\text{PPh}_2\text{H})_3$	Orange to green; after 75 min yellow.	20%	see text
$\text{HRu}_3(\text{CO})_{10}(\mu\text{-PPh}_2)$	No changes	80%	3 (10%), 4 (1%), 5 (5%); 8 (1%)
$\text{HRu}_3(\text{CO})_9(\mu\text{-PPh}_2)$	No changes	90%	as above
$\text{H}_2\text{Ru}_3(\text{CO})_8(\mu\text{-PPh}_2)_2$	Orange to green; after 30 min yellow	30–40%	parent (1%), 4 (1%), 5 (1%); 8 (15%)
$\text{HRu}_3(\text{CO})_7(\mu\text{-PPh}_2)_3$	Brown to orange	60–70%	3 (5%), 5 (5%); 8 (10%), 9 (5%)
$\text{Ru}_2(\text{CO})_6(\mu\text{-PPh}_2)_2$	Yellow to green; after 15 min orange	60%	3 (tr), parent (5%); 8 (20%)
Complex 8	Formation of a grey suspension	100%	—
Complex 9	Red colour darkens	60%	parent (20%); unidentified red product

^a Maximum decomposition after the longest reaction time. ^b The solutions of the vials of each run were kept together, filtered and reduced to small volume, then purified by TLC; the percentages are only tentative.

Treatment of **2** (150 mg, 0.202 mmol) with 0.2 ml of alkyne in n-octane under N_2 (in conventional glassware) gave only complexes **3**, **4**, and **5** in small amounts.

Treatment of **3** (150 mg, 0.167 mmol) for 10 min with 0.2 ml (1.63 mmol) of alkyne under the same conditions gave traces of **4**, about 10% of **8**, and 5% of **9**; some parent cluster was recovered.

Treatment of **4** (1.0 g, 0.95 mmol) with 2.0 ml of alkyne for 15 min under the above conditions gave about 15% of **8** and 5% of **9**, along with decomposition products.

Finally, treatment of **5** (0.5 g, 0.68 mmol) with 2.5 ml of alkyne (20.4 mmol) for 15 min under H_2 in a 400 ml sealed vial, as described above, gave about 5% each of **4** and **9** and 30–40% of **8**, together with some unchanged **5** and decomposition products; similar results were obtained after 30 min reflux under N_2 .

Behaviour of complexes 8, 9 in solution. These two complexes are eluted very close together on the TLC plates, and are difficult to obtain pure. Attempts to crystallize **8**, by keeping its solution in hexane under N_2 at -15°C for 24 h, resulted in deposition of a black-green crystalline powder unsuitable for X-ray analyses. Other solvent mixtures were also used (including hexane/chloroform, hexane/toluene, and toluene), but no crystals suitable for X-ray studies were obtained. Complex **9** under the same conditions deposited a dark red crystalline powder, sometimes contaminated by small amounts of **4**.

Treatment of **8** in a sealed vial under H_2 for 15 min at 120°C gave 3,3-dimethyl-1-butene and some decomposition products; complex **9** kept under the same conditions for 45 min gave 78% of 2,2-dimethyl-butane, 19%, of 3,3-dimethyl-1-butene, and 2.7% of t-butylacetylene. The cluster had only partly decomposed.

Results and discussion

Hydrogenation of t-butylacetylene in the presence of clusters 1–7. The results of these experiments are shown in Table 3.

All the clusters 1–7 gave similar results, involving a 30–40% conversion of the substrate after 90 min reaction; turnovers between 70 and 110 (mol of substrate transformed per mol of cluster) were observed, except for the binuclear complex 5, which is less reactive. There is considerable selectivity towards 3,3-dimethyl-1-butene, and only a 3–7% of the fully hydrogenated 2,2-dimethylbutane was formed.

The main differences in the behaviour of the above clusters are: (i) complex 5 and clusters 6, 7 give lower conversions during the first 15–30 min, than the complexes 1–4; (ii) of the latter, better initial conversions are obtained for 1 and 4. This behaviour can be accounted for by postulating a trinuclear catalytic species containing μ -PPh₂ bridges; the formation of this species would require longer times for 5, 6 and 7.

After the first 15 or 30 min reaction, however, the reactions apparently stop, and the extent of conversion remains almost constant over longer time. This behaviour is shown in Fig. 1. From Fig. 1 and Table 2 it can be seen that the reactions tend to stop when the green colour due to the presence of complex 8 begins to disappear. These observations indicate that the catalytic species is a cluster containing μ -PPh₂ bridges; this is formed more or less readily from all the compounds 1–7. In the

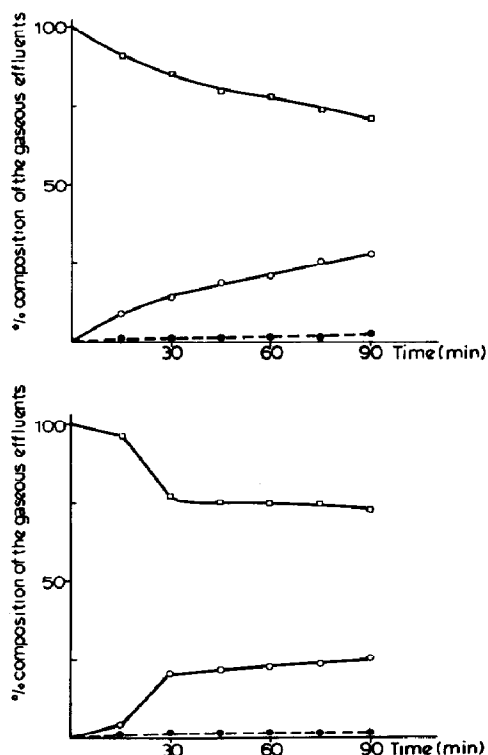


Fig. 1. Comparison of the behaviour of $\text{H}_2\text{Ru}_3(\text{CO})_8(\mu\text{-PPh}_2)_2$ (top) and $\text{Ru}_3(\text{CO})_{10}(\text{PPh}_2\text{H})_2$ in the hydrogenation of *t*-butylacetylene. $\square$, residual *t*-butylacetylene; $\circ$, 3,3-dimethyl-1-butene; $\bullet$, 2,2-dimethylbutane.

Table 3

Hydrogenation of t-butylacetylene in the presence of clusters 1–7

Cluster	Reaction time (min)	Turnover ^a	Conversion	Selectivity to:	
				2,2-dimethyl-butane	3,3-dimethyl-1-butene
$\text{Ru}_3(\text{CO})_{10}(\text{PPh}_2\text{H})_2$	15	8.7	2.8	3.57	96.43
	30	67.3	21.6	2.78	97.22
	45	70.7	22.7	3.18	96.92
	60	74.5	23.9	3.46	96.65
	75	76.0	24.4	3.69	96.31
	90	87.0	27.9	4.49	95.70
$\text{Ru}_3(\text{CO})_9(\text{PPh}_2\text{H})_3$	15	12.9	4.4	6.8	93.2
	30	69.1	23.5	2.98	97.02
	45	82.4	28.0	2.86	97.14
	60	83.6	28.4	3.17	96.83
	75	90.3	30.7	4.23	95.77
	90	99.4	33.8	4.73	95.27
$\text{HRu}_3(\text{CO})_{10}(\mu\text{-PPh}_2)$	15	59.0	25.6	3.50	96.50
	30	60.0	27.1	3.32	96.68
	45	70.0	31.8	3.77	96.23
	60	81.0	36.6	3.83	96.17
	75	90.0	40.5	3.70	96.30
	90	98.0	44.3	4.29	95.71
$\text{HRu}_3(\text{CO})_9(\mu\text{-PPh}_2)$	15	39.0	16.2	3.70	96.30
	30	65.0	26.9	2.97	97.03
	45	69.0	28.7	3.14	96.86
$\text{H}_2\text{Ru}_3(\text{CO})_8(\mu\text{-PPh}_2)$	15	29.0	9.9	6.06	93.94
	30	43.0	14.8	5.41	94.59
	45	59.0	20.0	4.00	96.00
	60	62.0	21.0	4.29	95.71
	75	79.0	26.8	3.73	96.27
	90	84.0	28.6	3.50	96.50
$\text{HRu}_3(\text{CO})_7(\mu\text{-PPh}_2)_3^a$	15	59.0	25.3	6.32	93.68
	30	74.0	31.7	5.36	94.64
	45	104	44.1	6.80	93.88
$\text{HRu}_3(\text{CO})_7(\mu\text{-PPh}_2)_3^b$	15	65.0	18.8	3.19	96.81
	30	89.0	25.9	2.32	97.68
	45	91.0	26.4	2.65	97.35
	60	99.0	28.7	2.79	97.21
	75	102.0	29.7	2.69	97.31
	90	111.0	32.2	2.80	97.20
$\text{Ru}_2(\text{CO})_6(\mu\text{-PPh}_2)_2^c$	10	12.0	11.5	4.35	95.65
	30	28.0	27.3	4.03	95.60
	45	33.0	31.8	3.77	96.23
$\text{Ru}_2(\text{CO})_6(\mu\text{-PPh}_2)_2^d$	15	49.0	15.7	3.82	96.18
	30	74.0	23.4	2.56	97.44
	45	81.0	25.8	2.71	97.29
	60	84.0	26.6	3.01	96.99
	75	89.0	28.4	3.17	96.83
	90	97.0	30.8	3.57	96.43

^a Substrate/cluster molar ratio 235. ^b substrate/cluster molar ratio 344. ^c Substrate/complex molar ratio 103. ^d substrate/complex molar ratio 315.

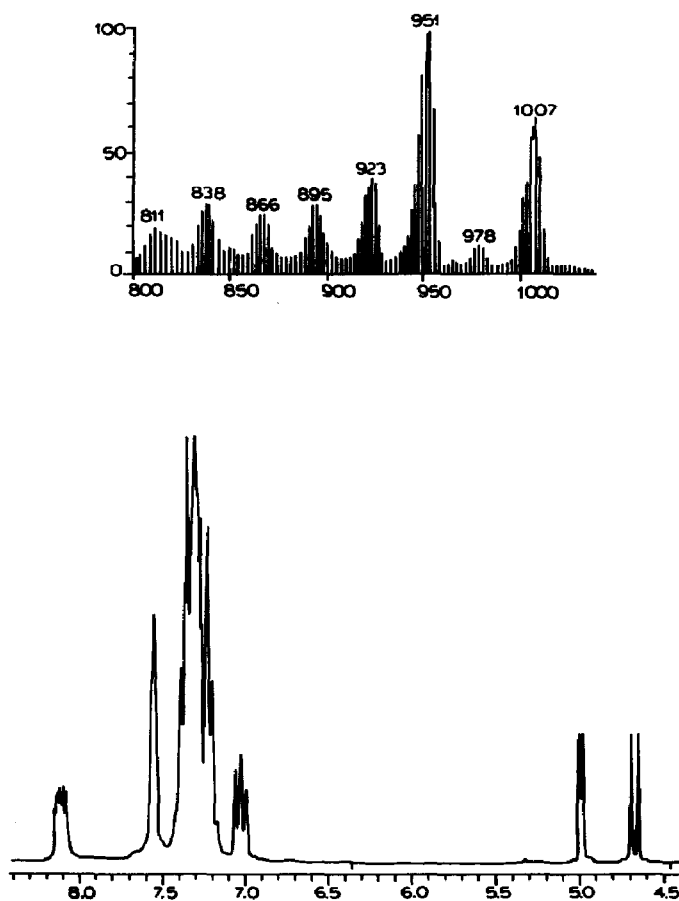


Fig. 2. FAB mass spectrum and ^1H NMR spectrum of complex **8**.

presence of the alkyne, this common species gives the cluster complex **8**, which is probably a reaction intermediate, as well as complex **9**; the natures of these derivatives are discussed below.

Finally, the reactions tend to stop when the active cluster catalyst and the green intermediate **8** begin to decompose; this is in accord with observations in other cases of "cluster catalysis" [6,7,15].

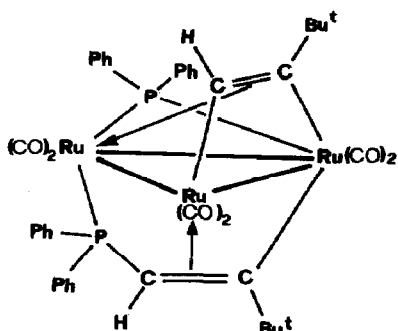


Fig. 3. Proposed structure for complex **8**.

Table 4

Analytical and spectroscopic data for complexes **8** and **9****Complex 8**

Elemental analysis: Found: C, 51.1; H, 4.2; P, 5.97; Ru, 29.4. $C_{42}H_{40}O_6P_2Ru_3$ calcd.: C, 50.15; H, 4.01; P, 6.16; Ru, 30.14%.

FAB mass spectrum: $P^+ = 1008$ m/e . Isotopic pattern Ru_3 . Loss of 6 CO's followed by complex fragmentation.

IR (ν (CO) (hexane/toluene): 2048 s, 2000 vs, 1992 s, 1966 m, 1953 m, 1942 s, cm^{-1} .

1H NMR ($CDCl_3$, 25 °C): δ 8.11 (mm, 2H, Ph), 7.55 (m, 2H, Ph), 7.39–7.20 (mm, 14H, Ph), 7.01 (m, 2H, Ph), 4.99–4.98 (d, 1H, C–H alkyne; $J(P-H)$ 3.48 Hz), 4.69–4.63 (d, 1H, C–H alkyne; $J(P-H)$ 11.46 Hz), 1.26 (s, 9H, Bu^t), 0.70 (s, 9H, Bu^t).

^{31}P NMR ($CDCl_3$, 25 °C, H_3PO_4): +239.75, +238.10 d (1) ($J(P-P)$ 80.0 Hz) +130.94, +127.30 d (1) ($J(P-P)$ 81.0 Hz)

^{13}C NMR ($CDCl_3$, 25 °C, C–H decoupled): 14.0, 30.7, 31.55, 33.04 (Bu^t) 81.89 s (C alkyne?): 113.7 d, 127.8–129.9 m, 130.5 d, 131.6–131.9 d, 133.0–133.1 d, 133.3–133.5 d (Ph): 137.9 (C alkyne?): 180.8 (broad: CO's?).

Complex 9

Elemental analysis: Found: C, 56.1; H, 4.6; P, 7.92; Ru, 26.1. $C_{52}H_{49}O_4P_3Ru_3$ Calcd.: C, 55.02; H, 4.44; P, 8.19; Ru, 26.71%.

FAB mass spectrum: $P^+ = 1136$ m/e . Isotopic pattern Ru_3 . Loss of 4 CO's then complex fragmentation. IR (ν (CO), hexane): 2056 vs, 2044 sh, 2020vs, 1996 vs, 1981 m, 1968 vs(b), 1956 vs(b), cm^{-1} .

1H NMR ($CDCl_3$, 25 °C): 8.11 mm, 7.60 mm, 7.33 mm, 7.07 mm, 6.70 mm (30 H, Ph); 6.0–5.93 (1H, C–H alkyne; $J(P-H)$ 21 Hz), 1.45 s (9H, Bu^t), 1.03 s (9H, Bu^t).

^{31}P NMR ($CDCl_3$, 25 °C, H_3PO_4): +248.4, +246.8 d (1) ($J(P-P)$ 29.1), +233.0 s (1), +193.9, +192.3 d (1) ($J(P-P)$ 24.1).

^{13}C NMR ($CDCl_3$, 25 °C, C–H decoupled): 30.3, 31.06, 31.5, 38.3 (Bu^t): 126.6–129.3 mm, 131.3–132.4 mm, 133.6 d (C, Ph).

Spectroscopic characterization and structural hypotheses for complexes 8, 9. The analytic and spectroscopic data for clusters **8** and **9** are listed in Table 4.

The elemental analyses and the FAB mass spectrum indicate that complex **8** has formula $Ru_3(CO)_6[Ph_2PC(H)C(Bu^t)](HC_2Bu^t)(\mu-PPh_2)$; in particular, in the FAB mass spectrum a parent ion at $m/e = 1008$ is observed together with ions arising from loss of 6 CO's followed by a complex fragmentation. The isotope pattern of the parent ion is typical of a Ru_3 cluster [16]; the FAB spectrum and the more relevant features of the 1H NMR spectrum of **8** are shown in Fig. 2.

The ^{31}P NMR spectrum indicates the presence of two non-equivalent phosphorus atoms with different relaxation times; these are coupled ($J(P-P)$ 80 Hz). In the 1H NMR spectrum there is a complex pattern for the phenyl hydrogens, together with two doublets attributable to C–H (alkynic) hydrogens; two distinct signals from the Bu^t protons are also observed. Selective irradiation of the signals centered at 8.11 and 7.0 ppm results in a simplification of the phenyl pattern; irradiation of the signals at 7.55–7.20 ppm results in the simplification of the former signals, which are thus attributed to phenyl hydrogens; the integrated spectrum is also in accord with this assignment. The two doublets attributed to the acetylenic hydrogens and the two different signals for Bu^t groups indicate the presence of two differently bound alkynes; the C–H hydrogens show different coupling constants with the P atoms ($J(P-H)$ 3.48 and $J(P-H)$ 11.5 Hz), which could point to the presence of hydrogens, respectively, *cis* or *trans* to the phosphorus atoms [17].

Among the many structures that can be proposed for **8**, we favour that shown in

Fig. 3, which is in accord with all the above data; complex **8** would be a 48 electron precise, diamagnetic cluster, resulting from insertion of an alkyne into a metal phosphorus bond (a feature further discussed below).

Unfortunately the ^{13}C NMR spectrum shows only a broad signal in the CO region; this indicates that there is fluxionality at room temperature, so that no information about the position of CO ligands relative to the phosphorus atoms can be obtained (low temperature studies were not possible owing to the poor solubility of the complex).

The characterization of complex **9** was more difficult because it was obtained in lower yield. The FAB mass spectrum shows a parent ion at $m/e = 1136$, then loss of 4 CO's, followed by a very complex fragmentation. Once again, the isotopic pattern of the parent ion is in accord with a Ru_3 cluster. The FAB spectrum and the elemental analysis are consistent with the proposed formulation as $\text{Ru}_3(\text{CO})_4[\text{Ph}_2\text{PC}(\text{H})\text{C}(\text{Bu}^t)][(\text{Ph}_2\text{PCC}(\text{Bu}^t))(\text{PPh}_2)]$.

The ^{31}P NMR spectrum shows three sets of signals (two doublets and a singlet), in 1/1/1 intensity ratio, which indicates the presence of two phosphorus atoms coupled together ($J(\text{P}-\text{P})$ 24 Hz) and of one uncoupled. In the ^1H NMR there is a complex pattern for the phenyl hydrogens, together with a doublet centered at 5.96 ppm (alkynic C-H) and two different Bu^t resonances; no other C-H signals can be detected (though some could be observed by the Ph resonances). Once again CO fluxionality is observed in the ^{13}C NMR spectrum.

The FAB mass spectrum and the ^{31}P NMR spectrum of **9** are shown in Fig. 4. In the light of the above data we propose the structure shown in Fig. 5, which would account for all the observed features. Complex **9** is diamagnetic; if the proposed structure is correct, it is a 46 electron cluster.

The structures proposed for **8** and **9** indicate that insertion of the alkyne (or of an acetylide) into the M-P bonds must have occurred; this is frequently observed for phosphinidene [18*,19] and for phosphido-bridged derivatives [20]. In particular, complex **4** undergoes insertion of diphenylacetylene into an M-P bond, with reductive elimination of one phosphorus bound phenyl and of the hydridic hydrogen to form benzene [21]. However, insertion of an acetylide into M-P bonds is not often observed, although phosphino-alkynes coordinated to clusters in multi-site fashion have been reported [22].

Some comments on the formation of common intermediates and their role in catalysis. The results discussed above indicate that clusters **1-7** are selective hydrogenation catalysts for *t*-butylalkyne, and that clusters **8** and **9** are probably reaction intermediates; it is also evident, however, that several processes occur in solution to give a common catalytic species. It is possible that there is M-M fragmentation (reversible or not) in solution, together with recombination of metal fragments as shown by the formation of **8** from **5**; other possible processes are the observed insertion into M-P bonds, and/or M-P bond hydrogenolysis to give $\sigma\text{-PPh}_2\text{H}$ from $\mu\text{-PPh}_2$.

Several of the above processes have been observed for clusters **1-7**; Geoffroy and coworkers reported that $\text{Ru}_3(\text{CO})_9(\text{PPh}_2\text{H})_3$ (**7**) under photochemical conditions gave **4** and **5** in substantial yields, together with **3** and $\text{H}_2\text{Ru}_3(\text{CO})_7(\text{PPh}_2\text{H})(\mu\text{-PPh}_2)_2$ [11]. The results observed were explained in terms of the initial formation of the common intermediate $\text{HRu}_3(\text{CO})_7(\mu\text{-PPh}_2)(\text{PPh}_2\text{H})_2$; M-M bond cleavage in the primary photochemical event was considered probable [23].

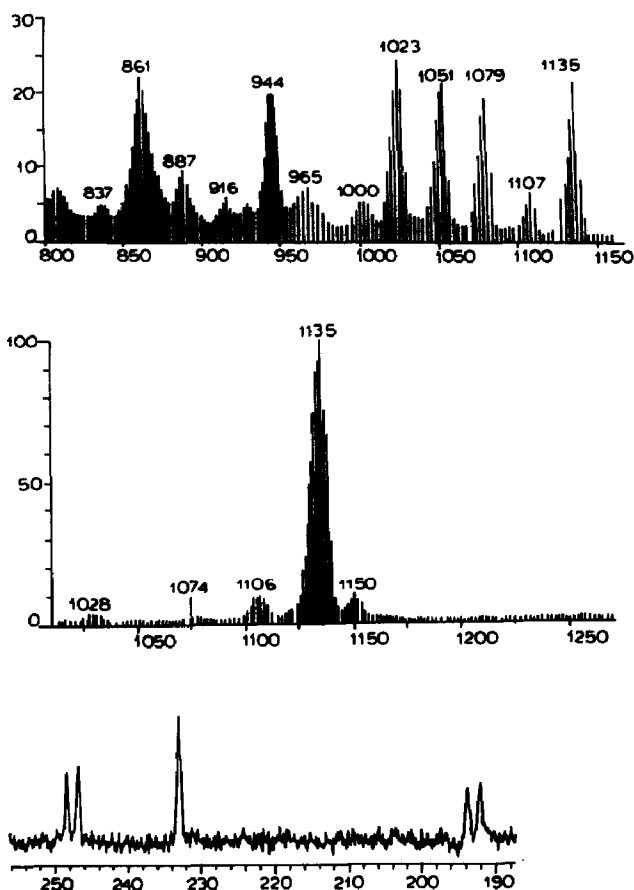


Fig. 4. Positive and negative ion FAB mass spectra (top and bottom, respectively) and ^{31}P NMR spectrum of complex 9.

Carty and coworkers found that the reaction of $\text{Ru}_3(\text{CO})_{12}$ in the presence of sodium benzophenone ketyl gave complex 1, which, depending on the reaction conditions, yields 2 [9] or 3–5 [10].

Finally, we have found that treatment of $\text{Ru}_3(\text{CO})_{12}$ with PPh_2H in the presence of Me_3NO gives $\text{Ru}_3(\text{CO})_{12-n}(\text{PPh}_2\text{H})_n$ ($n = 1-3$), which under thermal conditions

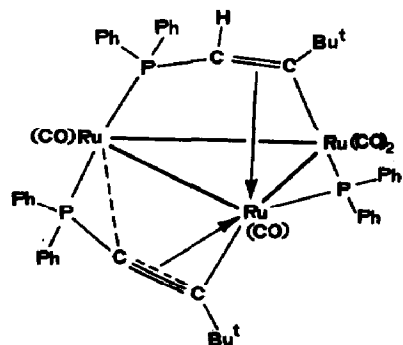


Fig. 5. Proposed structure for complex 9.

give mainly **4** and **5**, and smaller amounts of **3** [6]. Thus, different synthetic procedures lead to mixtures of the same phosphido-bridged clusters, and so it seems very probable that a common intermediate cluster species may be formed.

In our opinion, this intermediate cluster species acts as a hydrogenation catalyst in the reactions described above; indirect evidence for this hypothesis are: (i) after long reaction times, when the presence of metal fragments is more likely, the reactions tend to stop; (ii) complex **5** is less efficient, at least for short reaction times, and gives cluster intermediate derivatives (mainly **8**); (iii) the selectivity for formation of ethylenes indicates the presence of organometallic catalytic species; (iv) the formation of clusters **8** and **9** as probable intermediates also points to cluster catalysis; (v) preliminary results indicate that complexes formed by insertion of C_2Ph_2 into M–P bonds give stilbenes by hydrogenation [24]; (vi) different results could be expected to arise from clusters **1–5**, which have various numbers of μ -PPh₂ bridges and hydride ligands and have different cluster sizes. In fact similar results were obtained in all cases, in accord with Geoffroy's hypothesis of the participation of a common intermediate.

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