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Reactivity of a cationic triruthenium hydridoalkenylcarbonyl cluster complex toward nucleophilic reagents. Carbonyl substitution versus alkene elimination reactions

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Abstract

The reactions of the cationic hydridoalkenyl cluster complex $[\text{Ru}_3(\mu\text{-H})(\mu_3\text{-ampy})(\mu\text{-PhC=CHPh})(\text{CO})_8][\text{BF}_4]$ (**1**) (Hampy = 2-amino-6-methylpyridine) with neutral and anionic nucleophiles have been studied. Complex **1** reacts with different amounts of triphenylphosphine to replace CO giving $[\text{Ru}_3(\mu\text{-H})(\mu_3\text{-ampy})(\mu\text{-PhC=CHPh})(\text{PPh}_3)(\text{CO})_7][\text{BF}_4]$ (two isomers), $[\text{Ru}_3(\mu\text{-H})(\mu_3\text{-ampy})(\mu\text{-PhC=CHPh})(\text{PPh}_3)_2(\text{CO})_6][\text{BF}_4]$ and $[\text{Ru}_3(\mu\text{-H})(\mu_3\text{-ampy})(\mu\text{-PhC=CHPh})(\text{PPh}_3)_3(\text{CO})_5][\text{BF}_4]$ (two isomers). Analogous results are obtained using tri-4-tolylphosphine. The reaction of compound **1** with two equivalents of bis(diphenylphosphino)methane (dppm) induces the reductive elimination of *cis*-stilbene, yielding $[\text{Ru}_3(\mu_3\text{-ampy})(\mu\text{-dppm})(\text{dppm})(\text{CO})_7][\text{BF}_4]$. Complex **1** undergoes deprotonation upon treatment with NaOMe to give $[\text{Ru}_3(\mu_3\text{-ampy})(\mu\text{-PhC=CHPh})(\text{CO})_8]$. However, a similar reaction with NaOH yields *cis*-stilbene and the neutral hydride $[\text{Ru}_3(\mu\text{-H})(\mu_3\text{-ampy})(\text{CO})_9]$.

Keywords: Ruthenium; Cluster; Carbonyl; Alkenyl; Cationic clusters; Phosphine ligands

1. Introduction

Cationic carbonyl metal cluster compounds not containing hydride ligands are still very rare [1–4]. In most cases, they have been prepared by chemical oxidation of their neutral precursors [2] or by addition of $[\text{M}(\text{PPh}_3)]^+$ ($\text{M} = \text{Cu}, \text{Ag}, \text{or Au}$) fragments to compounds with electron-rich metal–metal bonds [3].

Recently, we have succeeded in the preparation of the first cationic 48-electron triruthenium carbonyl cluster compound without hydride ligands [4], $[\text{Ru}_3(\mu\text{-ampy})(\text{CO})_{10}][\text{BF}_4]$ (Hampy = 2-amino-6-methylpyridine), and we have shown that this complex has a rich and unusual derivative chemistry [5]. The synthesis of $[\text{Ru}_3(\mu\text{-ampy})(\text{CO})_{10}][\text{BF}_4]$ involves the reaction of the cationic hydridoalkenyl complex $[\text{Ru}_3(\mu\text{-H})(\mu_3\text{-ampy})(\mu\text{-PhC=CHPh})(\text{CO})_8][\text{BF}_4]$ (**1**) with carbon monoxide (Scheme 1) [4]. The result of this reaction seems to show that the formation of the non-hydridic

cationic cluster complex is preceded by the reductive elimination of the corresponding alkene, which is in turn induced by the addition of a 2-electron donor nucleophile (CO) to complex **1**.

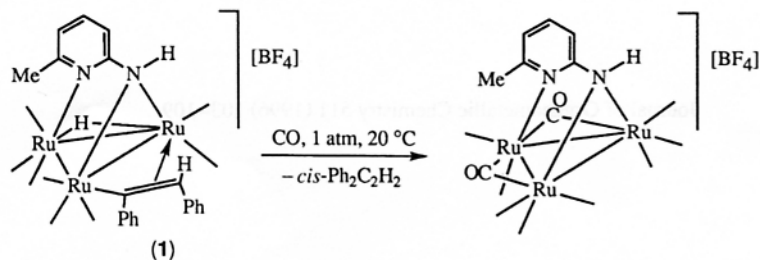
This article reports the reactivity of complex **1** with phosphines and other neutral and anionic nucleophilic reagents. We carried out this study in order to establish whether the chemical behaviour shown in Scheme 1 could be extended to 2-electron donor nucleophiles other than CO. This would imply, for neutral nucleophiles, that cationic hydrido-alkenyl cluster compounds, which can be easily made by protonation of neutral alkenyl clusters [6], are convenient starting materials for the synthesis of non-hydridic cationic cluster complexes.

2. Results and discussion

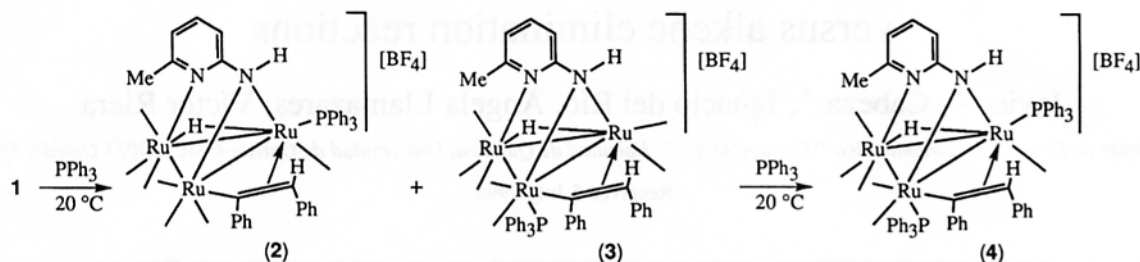
2.1. Reactions with neutral nucleophiles

The reaction of $[\text{Ru}_3(\mu\text{-H})(\mu_3\text{-ampy})(\mu\text{-PhC=CHPh})(\text{CO})_8][\text{BF}_4]$ (**1**) with one equivalent of triph-

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Scheme 1.



Scheme 2.

enylphosphine led to a mixture of two isomeric complexes (2 and 3; Scheme 2) which could not be separated. The same mixture was obtained when the neutral phosphine-substituted alkenyl cluster $[\text{Ru}_3(\mu_3\text{-ampy})(\mu\text{-PhC=CHPh})(\text{PPh}_3)(\text{CO})_7]$ [7] was protonated with $\text{HBF}_4 \cdot \text{OEt}_2$ (Scheme 3). Their NMR spectra (Tables 1 and 2) are consistent with the presence of alkenyl, hydride and PPh_3 ligands in the complexes. However, the exact position of the phosphines in the clusters could not be determined directly by spectroscopic methods, but was inferred by comparing the NMR spectra of 2 and 3 with those of the disubstituted complex 4 (see below).

Complex 1 reacted with two equivalents of triph-

enylphosphine to give a single product, the disubstituted derivative $[\text{Ru}_3(\mu\text{-H})(\mu_3\text{-ampy})(\mu\text{-PhC=CHPh})(\text{PPh}_3)_2(\text{CO})_6][\text{BF}_4]$ (4). This implies that both mono-substituted complexes 2 and 3 react with triphenylphosphine to give the same disubstituted product (Scheme 2). Complex 4 was also prepared by treating the X-ray-characterized neutral disubstituted precursor $[\text{Ru}_3(\mu_3\text{-ampy})(\mu\text{-PhC=CHPh})(\text{PPh}_3)_2(\text{CO})_6]$ [8] with $\text{HBF}_4 \cdot \text{OEt}_2$ (Scheme 3). The spectroscopic data of complex 4 (Tables 1 and 2) indicate that both phosphines are in the same positions as in the neutral compound $[\text{Ru}_3(\mu_3\text{-ampy})(\mu\text{-PhC=CHPh})(\text{PPh}_3)_2(\text{CO})_6]$ [8]. The ^1H NMR spectrum shows the hydride resonance as a doublet (note that in complexes 2 and 3 the hydride resonances

Table 1
Selected ^1H NMR data for compounds 2–6^a

Compound	H ¹	H ²	H ³	H ⁴	H ⁵	NH	Me
2 ^b	−11.32 (d) [15.7] ^c	4.10 (s) ^c	^d	^d	^d	4.96 (s) ^c	2.67 (s)
3 ^b	−12.20 (s)	4.13 (s)	^d	^d	^d	5.38 (s) ^c	2.86 (s)
4 ^b	−11.48 (d) [15.7] ^c	5.83 (d) [7.9] ^c	5.84 (d) [7.8]	6.49 (t) [7.8]	6.12 (d) [7.8]	2.45 (d) ^c [3.3]	2.65 (s)
5 ^f	−11.32 (t) [13.0] ^{c,g}	4.37 (d) [8.0] ^c	5.38 (d) [7.8]	5.95 (t) [7.8]	5.64 (d) [7.8]	2.71 (d) ^c [5.0]	2.22 (s)
6 ^f	−10.29 (dd) [13.1] ^c [7.7] ^g	4.43 (d) [8.1] ^c	6.32 (d) [7.8]	^d	6.56 (d) [7.8]	2.65 (s) ^c	2.13 (s)

^a Assignments as in Fig. 1, chemical shifts (δ) in ppm, multiplicities in parentheses, coupling constants (Hz) in square brackets.

^b In CDCl_3 .

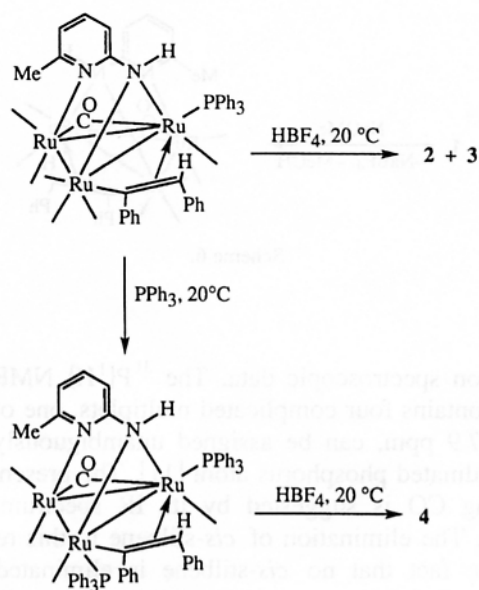
^c Broad signal.

^d Obscured by other signals.

^e $J(\text{H-P}^1)$.

^f In CD_2Cl_2 .

^g $J(\text{H-P}^3)$.



Scheme 3.

are a doublet and a singlet respectively) and the ^{31}P chemical shifts of the phosphines are similar to those observed for the mixture of complexes **2** and **3**. These data strongly support the structural assignments depicted for compounds **2**, **3** and **4** in Scheme 2 and Fig. 1.

Thus, the addition of one or two equivalents of triphenylphosphine to solutions of complex **1** does not induce the reductive elimination of *cis*-stilbene, but leads to CO-replacement. In order to prepare non-hydridic cationic compounds, the reaction of complex **1** with a large excess of triphenylphosphine (1:4 mol ratio) was carried out. At room temperature, only the disubstituted derivative **4** was formed, but under more forcing conditions (1,2-dichloroethane, reflux tempera-

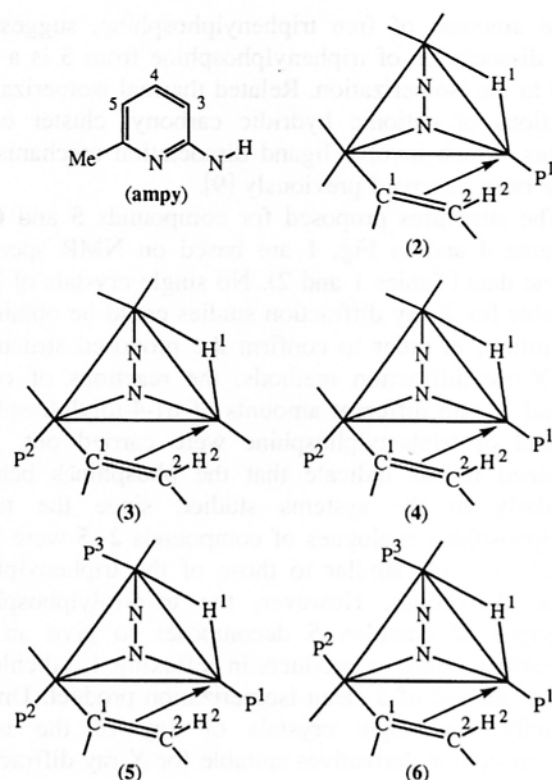


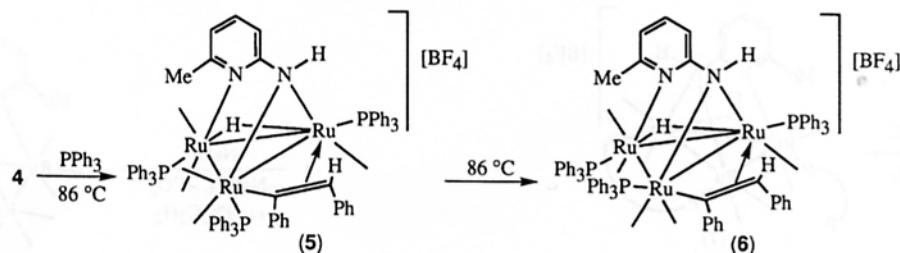
Fig. 1. Atomic labelling scheme used for NMR assignments in Tables 1 and 2. Axial CO ligands have been omitted for clarity.

ture, 15 min), a trisubstituted derivative, $[\text{Ru}_3(\mu\text{-H})(\mu_3\text{-ampy})(\mu\text{-PhC=CHPh})(\text{PPh}_3)_3(\text{CO})_5][\text{BF}_4]$ (**5**), was obtained (Scheme 4). Curiously, the use of longer reaction times (ca. 2.5 h) led to an isomer (**6**) of complex **5** while the intermediacy of complex **5** was observed by IR spectroscopy. In subsequent experiments we proved that the rate of this isomerization reaction is strongly retarded when the solution contains

Table 2
 $^{31}\text{P}\{^1\text{H}\}$ NMR data for compounds **2**–**6**^a

Compound	$\delta(\text{P}^1)$	$\delta(\text{P}^2)$	$\delta(\text{P}^3)$	$J(\text{P}^1\text{--P}^2)$	$J(\text{P}^1\text{--P}^3)$	$J(\text{P}^2\text{--P}^3)$
2 ^b	48.8 (s)					
3 ^b		31.8 (s)				
4 ^b	46.0 (d)	37.1 (d)		20.0		
5 ^c	48.5 (t)	38.2 (dd)	25.8 (dd)	23.0	23.0	6.3
6 ^c	48.1 (t)	34.1 (d)	23.9 (d)	28.6	28.6	0

^a Assignments as in Fig. 1, chemical shifts (δ) in ppm, multiplicities in parentheses, coupling constants J in Hz. ^b In CDCl_3 . ^c In CD_2Cl_2 .



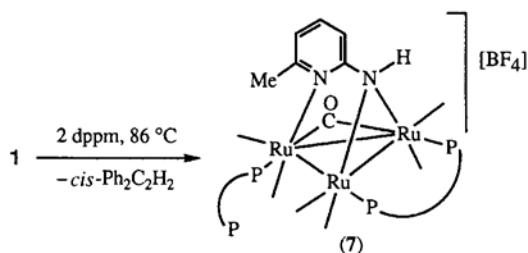
Scheme 4.

large amounts of free triphenylphosphine, suggesting that dissociation of triphenylphosphine from **5** is a key step in the isomerization. Related thermal isomerization reactions of cationic hydridic carbonyl cluster complexes, which involve ligand dissociation mechanisms, have been observed previously [9].

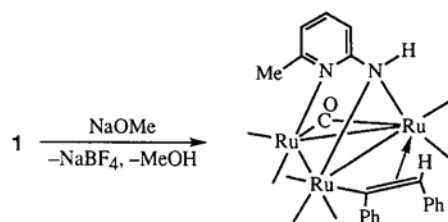
The structures proposed for compounds **5** and **6** in Scheme 4 and in Fig. 1 are based on NMR spectroscopic data (Tables 1 and 2). No single crystals of **2–6** suitable for X-ray diffraction studies could be obtained. Therefore, in order to confirm the proposed structures by X-ray diffraction methods, the reactions of compound **1** with different amounts of tri-4-tolylphosphine instead of triphenylphosphine were carried out. The obtained results indicate that the phosphines behave similarly in the systems studied since the tri-4-tolylphosphine analogues of compounds **2–5** were prepared in yields similar to those of the triphenylphosphine derivatives. However, the tri-4-tolylphosphine analogue of complex **5** decomposes to give an intractable mixture of products in refluxing 1,2-dichloroethane instead of a clean isomerization product. Unfortunately, no single crystals of any of the tri-4-tolylphosphine derivatives suitable for X-ray diffraction studies could be obtained.

Bis(diphenylphosphino)methane (dppm) is more basic than triphenylphosphine and the presence of the methylene group between the two phosphorus atoms often forces it to coordinate to two different metal atoms [9c,10]. Because of this, and after checking that triphenylphosphine does not induce the reductive elimination of *cis*-stilbene from complex **1** in any case, we decided to study the reactivity of complex **1** with dppm.

Compound **1** reacts with one equivalent of dppm to give a complex mixture of products which could not be separated. ^1H and ^{31}P NMR spectra of the mixture indicated the presence of starting material, complexes containing bridging dppm and complexes containing bridging and monocoordinated dppm. Fortunately, the reaction of complex **1** with two equivalents of dppm allowed the isolation of a pure product, $[\text{Ru}_3(\mu_3\text{-ampy})(\mu\text{-dppm})(\text{dppm})(\text{CO})_7][\text{BF}_4]$ (**7**). A GC analysis of the solution confirmed the presence of *cis*-stilbene. The structure proposed for compound **7** in Scheme 5 is



Scheme 5.



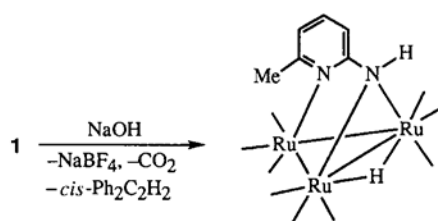
Scheme 6.

based on spectroscopic data. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum contains four complicated multiplets, one of them, at -17.9 ppm, can be assigned unambiguously to an uncoordinated phosphorus atom [11]. The presence of a bridging CO is suggested by its IR spectrum (1798 cm^{-1}). The elimination of *cis*-stilbene in this reaction, and the fact that no *cis*-stilbene is eliminated when tertiary phosphines are used, suggests that a bridging dppm occupies the coordination sites previously occupied by the alkenyl in complex **1**. Compound **7** is a rare example of a cationic cluster complex which contains no hydride ligands. However, despite attempts, no single crystals of this compound could be obtained and its structure could not be confirmed by X-ray diffraction methods.

We also carried out the reactions of compound **1** with the neutral nucleophiles PhNCS , $^t\text{BuNCO}$, $^t\text{BuNC}$, CS_2 , C_2H_2 , PhC_2H , Ph_2C_2 and C_2H_4 , but we were unable to isolate and characterize pure products.

2.2. Reactions with anionic nucleophiles

The reaction of complex **1** with sodium methoxide led to the known neutral alkenyl complex $[\text{Ru}_3(\mu_3\text{-ampy})(\mu\text{-PhC=CHPh})(\text{CO})_8]$ [6] (Scheme 6). However, an analogous reaction with sodium hydroxide led to *cis*-stilbene and to the known neutral hydride $[\text{Ru}_3(\mu\text{-H})(\mu_3\text{-ampy})(\text{CO})_9]$ [12] (Scheme 7). It seems that the methoxide anion prefers to deprotonate complex **1** whereas the hydroxide anion prefers to attack a coordinated CO to form CO_2 and a hydride ligand. A reductive elimination of the alkene from this intermediate would lead to a neutral unsaturated heptacarbonyl-hydrido derivative which would partially decompose to



Scheme 7.

give $[\text{Ru}_3(\mu\text{-H})(\mu_3\text{-ampy})(\text{CO})_9]$. So far, this different reactivity of the methoxide and hydroxide anions is unclear, since the formation of methoxycarbonyl ligands by nucleophilic attack of methoxide anions on coordinated CO of other cationic hydrido carbonyl clusters is an easy process [9] and the attack of hydroxide anions on coordinated CO to give hydrido derivatives is also known [5,13].

The reactions of complex **1** with some other anionic nucleophiles ($[\text{Bu}_4\text{N}]\text{I}$, $[\text{Et}_4\text{N}]\text{CN}$, $[\text{PPN}]\text{Cl}$, $[\text{PPN}]\text{NO}_2$) were also studied. In most cases, the presence of *cis*-stilbene in the solutions was confirmed by GC chromatography, but we were unable to isolate and characterize any pure product.

3. Experimental details

3.1. General data

Solvents were dried over sodium diphenyl ketyl (diethyl ether, hydrocarbons) or CaH_2 (dichloromethane, 1,2-dichloroethane) and distilled under dinitrogen prior to use. The reactions were carried out under dinitrogen (Schlenk-vacuum line techniques) and were monitored by solution IR spectroscopy (carbonyl stretching region). The compounds **1** [6], $[\text{Ru}_3(\mu_3\text{-ampy})(\mu\text{-PhC=CHPh})(\text{PPh}_3)(\text{CO})_7]$ [7] and $[\text{Ru}_3(\mu_3\text{-ampy})(\mu\text{-PhC=CHPh})(\text{PPh}_3)_2(\text{CO})_6]$ [8] were prepared as described previously. A ^{13}CO -enriched sample of compound **1** was prepared from ^{13}CO -enriched $[\text{Ru}_3(\text{CO})_{12}]$ [14]. This sample was subsequently used to make ^{13}CO -enriched **4–6**. All other reagents (reagent grade) were used as-received from commercial suppliers. Microanalyses were obtained by the University of Oviedo Analytical Service. IR spectra were recorded in solution with a Perkin-Elmer FT 1720-X spectrophotometer, using 0.1 mm CaF_2 cells. NMR spectra were run at 20°C in Bruker AC-200 and AC-300 spectrometers, using internal SiMe_4 (^1H , ^{13}C) or external 85% H_3PO_4 (^{31}P) as standards ($\delta = 0$ ppm). GC analyses were carried out with a Perkin-Elmer 8600 gas chromatograph, equipped with a 30 m Supelcowax-10TM capillary column (i.d. 0.25 mm) and a flame ionization detector.

3.2. Reaction of complex **1** with 1 equiv. PPh_3

A solution of PPh_3 (15 mg, 0.057 mmol) and complex **1** (50 mg, 0.055 mmol) in dichloromethane (10 ml) was stirred for 30 min. The solvent was removed under reduced pressure and the residue washed with diethyl ether (2×10 ml) to give a brown solid (40 mg, 64%) which consisted of a 2:3 mixture of the isomeric complexes **2** and **3** (by ^1H and ^{31}P NMR integration, Tables 1 and 2) and could not be separated. Anal.

Found: C, 45.83; H, 2.68; N, 2.29. $\text{C}_{45}\text{H}_{34}\text{BF}_4\text{N}_2\text{O}_7\text{PRu}_3$. Calc.: C, 46.33; H, 2.94; N, 2.40%.

3.3. Reaction of $[\text{Ru}_3(\mu_3\text{-ampy})(\mu\text{-PhC=CHPh})(\text{PPh}_3)(\text{CO})_7]$ with HBF_4

An excess of $\text{HBF}_4 \cdot \text{OEt}_2$ (ca. 0.5 ml) was added dropwise to a solution of $[\text{Ru}_3(\mu_3\text{-ampy})(\mu\text{-PhC=CHPh})(\text{PPh}_3)(\text{CO})_7]$ (50 mg, 0.048 mmol) in dichloromethane (5 ml). The original red changed immediately to brown. The solvent was removed under reduced pressure and the residue washed with diethyl ether (3×5 ml) to give a brown solid (48 mg, 86%). The IR and ^1H and ^{31}P NMR spectra of this solid indicated a ca. 1:1 mixture of compounds **2** and **3**.

3.4. Preparation of $[\text{Ru}_3(\mu\text{-H})(\mu_3\text{-ampy})(\mu\text{-PhC=CHPh})(\text{PPh}_3)_2(\text{CO})_6][\text{BF}_4]$ (**4**)

A solution of complex **1** (49 mg, 0.054 mmol) and PPh_3 (30 mg, 0.114 mmol) in dichloromethane (10 ml) was stirred at room temperature for 3 h. The solvent was removed under reduced pressure and the residue washed with diethyl ether (2×10 ml) and dried under vacuum to give complex **4** as a very dark brown, nearly black, solid (50 mg, 68%). Anal. Found: C, 54.75; H, 3.82; N, 1.95. $\text{C}_{62}\text{H}_{49}\text{BF}_4\text{N}_2\text{O}_6\text{P}_2\text{Ru}_3$. Calc.: C, 54.36; H, 3.61; N, 2.05%. IR (CH_2Cl_2): 2088 (vs), 2028 (vs), 1966 (m), 1953 (sh) cm^{-1} . $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): $\delta(\text{CO})$ 204.3 (d, $J = 14$ Hz, 1 C), 201.3 (d, $J = 9$ Hz, 1 C), 201.0 (s, 2 C), 198.7 (s, 1 C), 182.9 (s, 1 C); $\delta(\text{ampy})$: 173.5, 158.3, 141.7, 120.3, 113.0, 30.3 (all singlets); $\delta(\text{alkenyl})$: 217.3 (t, $J = 9.4$ Hz, C^1), 76.3 (s, C^2) ppm.

3.5. Reaction of $[\text{Ru}_3(\mu_3\text{-ampy})(\mu\text{-PhC=CHPh})(\text{PPh}_3)_2(\text{CO})_6]$ with HBF_4

An excess of $\text{HBF}_4 \cdot \text{OEt}_2$ (ca. 0.5 ml) was added dropwise to a solution of $[\text{Ru}_3(\mu_3\text{-ampy})(\mu\text{-PhC=CHPh})(\text{PPh}_3)_2(\text{CO})_6]$ (50 mg, 0.039 mmol) in dichloromethane (5 ml). The colour changed from red to brown. The solvent was removed under reduced pressure and the residue washed with diethyl ether (3×5 ml) to give complex **4** (45 mg, 84%).

3.6. Preparation of $[\text{Ru}_3(\mu\text{-H})(\mu_3\text{-ampy})(\mu\text{-PhC=CHPh})(\text{PPh}_3)_3(\text{CO})_5][\text{BF}_4]$ (**5**)

A solution of complex **1** (50 mg, 0.055 mmol) and PPh_3 (58.1 mg, 0.222 mmol) in 1,2-dichloroethane (10 ml) was stirred at reflux temperature for 15 min. The solvent was removed under reduced pressure and the residue washed with diethyl ether (2×10 ml) to give

complex **5** as a violet solid (75 mg, 84%). Anal. Found: C, 59.26; H, 4.12; N, 1.63. $C_{79}H_{64}BF_4N_2O_5P_3Ru_3$. Calc.: C, 59.15; H, 4.02; N, 1.75%. IR (THF): 2037 (vs), 2000 (m), 1977 (m), 1953 (w), 1929 (m) cm^{-1} . $^{13}C\{^1H\}$ NMR (CD_2Cl_2): $\delta(CO)$ 207.3 (d, $J = 15$ Hz, 1 C), 206.0 (d, $J = 9$ Hz, 1 C), 203.0 (s, 1 C), 201.9 (d, $J = 10$ Hz, 1 C), 194.7 (s, 1 C); $\delta(ampy)$: 175.3, 160.7, 139.4, 119.9, 111.7, 31.0 (all singlets); $\delta(alkenyl)$: 211.0 (t, $J = 9.8$ Hz, C^1), 76.6 (s, C^2) ppm.

3.7. Isomerization of complex **5** into complex **6**

A solution of complex **5** (50 mg, 0.031 mmol) in 1,2-dichloroethane (10 ml) was stirred at reflux temperature for 2.5 h. The colour changed from violet to dark green. The solvent was removed under reduced pressure and the residue washed with diethyl ether (2×10 ml) to give compound **6** as a green solid (44 mg, 88%). Anal. Found: C, 59.46; H, 3.96; N, 1.62. $C_{79}H_{64}BF_4N_2O_5P_3Ru_3$. Calc.: C, 59.15; H, 4.02; N, 1.75%. IR (CH_2Cl_2): 2058 (w), 2029 (vs), 1975 (s), 1940 (m), 1928 (m) cm^{-1} . $^{13}C\{^1H\}$ NMR (CD_2Cl_2): $\delta(CO)$ 208.9 (d, $J = 14$ Hz, 1 C), 204.4 (m, 3 C), 195.1 (d, $J = 4$ Hz, 1 C); $\delta(ampy)$: 172.8, 161.2, 140.4, 119.3, 112.9, 30.2 (all singlets); $\delta(alkenyl)$: 171.5 (s, C^1), 82.3 (s, C^2) ppm.

3.8. Preparation of $[Ru_3(\mu_3-ampy)(\mu-dppm)(dppm)(CO)_7][BF_4]$ (**7**)

A solution of dppm (48 mg, 0.123 mmol) and complex **1** (55.4 mg, 0.061 mmol) in 1,2-dichloroethane (10 ml) was stirred at reflux temperature for 15 min. A GC analysis of the solution confirmed the presence of *cis*-stilbene. The solvent was removed under reduced pressure and the residue washed with diethyl ether (2×10 ml) to give complex **7** as an orange solid (70 mg, 78%). Anal. Found: C, 51.91; H, 3.76; N, 1.58. $C_{63}H_{51}BF_4N_2O_7P_4Ru_3$. Calc.: C, 51.76; H, 3.52; N, 1.92%. IR (CH_2Cl-CH_2Cl): 1997 (vs), 1989 (sh), 1964 (s), 1939 (m), 1914 (w), 1789 (w,br) cm^{-1} . 1H NMR (CD_2Cl_2): 8.2–6.8 (m, 8 Ph), 6.66 (d, $J = 7.9$ Hz, 1 H), 6.38 (t, $J = 7.9$ Hz, 1 H), 5.88 (d, $J = 7.9$ Hz, 1 H), 3.80 (s, br, NH), 3.70 (m, 2 H), 1.81 (m, 2 H), 1.62 (s, Me) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 4.1 (m, 1 P), 1.0 (m, 1 P), –4.5 (m, 1 P), –17.9 (m, 1 P) ppm.

3.9. Reaction of complex **1** with NaOMe

A solution of NaOMe in methanol (0.6 ml, 0.1 M, 0.06 mmol) was added dropwise to a solution of compound **1** (50 mg, 0.055 mmol) in dichloromethane. The reaction was instantaneous. A spot TLC analysis of the solution showed the presence of three products. Column chromatography separation on Florisil (1:1 hexane-dichloromethane) allowed the isolation of the major component of the mixture, which was identified as

$[Ru_3(\mu_3-ampy)(\mu-PhC=CHPh)(CO)_8]$ (**6**) (27 mg, 60%).

3.10. Reaction of complex **1** with NaOH

An excess of solid NaOH (20 mg, 0.5 mmol) was added to a solution of complex **1** (30 mg, 0.033 mmol) in dichloromethane (10 ml). The mixture was stirred for 30 min and it became dark brown. A GC analysis of the solution showed the presence of *cis*-stilbene. The filtered solution was evaporated to dryness and the residue chromatographed on neutral alumina (activity I, 1:1 hexane-dichloromethane). Only one compound was eluted, which was identified as the neutral hydride $[Ru_3(\mu-H)(\mu_3-ampy)(CO)_9]$ (**12**) (10 mg, 45%).

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