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Synthesis, structure and hydrogenation catalytic activity of $[Ru_3(\mu_3,\eta^2\text{-ampy})(\mu,\eta^1{:}\eta^2\text{-PhC=CHPh})(CO)_6(PPh_3)_2]$ (Hampy = 2-amino-6-methylpyridine)

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Abstract

The compound $[Ru_3(\mu_3,\eta^2\text{-ampy})(\mu,\eta^1{:}\eta^2\text{-PhC=CHPh})(CO)_6(PPh_3)_2]$ (**1**) (ampy = 2-amino-6-methylpyridinate) has been prepared by reaction of $[Ru_3(\mu_3,\eta^2\text{-ampy})(\mu,\eta^1{:}\eta^2\text{-PhC=CHPh})(CO)_7(PPh_3)]$ with triphenylphosphine at room temperature. However, the reaction of $[Ru_3(\mu\text{-H})(\mu_3,\eta^2\text{-ampy})(CO)_7(PPh_3)_2]$ with diphenylacetylene requires a higher temperature (110°C) and does not give complex **1** but the phenyl derivative $[Ru_3(\mu_3,\eta^2\text{-ampy})(\mu,\eta^1{:}\eta^2\text{-PhC=CHPh})(\mu\text{-PPh}_2)(Ph)(CO)_5(PPh_3)]$ (**2**). The thermolysis of complex **1** (110°C) also gives complex **2** quantitatively. Both **1** and **2** have been characterized by X-ray diffraction methods. Complex **1** is a catalyst precursor for the homogeneous hydrogenation of diphenylacetylene to a mixture of *cis*- and *trans*-stilbene under mild conditions (80°C, 1 atm. of H_2), although progressive deactivation of the catalytic species is observed. The dihydride $[Ru_3(\mu\text{-H})_2(\mu_3,\eta^2\text{-ampy})(\mu,\eta^1{:}\eta^2\text{-PhC=CHPh})(CO)_5(PPh_3)_2]$ (**3**), which has been characterized spectroscopically, is an intermediate in the catalytic hydrogenation reaction.

Key words: Ruthenium; X-ray diffraction; Hydrogenation; Homogenous catalysis; Clusters; Phosphine

1. Introduction

It is now well known that many transition metal carbonyl cluster complexes are efficient catalyst precursors for the hydrogenation of unsaturated organic substrates under homogeneous conditions [1]. However, there are very few examples in which the participation of polynuclear catalytic species in these processes has actually been proved [1–3]; and, in most cases, the nuclearity of the catalytic species is unknown [1,4]. In this context, we have recently reported [2,5] the catalytic activity of the cluster complexes $[Ru_3(\mu\text{-H})(\mu_3,\eta^2\text{-ampy})(CO)_8(PPh_3)]$ [6] (Hampy = 2-amino-6-methylpyridine) and $[Ru_3(\mu\text{-H})(\mu,\eta^1{:}\eta^2\text{-}C_8H_{11}N_2)(CO)_9]$ [7] ($C_8H_{12}N_2$ = 1,2-diamino-4,5-dimethylbenzene) in the homogeneous hydrogenation of diphenylacetylene. Kinetic and chemical studies have demonstrated that the catalytic species are actually trinuclear in the former case [2] and mononuclear in the latter [5].

The results obtained with $[Ru_3(\mu\text{-H})(\mu_3,\eta^2\text{-ampy})(CO)_8(PPh_3)]$ prompted us to study the hydrogenation catalytic activity of the disubstituted derivative $[Ru_3(\mu\text{-H})(\mu_3,\eta^2\text{-ampy})(CO)_7(PPh_3)_2]$ [8]. Disappointingly, under the reaction conditions, this cluster led to catalytically inactive trinuclear compounds [9]. However, since the σ,π-alkenyl derivative $[Ru_3(\mu_3,\eta^2\text{-ampy})(\mu,\eta^1{:}\eta^2\text{-PhC=CHPh})(CO)_7(PPh_3)]$ is a catalytic intermediate for hydrogenation of diphenylacetylene promoted by $[Ru_3(\mu\text{-H})(\mu_3,\eta^2\text{-ampy})(CO)_8(PPh_3)]$ [2], we thought it of interest to study the hydrogenation catalytic activity of the bis(triphenylphosphine)-σ,π-alkenyl derivative $[Ru_3(\mu_3,\eta^2\text{-ampy})(\mu,\eta^1{:}\eta^2\text{-PhC=CH-}$

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$Ph)(CO)_6(PPh_3)_2]$ (**1**). We now describe the synthesis, X-ray structure and hydrogenation catalytic activity of this complex.

2. Results and discussion

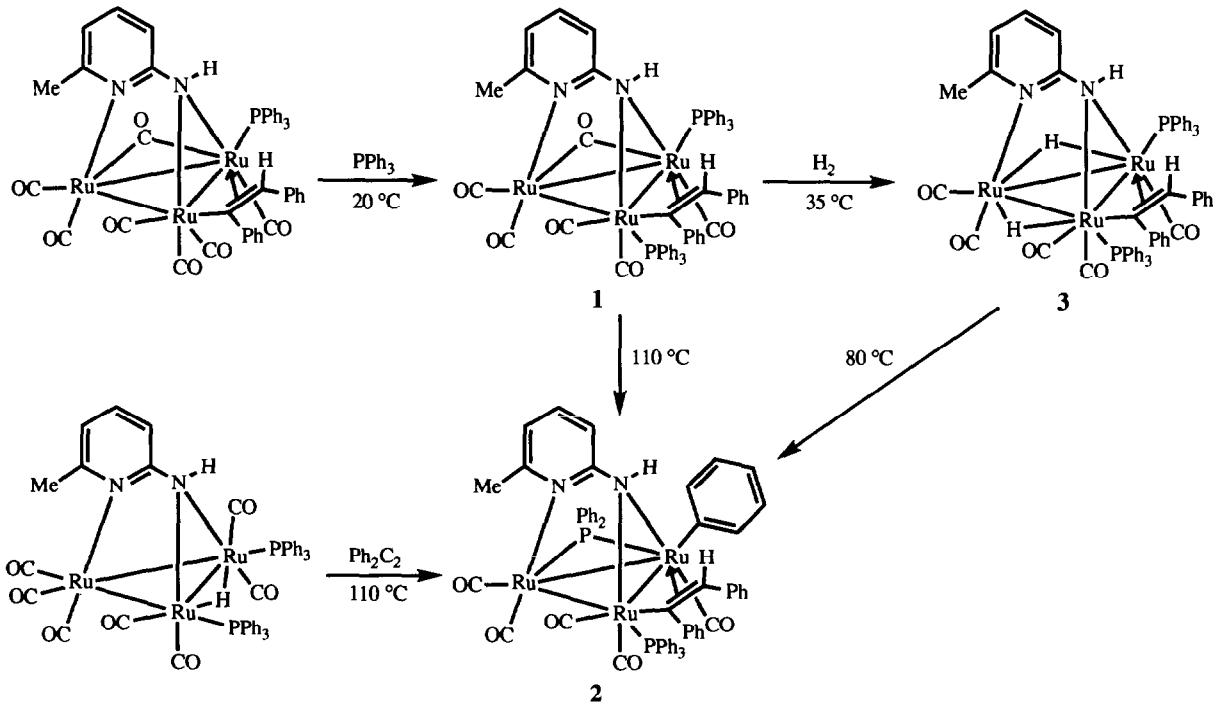
2.1. Synthesis of $[Ru_3(\mu_3,\eta^2\text{-ampy})(\mu,\eta^1{:}\eta^2\text{-PhC=CHPh})(CO)_6(PPh_3)_2]$ (1)

The preparation of complex **1** was attempted by following two different synthetic approaches: (a) the reaction of $[Ru_3(\mu\text{-H})(\mu_3,\eta^2\text{-ampy})(CO)_7(PPh_3)_2]$ with diphenylacetylene, and (b) the reaction of $[Ru_3(\mu_3,\eta^2\text{-ampy})(\mu,\eta^1{:}\eta^2\text{-PhC=CHPh})(CO)_7(PPh_3)]$ with triphenylphosphine.

No reaction was observed when $[Ru_3(\mu\text{-H})(\mu_3,\eta^2\text{-ampy})(CO)_7(PPh_3)_2]$ was treated with diphenylacetylene in THF at reflux temperature. However, a clean reaction took place in refluxing toluene to give the σ-phenyl-μ-diphenyphosphido derivative $[Ru_3(\mu_3,\eta^2\text{-ampy})(\mu,\eta^1{:}\eta^2\text{-PhC=CHPh})(\mu\text{-}PPh_2)(Ph)(CO)_5(PPh_3)]$ (**2**) (Scheme 1). This results contrast with those obtained with the monosubstituted cluster $[Ru_3(\mu\text{-H})(\mu_3,\eta^2\text{-ampy})(CO)_8(PPh_3)]$, which reacts with diphenylacetylene in refluxing THF to give $[Ru_3(\mu_3,\eta^2\text{-ampy})(\mu,\eta^1{:}\eta^2\text{-PhC=CHPh})(CO)_7(PPh_3)]$ [2]. The ^1H and $^{13}C\{^1H\}$ NMR spectra of compound **2** are quite difficult to interpret, but the $^{31}P\{^1H\}$ NMR spectrum shows the presence of one diphenylphosphido group (232.3 ppm, d, $J = 8.2$ Hz) and one triphenylphosphine (42.7 ppm, d, $J = 8.2$ Hz) in the molecule. All these spectroscopic data were insufficient to inequivocally assign a structure to the complex, therefore a single-crystal X-ray diffraction study was carried out. The results of this structural study have already been published as a communication [9] and will not be discussed further here.

It should be noted that complex **2** represents a very rare example of a σ-phenyl cluster complex. Although many examples of activation of P–C bonds of triarylphosphines by transition metal compounds are now known [10], these reactions lead to bridging diphenylphosphide as well as to benzene [11], benzaldehyde [12] or biphenyl [13], but σ-phenyl-μ-diphenylphosphido derivatives have been isolated in very few instances [14], although they have been claimed as intermediates in these processes [13,15].

In contrast, the room temperature reaction of $[Ru_3(\mu_3,\eta^2\text{-ampy})(\mu,\eta^1{:}\eta^2\text{-PhC=CHPh})(CO)_7(PPh_3)]$ with triphenylphosphine gave the expected disubstituted derivative $[Ru_3(\mu_3,\eta^2\text{-ampy})(\mu,\eta^1{:}\eta^2\text{-PhC=CHPh})(CO)_6(PPh_3)_2]$ (**1**) (Scheme 1). Both carbon atoms of the σ,π-coordinated alkenyl were clearly observed in the $^{13}C\{^1H\}$ NMR spectrum of **1** (*C*=CH: 154.1 ppm; C=*C*H: 80.1 ppm), its $^{31}P\{^1H\}$ NMR spec-



Scheme 1.

TABLE 1. Selected bond distances (Å) and angles (°) in complex 1

Ru(1)–Ru(2)	2.8093(7)	Ru(1)–Ru(3)	2.8287(7)
Ru(2)–Ru(3)	2.7690(7)	Ru(1)–N(2)	2.246(5)
Ru(2)–N(1)	2.172(5)	Ru(3)–N(1)	2.125(5)
Ru(2)–P(2)	2.378(2)	Ru(3)–P(3)	2.383(2)
Ru(2)–C(7)	2.275(6)	Ru(2)–C(8)	2.253(6)
Ru(3)–C(8)	2.108(6)	C(7)–C(8)	1.436(9)
Ru(1)–C(1)	1.886(8)	Ru(1)–C(4)	1.972(7)
Ru(1)–C(5)	1.848(8)	Ru(2)–C(2)	1.855(7)
Ru(2)–C(4)	2.135(7)	Ru(3)–C(3)	1.864(7)
Ru(3)–C(6)	1.954(7)		
Ru(1)–C(4)–Ru(2)	86.2(3)	Ru(2)–N(1)–Ru(3)	80.3(2)
Ru(2)–C(8)–Ru(3)	78.8(2)	Ru(2)–C(7)–C(8)	70.7(4)
Ru(2)–C(8)–C(7)	72.4(3)	P(2)–Ru(2)–C(7)	92.9(2)
P(2)–Ru(2)–C(8)	129.7(2)	P(3)–Ru(3)–C(8)	97.6(2)

trum shows the two phosphines as two doublets (40.5 and 37.7 ppm, $J = 35.1$ Hz), and the presence of a bridging carbonyl was indicated by its IR spectrum (1763 cm^{-1}), but again, all these spectroscopic data were not enough to assign unequivocally a structure to the complex, and an X-ray diffraction study was carried out.

2.2. X-ray structure of complex 1

Figure 1 shows the molecular structure of complex 1. Selected bond distances and angles are given in Table 1. The cluster consists of a triangular array of ruthenium atoms with the ampy ligand occupying three axial sites, being bonded to Ru(1) through the pyridine nitrogen and to both Ru(2) and Ru(3) through the amido-fragment. The Ru(2)–Ru(3) edge is also bridged by the alkenyl, which is σ-bonded to Ru(3) and π-bonded to Ru(2). The coordination features of the alkenyl fragment are comparable to those found in other cluster complexes containing this ligand [16]. The coordination shell of the cluster is completed by two triphenylphosphines (in equatorial positions, on Ru(2) and Ru(3), *cis* to the alkenyl) and by six carbonyls (three in axial sites, *trans* to the nitrogen atoms of the ampy, and three in equatorial sites, one of the latter bridging the Ru(1)–Ru(2) edge).

2.3. Catalytic hydrogenation of diphenylacetylene promoted by complex 1

Complex 1 promotes the homogeneous catalytic hydrogenation of diphenylacetylene to a mixture of *cis*- and *trans*-stilbene under mild conditions (80°C, toluene, 1 atm. of H_2). As can be observed from Fig. 2, the catalytic reaction shows an activation period of *ca.* 25 min and undergoes a reduction of the hydrogenation rate after *ca.* 350 min. In order to explain these observations and to obtain information on the mechanism of this reaction, the behaviour of complex 1 in its stoichiometric reaction with dihydrogen and its thermal stability were studied.

Complex 1 releases CO upon reaction with dihydro-

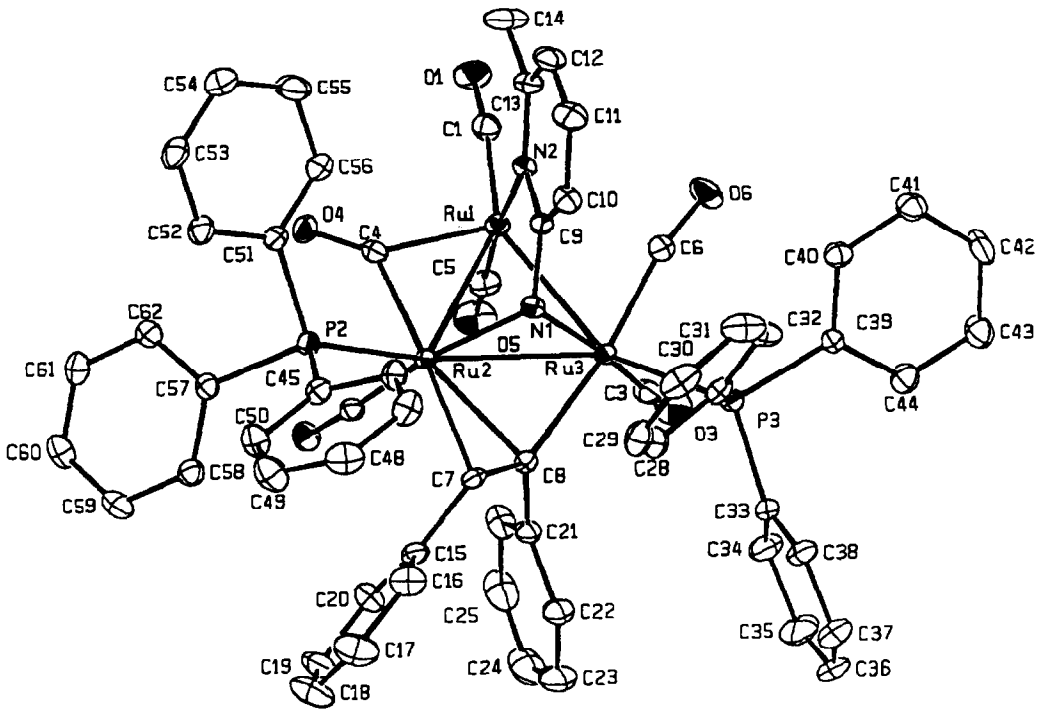


Fig. 1. Molecular structure of complex 1 showing the atom labelling scheme (30% thermal ellipsoids).

gen (35°C, 10.5 h, 1 atm.) to give the dihydride derivative [$Ru_3(\mu$-H)$_2(\mu_3,\eta^2$-ampy)(μ,η^1:η^2-PhC=CHPh)$(CO)_5(PPh_3)_2$] (3) (Scheme 1). This compound is rather unstable and could not be isolated in a pure form, but it was characterized spectroscopically. All the organic ligands were clearly observed in the ^{1}H NMR spectrum, which also shows the hydride resonances (−8.66 ppm, t, J = 5.0 Hz; −10.83 ppm, d, J = 15.8 Hz). The number of CO ligands was deduced from the ^{13}C {^{1}H} NMR spectrum, which shows five carbonyl resonances as well as the signals of all the organic ligands. Two doublets were observed in the ^{31}P{^{1}H} NMR spectrum (48.0 and 43.1 ppm, J = 34.2 Hz). These spectra strongly support the structure proposed for this complex in Scheme 1.

A mechanism for the homogeneous hydrogenation of diphenylacetylene promoted by complex **1** is proposed in Scheme 2. This mechanism implies the engagement of only trinuclear species in the catalytic cycle. It is supported by the fact that complex **3** is the major species observed in the catalytic solutions by IR and NMR spectroscopies. This implies that the transformation of **3**, which already contains coordinated hydrogen and the alkyne, should be the rate-determining step of the catalytic cycle. However, the coupling of a hydride with the alkenyl in **3** to give stilbene cannot be possible in one elemental reaction because the alkenyl α-carbon atom is not *cis* to any of the hydrides. Therefore, the rate-determining step cannot be the reductive elimination of stilbene but a previous isomerization reaction which would place a hydride and the alkenyl α-carbon atom in a *cis* arrangement (**3'**). The release of stilbene from **3'** would give a very unsaturated species which would rapidly add diphenylacetylene and dihydrogen (or CO) to close the catalytic

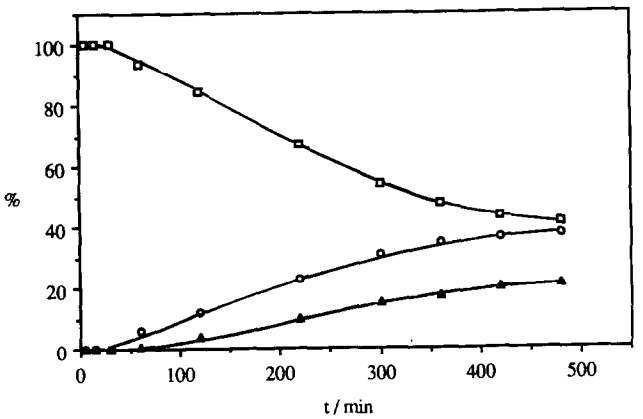
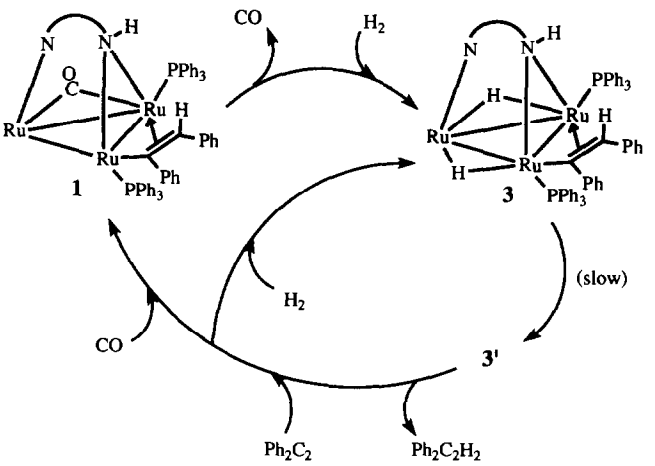


Fig. 2. Progress of the catalytic hydrogenation of diphenylacetylene promoted by complex **1** (reaction conditions: T = 80°C, 8 ml of toluene, $P(H_2)$ = 1 atm, $[1]_{t=0} = 0.146 \times 10^{-2}$ M, $[Ph_2C_2]_{t=0}$ = 0.146 M).



Scheme 2. Proposed mechanism for the catalytic hydrogenation of diphenylacetylene promoted by complex **1**. Terminal CO ligands have been omitted for clarity.

cycle. Unfortunately, the slow reaction rate prevented the measurement of the reaction kinetics which might further support the proposed mechanism. A similar mechanism, which was supported by kinetic experiments, has been proposed for the hydrogenation of diphenylacetylene promoted by [$Ru_3(\mu$-H)$(\mu_3,\eta^2$-ampy)$(CO)_8(PPh_3)$] [2]. In this case, no activation period nor catalyst deactivation were observed.

In the present case, the activation period probably results from the fact that the activation energy for the release of CO from **1** (to create the necessary vacant site for the subsequent reaction with dihydrogen to give **3**) is rather high because **1** contains only six CO ligands (it is known that carbonyl cluster complexes with less than six CO ligands are very difficult to prepare [8]).

Concerning the catalyst deactivation detected in the catalytic reaction after long reaction times (Fig. 2), we observed that the thermolysis of complexes **1** and **3** under nitrogen gave complex **2**, which is catalytically inactive. However, this product was not even detected when the thermolysis reactions were carried out under dihydrogen: complex **1** gave **3**, and **3** gave *cis*- and *trans*-stilbene (GC) and a complex mixture of products which do not contain phosphido ligands (^{31}P NMR). The same mixture of products was observed in the catalytic solutions after long reaction times (^{31}P NMR spectroscopy). These results imply that **2** is not responsible for the catalyst deactivation, and suggest that the catalyst deactivation occurs after the reductive elimination of stilbene from **3'**. At relatively low concentrations (or in the absence) of diphenylacetylene, the unsaturated species formed decompose to give catalyticaly inactive products. Most probably these inactive

products are species containing orthometallated phosphines, because it is well known that the orthometallation of triphenylphosphines in coordinatively unsaturated complexes is an easy process [17]. Unfortunately, we have been unable to isolate and characterize any of these products.

In conclusion, although the catalytic results are far from being of practical importance, the present work is one of the very few examples of the participation of cluster complexes in a homogeneous catalytic reaction [1].

3. Experimental details

Solvents were dried over sodium diphenyl ketyl (THF, diethyl ether, hydrocarbons) or CaH_2 (CH_2Cl_2) and distilled under dinitrogen prior to use. All reactions were carried out under dinitrogen using standard Schlenk techniques and were routinely monitored by solution IR spectroscopy. The compounds $[Ru_3(\mu\text{-H})(\mu_3,\eta^2\text{-ampy})(CO)_7(PPh_3)_2]$ [8] and $[Ru_3(\mu_3,\eta^2\text{-ampy})(\mu,\eta^1{:}\eta^2\text{-PhC=CHPh})(CO)_7(PPh_3)]$ [18] were prepared as described previously. All other reagents (reagent or analytical grade) were used as received from commercial suppliers. IR spectra were recorded on a Perkin-Elmer FT 1720-X spectrophotometer. ^1H and $^{31}P\{^1H\}$ NMR spectra were run at 23°C with Bruker AC-200 and AC-300 instruments, using internal $SiMe_4$ (^1H, ^{13}C) or external 85% H_3PO_4 (^{31}P) as standards ($\delta = 0$ ppm). Microanalyses were obtained from the University of Oviedo Analytical Service. GC analyses were performed at 160°C on a Perkin-Elmer 8600 gas chromatograph, equipped with a 12 m AQ2 capillary column and a flame ionization detector, quantification was achieved with a PE-Nelson 1020 integrator. An Enraf-Nonius CAD4 diffractometer was used for the X-ray diffraction study.

3.1. $[Ru_3(\mu_3,\eta^2\text{-ampy})(\mu,\eta^1:\eta^2\text{-PhC=CHPh})(CO)_6(PPh_3)_2]$ (1)

An excess of triphenylphosphine (157 mg, 0.600 mmol) was added to a solution of $[Ru_3(\mu_3,\eta^2\text{-ampy})(\mu,\eta^1:\eta^2\text{-PhC=CHPh})(CO)_7(PPh_3)]$ (238 mg, 0.227 mmol) in THF (10 ml). The solution was stirred for 14 h, the solvent was removed under reduced pressure, and the solid residue washed with diethyl ether (3 × 8 ml) to give complex **1** as a red powder (180 mg, 62%). Anal. Found: C, 58.08; H, 3.77; N, 2.18. $C_{62}H_{48}N_2O_6P_2Ru_3$ calc.: C, 58.33; H, 3.85; N, 2.09%. IR (THF): ν(CO) 2002 (s), 1968 (m), 1952 (w), 1924 (m), 1901 (m), 1763 (w) cm^{-1}. ^1H NMR ($CDCl_3$): 8–5 (complex mixture of signals); 2.28 (s, Me) ppm. Selected $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 175.2 (s), 161.8 (s), 138.5 (s), 118.3 (s), 112.4 (s), 31.7 (s) (ampy ligand); 154.1 (s) (alkenyl *C*=CH), 80.1 (s) (alkenyl C=*CH*) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): 40.5 (d, $J = 35.1$ Hz), 37.7 (d, $J = 35.1$ Hz) ppm. Crystals of **1** · CH_2Cl_2 suitable for X-ray diffraction studies were obtained by diffusion of pentane layered onto a solution of the complex in dichloromethane at −20°C.

3.2. $[Ru_3(\mu_3,\eta^2\text{-ampy})(\mu,\eta^1:\eta^2\text{-PhC=CHPh})(\mu\text{-}PPh_2)(Ph)(CO)_5(PPh_3)]$ (2)

A toluene solution (10 ml) of $[Ru_3(\mu\text{-H})(\mu_3,\eta^2\text{-ampy})(CO)_7(PPh_3)_2]$ (49.4 mg, 0.044 mmol) and diphenylacetylene (8 mg, 0.045 mmol) was stirred at reflux temperature for 75 min. The solvent was removed under vacuum and the residue washed with diethyl ether (3 × 8 ml) to give the toluene solvate **2** · C_7H_8 as a purple solid (40 mg, 71%). Anal. Found: C, 61.47; H, 4.07; N, 2.00. $C_{61}H_{48}N_2O_5P_2Ru_3 \cdot C_7H_8$ calc.: C, 60.67; H, 4.19; N, 2.08%. IR (THF): ν(CO) 2003 (s), 1968 (w), 1941 (m), 1926 (m), 1912 (sh) cm^{-1}. ^1H NMR ($CDCl_3$): 8.3–5.8 (complex mixture of signals); 5.23 (s, alkenyl CH); 2.82 (s, NH); 2.28 (s, Me); 2.17 (s, toluene Me) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): 232.3 (d, $J = 8.2$ Hz), 42.7 (d, $J = 8.2$ Hz) ppm.

TABLE 2. Crystallographic and refinement data for 1·CH_2Cl_2

Formula	$C_{62}H_{48}N_2O_6P_2Ru_3 \cdot CH_2Cl_2$
Formula weight	1367.17
Crystal system	monoclinic
Space group	$P2_1/c$
a, Å	14.515(2)
b, Å	19.179(3)
c, Å	20.902(11)
β, °	100.63(2)
V, Å^3	5719(3)
Z	4
$F(000)$	2744
D_c, g cm^{-3}	1.588
Crystal size, mm	0.5 × 0.1 × 0.05
Radiation (λ, Å)	Mo Kα (0.71073)
Monochromator	graphite
μ(Mo Kα), cm^{-1}	9.685
Scan-method	θ–2θ
h, k, l range	0–17, 0–22, −24–24
2θ limits, °	2–50
Unique reflections	10060
Reflections with $I \geq 3\sigma(I)$	5819
Variables	689
$R(F)$	0.038
$R_w(F)$ [a]	0.048
GOF	1.186
$(\Delta/\sigma)_{max}$	0.73
Max, min $\Delta\rho$, e Å^{-3}	0.932, −0.165

[a] $w = 4F_0^2/[\sigma^2(I)+(0.06|F_0|^2)^2]$.

3.3. $[Ru_3(\mu\text{-}H)_2(\mu_3,\eta^2\text{-ampy})(\mu,\eta^1{:}\eta^2\text{-PhC=CHPh})(CO)_5(PPh_3)_2]$ (3)

Dihydrogen was bubbled for 10.5 h through a dichloromethane solution (30 ml) of compound **1** (44.2 mg, 0.044 mmol) at reflux temperature. The solvent was removed under reduced pressure to give an oily residue. Its NMR spectra indicated the presence of an almost pure (greater than 95%) compound identified as complex **3**, but all attempts to recrystallize this material led to partial or total decomposition. IR (CH_2Cl_2): ν(CO) 2014 (s), 1967 (sh), 1947 (s), 1921 (sh) cm^{-1}. ^1H NMR (CD_2Cl_2): 8.2–5.9 (complex mixture of signals); 4.81 (d, $J = 8.1$ Hz, alkenyl CH); 2.75 (s, Me); −8.66 (t, $J = 5.0$ Hz, μ–H); −10.83 (d, $J = 15.8$ Hz, μ–H) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 48.0 (d, $J = 34.2$ Hz) 43.1 (d, $J = 34.2$ Hz) ppm. Selected $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 210.9 (d, $J = 5.8$ Hz), 207.2 (s), 204.6 (d, $J = 8.5$ Hz), 202.1 (dd, $J = 11.3$ and 5.5 Hz), 198.3 (d, $J = 5.0$ Hz) (5 CO ligands); 174.4 (s), 160.3 (s), 137.5 (s), 117.1 (s), 111.7 (s), 31.8 (s) (ampy ligand); 153.1 (s) (alkenyl *C*=CH), 70.9 (s) (alkenyl C=*C*H) ppm.

TABLE 3. Fractional atomic coordinates and equivalent isotropic thermal factors for the non-H atoms of $1 \cdot CH_2Cl_2$

Atom	x	y	z	B_{eq} (Å^2) [a]
Ru1	0.09230(3)	0.14984(3)	0.34664(2)	2.51(1)
Ru2	0.16848(3)	0.15562(3)	0.23257(2)	2.023(9)
Ru3	0.24736(3)	0.06614(3)	0.33161(2)	2.084(9)
P2	0.0757(1)	0.17176(8)	0.12734(8)	2.51(3)
P3	0.3229(1)	−0.04450(9)	0.33581(8)	2.52(3)
O1	−0.0330(4)	0.2109(3)	0.4326(2)	4.9(1)
O2	0.2323(3)	0.3040(2)	0.2337(2)	3.9(1)
O3	0.3782(4)	0.1241(3)	0.4484(2)	4.8(1)
O4	0.0127(3)	0.2586(3)	0.2522(2)	4.1(1)
O5	0.2232(4)	0.2606(3)	0.4086(3)	5.5(1)
O6	0.1437(4)	0.0166(3)	0.4397(2)	4.7(1)
N1	0.1404(3)	0.0466(3)	0.2495(2)	2.3(1)
N2	0.0090(3)	0.0588(3)	0.2995(2)	2.5(1)
C1	0.0104(5)	0.1822(4)	0.4005(3)	3.4(2)
C2	0.2106(4)	0.2470(3)	0.2331(3)	2.6(1)
C3	0.3321(4)	0.1022(3)	0.4018(3)	2.9(1)
C4	0.0594(4)	0.2090(3)	0.2686(3)	2.9(1)
C5	0.1742(5)	0.2177(4)	0.3855(3)	3.5(2)
C6	0.1743(5)	0.0390(3)	0.3973(3)	2.9(1)
C7	0.2871(4)	0.1047(3)	0.1920(3)	2.5(1)
C8	0.3147(4)	0.1125(3)	0.2612(3)	2.6(1)
C9	0.0541(4)	0.0212(3)	0.2595(3)	2.3(1)
C10	0.0173(5)	−0.0400(4)	0.2294(3)	3.3(1)
C11	−0.0693(5)	−0.0620(4)	0.2376(4)	4.2(2)
C12	−0.1174(5)	−0.0226(4)	0.2752(4)	4.3(2)
C13	−0.0783(4)	0.0365(4)	0.3066(3)	3.4(1)
C14	−0.1314(5)	0.0788(5)	0.3474(5)	5.9(2)
C15	0.3332(4)	0.1380(4)	0.1406(3)	3.0(1)
C16	0.3325(5)	0.1008(4)	0.0845(4)	4.6(2)
C17	0.3729(7)	0.1264(6)	0.0330(4)	6.7(2)
C18	0.4153(6)	0.1908(6)	0.0391(4)	6.7(2)
C19	0.4153(6)	0.2288(5)	0.0952(4)	5.4(2)
C20	0.3752(5)	0.2025(4)	0.1444(3)	3.9(2)
C21	0.4037(4)	0.1536(4)	0.2842(3)	3.3(1)
C22	0.4864(5)	0.1301(5)	0.2666(4)	5.1(2)
C23	0.5699(6)	0.1690(6)	0.2854(5)	8.2(3)
C24	0.5692(6)	0.2292(5)	0.3197(5)	7.4(3)
C25	0.4902(6)	0.2502(5)	0.3382(4)	5.9(2)
C26	0.4072(5)	0.2139(4)	0.3217(4)	4.3(2)
C27	0.2746(4)	−0.1001(4)	0.2659(3)	2.9(1)
C28	0.2881(5)	−0.0773(4)	0.2048(4)	3.7(2)
C29	0.2518(6)	−0.1145(4)	0.1496(4)	4.5(2)
C30	0.1988(6)	−0.1712(5)	0.1528(4)	5.2(2)
C31	0.1827(5)	−0.1943(4)	0.2125(4)	5.2(2)
C32	0.2225(5)	−0.1592(4)	0.2698(4)	4.2(2)
C33	0.4487(4)	−0.0484(3)	0.3338(3)	3.0(1)
C34	0.5082(5)	−0.0010(4)	0.3700(4)	4.6(2)
C35	0.6057(5)	−0.0078(5)	0.3730(5)	6.7(3)
C36	0.6406(5)	−0.0598(5)	0.3425(5)	5.8(2)
C37	0.5831(6)	−0.1062(5)	0.3066(5)	5.8(2)
C38	0.4864(5)	−0.1018(4)	0.3021(4)	4.3(2)
C39	0.3153(4)	−0.0969(3)	0.4087(3)	2.9(1)
C40	0.2283(5)	−0.1159(4)	0.4223(4)	3.4(2)
C41	0.2180(5)	−0.1506(4)	0.4781(4)	3.9(2)
C42	0.2976(6)	−0.1670(4)	0.5218(4)	5.2(2)
C43	0.3848(6)	−0.1500(5)	0.5097(4)	5.2(2)
C44	0.3931(5)	−0.1149(4)	0.4534(4)	3.9(2)
C45	0.0968(4)	0.1137(4)	0.0618(3)	3.0(1)
C46	0.0990(5)	0.0423(4)	0.0742(3)	3.2(2)
C47	0.1134(5)	−0.0054(4)	0.0273(4)	4.1(2)
C48	0.1271(6)	0.0180(4)	−0.0320(4)	4.9(2)
C49	0.1240(6)	0.0871(4)	−0.0446(4)	5.1(2)
C50	0.1075(6)	0.1357(4)	0.0002(4)	4.1(2)
C51	−0.0530(4)	0.1625(3)	0.1158(3)	2.7(1)
C52	−0.1074(5)	0.1776(4)	0.0541(3)	3.5(2)
C53	−0.2024(5)	0.1707(4)	0.0444(4)	4.2(2)
C54	−0.2470(5)	0.1489(5)	0.0931(5)	5.2(2)
C55	−0.1956(5)	0.1334(5)	0.1534(4)	5.1(2)
C56	−0.0985(5)	0.1402(4)	0.1639(4)	4.1(2)
C57	0.0887(4)	0.2599(3)	0.0968(3)	2.7(1)
C58	0.1670(5)	0.2787(4)	0.0717(3)	3.3(2)
C59	0.1792(5)	0.3464(4)	0.0534(3)	4.0(2)
C60	0.1146(6)	0.3973(4)	0.0625(4)	4.3(2)
C61	0.0392(5)	0.3797(4)	0.0882(4)	4.0(2)
C62	0.0241(5)	0.3117(4)	0.1057(3)	3.0(1)
Cl1	−0.5358(4)	−0.0647(3)	0.0780(3)	15.0(2) [b]
Cl2	−0.3546(5)	−0.0293(4)	0.1459(4)	22.7(3) [b]
C63	−0.453(2)	−0.002(1)	0.127(1)	21.6(9) [b]

[a] $B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}a_i \cdot a_j$. [b] B_{iso}.

3.4. Thermolysis of complex 1

A solution of complex **1** (29 mg, 0.023 mmol) in toluene (5 ml) was stirred at reflux temperature for 15 min. The IR spectrum of the solution obtained showed complete transformation of complex **1** into complex **2**.

3.5. Thermolysis of complex 3

An unweighed amount of complex **3** (prepared *in situ*, as described above, from 50 mg of compound **1**

and dihydrogen) was stirred in THF (15 ml) at reflux temperature for 4 h. The IR spectrum of the solution obtained showed the complete transformation of complex **3** into complex **2**.

3.6. Thermolysis of complex 3 in a dihydrogen atmosphere

A stream of dihydrogen was bubbled for 4 h through a toluene solution (10 ml) of complex **3** (prepared *in situ*, as described above, from 50 mg of compound **1** and dihydrogen) at 80°C. The solvent was removed under vacuum and the residue analyzed by $^{31}P\{^1H\}$ NMR spectroscopy. The spectrum showed the resonances of a small amount of complex **3** accompanied by several singlet and doublet resonances in the 60–20 ppm region (no signals were observed above 60 ppm).

3.7. Catalytic hydrogenation of diphenylacetylene promoted by complex 1

Complex **1** (15 mg, 0.0117 mmol) and diphenylacetylene (208.2 mg, 1.17 mmol) were placed in a two-necked 25 ml flask; one neck was connected to a gas burette, which was in turn connected to a vacuum line. The flask was closed by a silicone septum and the system evacuated and filled with dihydrogen five times. Degassed toluene (8 ml) was then introduced into the flask and the pressure adjusted to 1 atm. in the gas burette. The flask was immersed in a thermostatted bath at 80°C and shaken at 600 min^{-1} with a Selecta shaker. An equilibration time of 5 min was allowed before acquiring any data. The catalytic reaction was followed by gas chromatography (Fig. 1).

In an attempt to characterize the catalytic intermediates, complex **1** (13 mg, 0.010 mmol), diphenylacetylene (21.5 mg, 0.119 mmol) and toluene-d_8 (0.8 ml) were placed in an NMR tube. Dihydrogen was bubbled continuously through the solution and the tube was immersed in a thermostatted bath at 80°C. After 1 h, the $^{31}P\{^1H\}$ NMR spectrum showed the signals of complex **3** accompanied by a group of low intensity signals in the 60–20 ppm region. After 5 h, the $^{31}P\{^1H\}$ NMR spectrum showed that complex **3** was a minor component of the mixture, while the intensity of the group of signals in the 60–20 ppm region had increased considerably. The pattern of these group of signals is comparable with that observed when complex **3** was thermolysed under a dihydrogen atmosphere (see above).

3.8. Crystal structure determination of $1 \cdot CH_2Cl_2$

The crystal data are summarised in Table 2. The cell dimensions were refined by least-squares methods from the setting angles of 25 centred reflections with $17 \leq 2\theta \leq 22°$. Intensities were collected by the θ–2θ scan method. Three standard reflections were measured every hour, revealing no intensity fluctuations. One set of reflections was collected up to $2\theta = 50°$. Lorentz and polarization corrections were applied. An absorption correction was applied using the DIFABS procedure.

The structure was solved by direct methods and successive Fourier difference syntheses, and was refined by full-matrix least-squares methods. After refinement of positional and anisotropic thermal parameters (β_{ij}) for the non-hydrogen atoms, the positions of the H atoms were calculated (C–H = 0.95 Å, $B_{eq} = 4$ Å^2) and included as a fixed contribution to F_c. Scattering factors and corrections for anomalous dispersion were taken from Ref. 19. All calculations were performed on a Micro Vax 3100 computer, using the Enraf-Nonius MoLen program package [20]. The final atomic coordinates are given in Table 3. Full data have been deposited with the Cambridge Crystallographic Data Centre.

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