Synthesis and reactivity of diphenylphosphine derivatives of $[Ru_3(\mu\text{-H})(\mu_3\text{-ampy})(CO)_9]$ and $[Ru_3(\mu\text{-H})_2(\mu_3\text{-ampy})(CO)_9][BF_4]$ (Hampy = 2-amino-6-methylpyridine)

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Abstract

The reactions of $[Ru_3(\mu\text{-H})(\mu_3\text{-ampy})(CO)_9]$ (**1**) (Hampy = 2-amino-6-methylpyridine) with one or two equivalents of PPh_2H give the complexes $[Ru_3(\mu\text{-H})(\mu_3\text{-ampy})(CO)_8(PPh_2H)]$ (**3**) or $[Ru_3(\mu\text{-H})(\mu_3\text{-ampy})(CO)_7(PPh_2H)_2]$ (**4**), in which the PPh_2H ligands are *cis* to the bridging NH fragment and *cis* to the hydride. Complex **3** eliminates hydrogen in refluxing tetrahydrofuran to give the phosphido-bridged derivative $[Ru_3(\mu_3\text{-ampy})(\mu\text{-}PPh_2)(\mu\text{-}CO)_2(CO)_6]$ (**5**), which contains the PPh_2 ligand spanning one of the two Ru–Ru edges unbridged by the amido moiety. Under similar conditions, complex **4** gives a separable mixture of two isomers of $[Ru_3(\mu\text{-H})(\mu_3\text{-ampy})(\mu\text{-}PPh_2)_2(CO)_6]$ in a 5:1 ratio; the major product (**6a**) has a plane of symmetry, whereas the minor one (**6b**) is asymmetric. Compound **6a** can also be prepared by reaction of **5** with PPh_2H. Complexes **3** and **4** undergo protonation with $HBF_4 \cdot OEt_2$ at an amido-unbridged P-bonded Ru–Ru edge, rendering $[Ru_3(\mu\text{-H})_2(\mu_3\text{-ampy})(CO)_8(PPh_2H)][BF_4]$ (**7a**) and $[Ru_3(\mu\text{-H})_2(\mu_3\text{-ampy})(CO)_7(PPh_2H)_2][BF_4]$ (**8**), respectively. Upon reaction with potassium methoxide, the cation **7a** regenerates the neutral complex **3**, while complex **8** gives a mixture of **4**, **6a** and **6b**. Treatment of the dihydride $[Ru_3(\mu\text{-H})_2(\mu_3\text{-ampy})(CO)_9][BF_4]$ (**2**) with PPh_2H gives $[Ru_3(\mu\text{-H})_2(\mu_3\text{-ampy})(CO)_8(PPh_2H)][BF_4]$ (**7b**), which has the PPh_2H ligand *cis* to the bridging NH moiety and *cis* to the hydride on the Ru atom bonded to only one hydride, being therefore an isomer of complex **7a**. The cation **7b** undergoes nucleophilic attack by potassium methoxide to give the neutral methoxycarbonyl derivative $[Ru_3(\mu\text{-H})_2(\mu_3\text{-ampy})(CO_2Me)(CO)_7(PPh_2H)]$ (**9**). Proton and ^{31}P $\{^1H\}$ NMR and IR spectra of all the compounds are included and discussed in relation to their structures.

Introduction

The chemistry of phosphido-bridged ruthenium carbonyl clusters has grown up considerably in the last decade [1–7]. This activity has been related to the very interesting structural aspects presented by many of these complexes and also to the search for polynuclear catalytic systems containing bridging ligands that prevent cluster fragmentation. However, this second point has not been successfully achieved using phosphido-bridged carbonyl clusters, i.e. the complexes $[Ru_3(\mu\text{-H})(\mu\text{-}PPh_2)(CO)_{10}]$ [5], $[Ru_3(\mu\text{-H})(\mu\text{-}PPh_2)(CO)_9]$ [5], $[Ru_3(\mu\text{-H})_2(\mu\text{-}PPh_2)_2(CO)_8]$ [5], $[Ru_3(\mu\text{-H})(\mu\text{-}PPh_2)_3(CO)_7]$ [5] and $[Ru_3\{\mu_3\text{-}PPh(C_5H_4N)\}(\mu\text{-}PPh_2)(\mu\text{-}CO)_2(CO)_6]$ [6, 7] are active hydrogenation catalyst precursors, but they all rearrange to mixtures of other complexes under catalytic conditions.

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In previous papers [8, 9] we have shown that the complex $[Ru_3(\mu\text{-H})(\mu_3\text{-ampy})(CO)_9]$ (**1**) (Hampy = 2-amino-6-methylpyridine) exhibits a rich substitution chemistry, that itself and its substituted products have Ru–Ru bonds electron-rich enough to be protonated under mild conditions, and that all these compounds are very stable towards fragmentation under high temperatures, probably owing to the presence of the triply-bridging ampy ligand. We now report the synthesis and some reactivity of diphenylphosphine derivatives of complex **1** and of its protonation product $[Ru_3(\mu\text{-H})_2(\mu_3\text{-ampy})(CO)_9][BF_4]$ (**2**). A small part of this work has been communicated in a preliminary form [10].

Results and discussion

Neutral complexes

The complex $[Ru_3(\mu\text{-H})(\mu_3\text{-ampy})(CO)_9]$ (**1**) reacted readily with one or two equivalents of di-

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phenylphosphine, at room temperature, to give the substituted compounds $[Ru_3(\mu\text{-H})(\mu_3\text{-ampy})(CO)_8(PPh_2H)]$ (**3**) and $[Ru_3(\mu\text{-H})(\mu_3\text{-ampy})(CO)_7(PPh_2H)_2]$ (**4**), respectively. In both cases, the displaced CO ligands were those *cis* to the NH fragment and *cis* to the hydride, as deduced from the low values of the *J* (P-hydride) coupling constants [8, 9] (*c.* 12 Hz) in their ^1H NMR spectra (Table 1). Small couplings (*c.* 3 Hz) between the hydrides and the PH hydrogens were also observed. A similar reactivity has been reported for complex **1** with triphenylphosphine, however the formation of the bis(triphenylphosphine) complex, the structure of which has been determined by X-ray diffraction [11], requires high temperature [8].

Thermolysis of complex **3** in refluxing tetrahydrofuran (thf) for 1.5 h resulted in the elimination of hydrogen and the formation of the phosphido-bridged compound $[Ru_3(\mu_3\text{-ampy})(\mu\text{-}PPh_2)(\mu\text{-CO})_2(CO)_6]$ (**5**). Its ^1H NMR spectrum showed no hydride ligands. Its ^{31}P $\{^1H\}$ NMR spectrum was a singlet at 386.9 ppm, which is among the highest chemical shifts ever reported for a μ-PPh_2 ligand [6], since in most other cases they appear below 200 ppm [1–4, 12]. Its IR spectrum (Table 2) showed the presence of bridging carbonyls and the absence of ν(PH) absorptions. The relative positions of the μ-CO and μ-PPh_2 ligands on the complex were deduced from a ^{13}C $\{^1H\}$ NMR spectrum, which revealed the presence of two bridging (doublets at δ 240.2 and 226.7 ppm) and six terminal (two doublets and four singlets) CO ligands, as expected for the structure depicted in Scheme 1, ruling out the possibility that the phosphido ligand spanned the same edge as the NH fragment. A structurally similar complex $[Ru_3\{\mu_3\text{-}PPh(C_5H_4N)\}(\mu\text{-}PPh_2)(\mu\text{-CO})_2(CO)_6]$ [6] has been reported as the product of the thermolysis of $[Ru_3\{\mu_3\text{-}PPh(C_5H_4N)\}(\mu\text{-O=CPh})(CO)_8(PPh_2H)]$ [13]. In an attempt to regenerate complex **3** from **5**, the latter was treated with hydrogen (thf, 1 atm., 20 °C, 3 h), but no reaction was observed by IR spectroscopy.

Thermolysis of the bis(diphenylphosphine) complex **4** in refluxing thf for 1.5 h gave a mixture of two isomers of $[Ru_3(\mu\text{-H})(\mu_3\text{-ampy})(\mu\text{-}PPh_2)_2(CO)_6]$ (**6a** and **6b**), in a 5:1 ratio, which was separated by thin layer chromatography on silica gel. The structures shown for these complexes in Scheme 1 are supported by their NMR (Table 1) and IR (Table 2) spectroscopic data, which clearly indicated that the major product **6a** bears the μ-PPh_2 ligands symmetrically arranged on the amido-unbridged Ru–Ru edges, whereas the minor one **6b** is asymmetric. It has been reported that the reaction of $[Ru_3\{\mu_3\text{-}PPh(C_5H_4N)\}(\mu\text{-}PPh_2)(\mu\text{-CO})_2(CO)_6]$ with diphenylphosphine gives an inseparable mixture of two isomers of $[Ru_3(\mu\text{-H})\{\mu\text{-}PPh(C_5H_4N)\}(\mu\text{-}PPh_2)_2(CO)_6]$ [6]; however, a similar reaction between complex **5** and diphenylphosphine afforded the symmetric complex **6a** as the only product detectable by NMR spectroscopy.

Cationic complexes

Cationic phosphido-bridged compounds are rare, and their systematic syntheses and potential reactivity have not been explored [14]. Having this in mind, we attempted the preparation of some cationic diphenylphosphido-bridged derivatives of complex **1** by two different routes: (i) thermolysis of the protonation products of complexes **3** and **4**, and (ii) preparation of diphenylphosphine derivatives of the

TABLE 1. Selected NMR data[a]

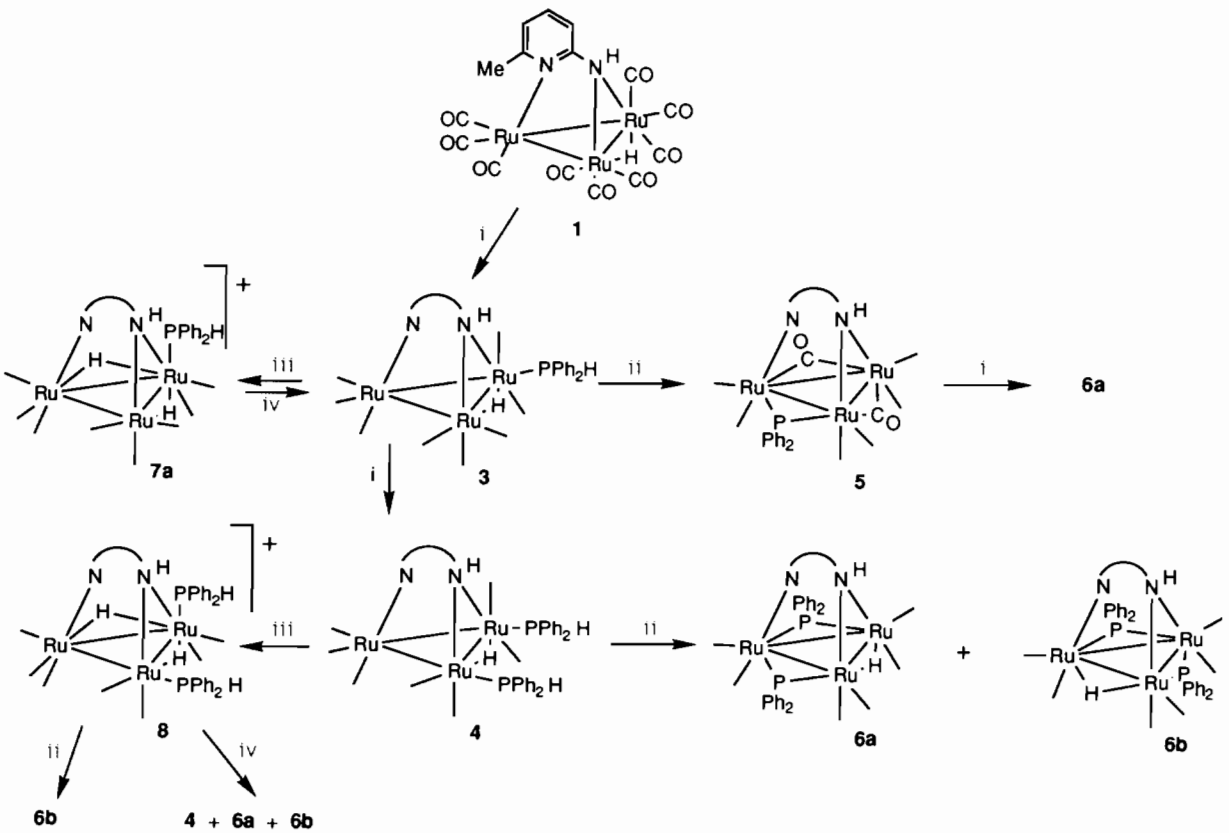
Compound	$\delta(\mu\text{-H})$	δ(PH)	δ(P)[b]
3	−11.15 (dd, 11.9[c], 3.1[d])	6.81 (dd, 346.5[c], 3.1[d])	2.0 (s)
4	−10.98 (tt, 11.7[c], 2.7[d])	6.06 (dd, 326.5[c], 2.7[d])	0.9 (s)
5			386.9 (s)
6a	−7.97 (t, 29.1[c])		246.2 (s)
6b	−8.40 (dd, 31.2[c], 29.8[c])		251.2 (d, 156.9[e]), 226.3 (d, 156.9[e])
7a	−12.35 (d, 33.8[c]), −14.03 (d, 14.6[c])	5.82 (d, 312.9[c])	7.2 (s)
7b	−13.11 (d, 3.3[c]), −14.56 (d, 17.8[c])	6.57 (d, 343.3[c])	9.7 (s)
8	−12.20 (dd, 22.6[c], 6.0[c]), −13.22 (dd, 14.0[c], 6.2[c])	f	6.8 (d, 11.8[c]), 1.3 (d, 11.8[c])
9[g]	−12.04 (d, 3.7[c]), −13.61 (d, 23.3[c])	6.59 (d, 334.5[c])	11.3 (s)

[a]Spectra recorded at 22 °C, in $CDCl_3$; δ (ppm) refered to internal $SiMe_4$ (^1H, 300.13 MHz) or external 85% H_3PO_4 (^{31}P, 121.5 MHz); multiplicities and coupling constants (Hz) in parentheses. [b]Proton-decoupled. [c]P–H coupling. [d]H–H coupling. [e]P–P coupling. [f]Obscured by the phenyl protons. [g]$\delta(CO_2Me)$ 3.65 (s).

TABLE 2. Selected IR data (cm^{-1})

Compound	ν(CO)	ν(NH)[a]	ν(PH)[a]
3	2058m, 2021vs, 1993s, 1979s, 1957m, 1940m[b]	3303m	2304m
4	2033s, 1994vs, 1978w, 1957s, 1944w, 1927w[c]	3298w	2321w, 2294w
5	2050s, 2014vs, 2006vs, 1976m, 1957m, 1878w, 1819m[b]	3319w	
6a	2028vs, 1997s, 1990s, 1950m, 1935s[b]	3318w	
6b	2026m, 2001s, 1987m, 1960m, 1940m, 1925m[b]	3312w	
7a	2100m, 2069vs, 2020s, 1995m, 1961w[b]	3285m	2300w
7b	2132s, 2083vs, 2057s, 2032s, 2013s, 1972w[c]	3303w	2295w
8	2077m, 2063s, 2020s, 1996m, 1965w[c]	3300w	2296w
9[d]	2068m, 2037s, 2015s, 1991m, 1976m, 1955w[b]	3269w	2302w

[a]In Nujol. [b]In tetrahydrofuran. [c]In dichloromethane. [d]ν(COOMe) 1601 (Nujol).



Scheme 1. (i) PPh_2H; (ii) thf, reflux; (iii) $HBF_4 \cdot OEt_2$; (iv) MeO^-.

cationic dihydride **2**, which can be easily made by protonation of **1** [9], followed by thermolysis. Although all these attempts were unsuccessful, they led to an interesting chemistry, which is discussed below.

Protonation of complex **3** with $HBF_4 \cdot OEt_2$ led to the cationic dihydride $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-ampy})(CO)_8(PPh_2H)][BF_4]$ (**7a**). As expected, its IR spectrum showed the ν(CO) absorptions shifted to higher wavenumbers than those of complex **3** (Table 2). Its ^1H NMR spectrum (Table 1) clearly indicated that protonation has taken place at the Ru–Ru edge containing the phosphine ligand, since it showed one hydride *trans* ($\delta - 12.35$ ppm, doublet, $J = 33.8$ Hz)

and the other one *cis* ($\delta - 14.03$ ppm, doublet, $J = 14.6$ Hz) to phosphorous. The spectrum also revealed that the PPh_2H ligand had moved from *cis* (in complex **3**) to *trans* (in complex **7a**) to the hydride which spans the amido-bridged Ru–Ru edge (see Scheme 1), because the protonation product of $[Ru_3(\mu\text{-}H)(\mu_3\text{-ampy})(CO)_8(PPh_3)]$ has a similar spectrum, and its structure has been confirmed by an X-ray diffraction analysis [9].

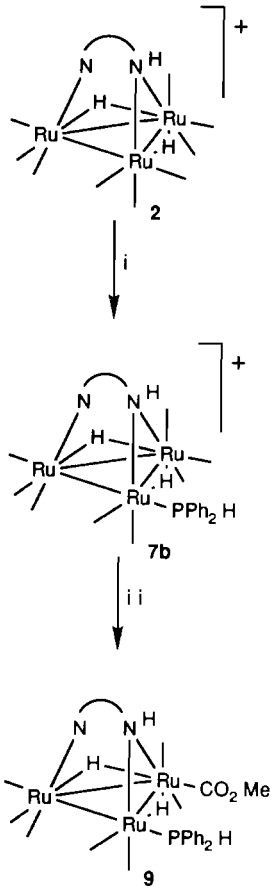
Protonation of the bis(diphenylphosphino) complex **4** gave the dihydride $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-ampy})(CO)_7(PPh_2H)_2][BF_4]$ (**8**). Its spectroscopic data (Tables 1 and 2), which follow the same trends as those of complex **7a**, confirm the structure depicted in Scheme 1.

Disappointingly, the thermolysis of complexes **7a** and **8** did not lead to cationic phosphido-bridged products. Complex **7a** remained unaltered after refluxing of a thf solution for 1.5 h. A similar treatment of complex **8** produced the elimination of hydrogen and HBF_4 giving the asymmetric neutral complex **6b** quantitatively. This reaction provides an appropriate method for the synthesis of **6b**, since this compound is only a minor product of the thermolysis of complex **4**. In subsequent experiments, we proved that complexes **5**, **6a** and **6b** do not undergo protonation with $HBF_4 \cdot OEt_2$.

Complex **7a** was deprotonated with one equivalent of potassium methoxide to regenerate **3**. However, an analogous reaction with complex **8** gave a mixture of **4**, **6a** and **6b** in a ratio of 17:1:11, as shown by ^{31}P NMR spectroscopy. These results indicate that the lateral hydride of complex **8** is probably the most acidic hydrogen, but the methoxide ion should also take either of the PH protons of complexes **8** or **4** to give an intermediate which subsequently produces **6a** and **6b**.

The reaction of the cationic dihydride $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-ampy})(CO)_9][BF_4]$ (**2**) with diphenylphosphine gave the substituted compound $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-ampy})(CO)_8(PPh_2H)][BF_4]$ (**7b**). The ^1H NMR spectrum (Table 1) showed two hydride ligands as doublets, with coupling constants one typical for a J_{cis} coupling (17.8 Hz) and the other one very small (3.3 Hz). Since the amido moiety is expected to be more *cis* labilizer than pyridine, these data suggest that substitution has taken place at an equatorial position *cis* to hydride and on the Ru atom bonded to only one hydride, as depicted in Scheme 2. Therefore, the complexes **7a** and **7b** are isomers.

The ^{31}P NMR spectrum of the solution obtained by refluxing complex **7b** in thf for 1.5 h showed the peaks of complexes **7b** and **7a** in a 3:1 ratio, as well as the resonances of some other unidentified minor products, but none of them in the μ-PPh_2 region.



Scheme 2. (i) PPh_2H; (ii) OMe^-.

As commented above, the reaction of **7a** with potassium methoxide produced deprotonation. However, a similar reaction with the isomer **7b** gave the neutral methoxycarbonyl derivative $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-ampy})(CO_2Me)(CO)_7(PPh_2H)]$ (**9**). The presence of the metoxycarbonyl ligand in the complex was confirmed by IR and NMR spectroscopies (Tables 1 and 2). Although with only these data it is impossible to locate precisely this ligand in the complex, we think that it ought to be in one of the two equatorial positions of the H–Ru–H moiety, as shown in Scheme 2, because the two equatorial carbonyls which are on the H–Ru–H moiety of complex **7b** should bear a higher positive partial charge than the other CO ligands, being therefore more susceptible to nucleophilic attack by the methoxide ion. Most probably, the equatorial CO ligand attached to the H–Ru–H moiety of complex **7a** is not electrophilic enough to react with potassium methoxide owing to the presence of the basic phosphine ligand on the same Ru atom. It is curious that in this case the methoxide ion prefers to attack nucleophilicly a coordinated CO ligand rather than acting as a base, abstracting protons, although the formation of methoxycarbonyl

ligands by this mechanism is well known [15]. An identical behaviour was observed upon reaction of $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-ampy})(CO)_8(PPh_3)][BF_4]$ with potassium methoxide [9].

Experimental

Solvents were dried and distilled prior to use. All reactions were carried out under nitrogen, using standard Schlenk techniques. Complexes **1** [16] and **2** [9] were prepared as described previously; diphenylphosphine was obtained from Strem; all the other reagents were obtained from Aldrich and used as received. Instrumentation was as follows: Perkin-Elmer FT 1720-X (IR), Bruker AC-300 (NMR), Perkin-Elmer 240-B (microanalysis). The ^{13}C $\{^1H\}$ NMR spectra were recorded using samples made from *c.* 30% ^{13}CO-enriched $[Ru_3(CO)_{12}]$ as starting material [17].

Preparation of $[Ru_3(\mu\text{-}H)(\mu_3\text{-ampy})(CO)_8(PPh_2H)]$ (3)

Diphenylphosphine (39 μl, 0.224 mmol) was injected into a solution of complex **1** (150 mg, 0.226 mmol) in thf (10 cm^3). After stirring for 1.5 h, the solvent was removed under reduced pressure and the residue washed with hexane (2 cm^3) to give a yellow–orange solid (120 mg, 65%). *Anal.* Found: C, 37.6; H, 2.35; N, 3.2. Calc. for $C_{26}H_{19}N_2O_8PRu_3$: C, 38.0; H, 2.3; N, 3.4%.

Preparation of $[Ru_3(\mu\text{-}H)(\mu_3\text{-ampy})(CO)_7(PPh_2]$ (4)

A solution of complex **1** (150 mg, 0.226 mmol) and diphenylphosphine (101 μl, 0.581 mmol) in thf (10 cm^3) was stirred for 2 h. The solvent was removed under reduced pressure and the residue washed with hexane (2 cm^3) to give an orange solid (140 mg, 63%). *Anal.* Found: C, 45.3; H, 3.3; N, 2.75. Calc. for $C_{37}H_{30}N_2O_7P_2Ru_3$: C, 45.35; H, 3.05; N, 2.85%.

Preparation of $[Ru_3(\mu_3\text{-ampy})(\mu\text{-}PPh_2)(\mu\text{-}CO)_2(CO)_6]$ (5)

A solution of complex **3** (215 mg, 0.262 mmol) in thf (15 cm^3) was stirred at reflux temperature for 1.5 h. The solvent was removed and the residue washed with hexane (two 1-cm^3 protions) to give a dark red solid (170 mg, 79%). *Anal.* Found: C, 38.2; H, 2.4; N, 3.3. Calc. for $C_{26}H_{17}N_2O_8PRu_3$: C, 38.1; H, 2.1; N, 3.4%. ^{13}C $\{^1H\}$ NMR ($CDCl_3$, 22 °C, 75.4 MHz): δ(CO) 240.2 (d, J = 55.2 Hz), 226.9 (d, J = 53.4 Hz), 200.3 (s), 199.2 (s), 197.8 (s), 197.6 (d, J = 8.1 Hz), 195.5 (s), 193.2 (d, J = 7.0 Hz) ppm.

Preparation of two isomers of $[Ru_3(\mu\text{-}H)(\mu_3\text{-ampy})(\mu\text{-}PPh_2)_2(CO)_6]$ (6a and 6b)

A solution of complex **4** (100 mg, 0.102 mmol) in thf (15 cm^3) was stirred at reflux temperature for 1.5 h. The solution was concentrated to *c.* 1 cm^3 and chromatographed on preparative tlc plates (silica gel). Hexane–toluene (2/1 vol./vol.) eluted two bands which were extracted from the support with thf. The first band, yellow, was worked up to give complex **6a** as a yellow solid (65 mg, 67%). *Anal.* Found: C, 45.5; H, 3.25; N, 2.7. Calc. for $C_{36}H_{28}N_2O_6P_2Ru_3$: C, 45.5; H, 2.95; N, 2.95%. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 22 °C, 75.4 MHz): δ(CO) 203.9 (m, 2 C), 199.3 (s, 2 C), 195.7 (d, J = 6.0 Hz, 2 C) ppm. The second band, red, was worked up to give the solvate **6b**·thf as a deep red solid (12 mg, 12%). *Anal.* Found: C, 47.3; H, 3.6; N, 2.7. Calc. for $C_{40}H_{36}N_2O_7P_2Ru_3$: C, 47.0; H, 3.55; N, 2.75%). ^{13}C $\{^1H\}$ NMR ($CDCl_3$, 22 °C, 75.4 MHz): δ(CO) 205.7 (d, J = 7.7 Hz), 203.2 (s), 200.8 (d, J = 8.1 Hz), 199.3 (t, J = 6.0 Hz), 198.7 (t, J = 8.8 Hz), 198.3 (s) ppm.

Reaction of complex 5 with diphenylphosphine

Complex **5** (37 mg, 0.045 mmol) and diphenylphosphine (8 μl, 0.045 mmol) were stirred in thf (5 cm^3) for 2.5 h. The ^{31}P $\{^1H\}$ NMR spectrum (D_2O external lock) of this solution indicated that it contained the complexes **5** and **6a** in a 1:3 ratio.

Protonation of complex 3

The addition of an excess of $HBF_4 \cdot OEt_2$ (0.1 cm^3) to a solution of complex **3** (95 mg, 0.119 mmol) in dichloromethane (10 cm^3) resulted in an instantaneous colour change from orange to yellow. The solution was evaporated to dryness and the oily residue washed with diethyl ether (five 2-cm^3 portions) to give the complex $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-ampy})(CO)_8(PPh_2H)][BF_4]$ (**7a**) as a yellow solid (70 mg, 67%). *Anal.* Found: C, 33.9; H, 2.4; N, 3.05. Calc. for $C_{26}H_{20}BF_4N_2O_8PRu_3$: C, 34.35; H, 2.2; N, 3.1%.

Deprotonation of complex 7a

A solution of KOH in methanol (0.58 cm^3, 0.1 mol dm^{-3}, 0.058 mmol) was added to a solution of complex **7a** (50 mg, 0.057 mmol) in thf (5 cm^3). The IR spectrum of the resulting solution only showed bands of complex **3**.

Protonation of complex 4

An excess of $HBF_4 \cdot OEt_2$ (0.1 cm^3) was added to a solution of complex **4** (120 mg, 0.123 mmol) in dichloromethane (5 cm^3). The resulting solution was worked up as above to give $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-ampy})(CO)_7(PPh_2H)_2][BF_4]$ (**8**) as a yellow–orange

solid (85 mg, 65%). *Anal.* Found: C, 41.6; H, 2.85; N, 2.5. Calc. for $C_{37}H_{31}BF_4N_2O_7P_2Ru_3$: C, 41.65; H, 2.95; N, 2.6%.

Thermal transformation of complex 8

A solution of complex **8** (35 mg, 0.033 mmol) in thf (10 cm^3) was heated at reflux temperature for 1.5 h and then evaporated to dryness. The IR and ^{31}P NMR spectra of the residue indicated complete conversion into complex **6b**.

Reaction of complex 8 with potassium methoxide

A solution of KOH in methanol (0.52 cm^3, 0.1 mol dm^{-3}, 0.052 mmol) was added to a solution of complex **8** (46 mg, 0.043 mmol) in thf (5 cm^3). The solution, which immediately changed from yellow to red, was evaporated to dryness. The ^{31}P $\{^1H\}$ NMR spectrum of the residue showed that it was a 17:1:11 mixture of the complexes **4**, **6a** and **6b**.

Preparation of $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-}ampy)(CO)_8(PPh_2H)][BF_4]$ (7b)

Complex **2** (109 mg, 0.145 mmol) and an excess of diphenylphosphine (62 μl, 0.357 mmol) were stirred in thf (10 cm^3) for 5 h. The solution was evaporated to dryness and the residue washed with diethyl ether (three 2-cm^3 portions) to give complex **7b** as an orange solid (107 mg, 81%). *Anal.* Found: C, 34.2; H, 2.3; N, 2.9. Calc. for $C_{26}H_{20}BF_4N_2O_8PRu_3$: C, 34.35; H, 2.2; N, 3.1%.

Preparation of $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-}ampy)(CO_2Me)(CO)_7(PPh_2H)]$ (9)

A solution of KOH in methanol (1.35 cm^3, 0.1 mol dm^{-3}, 0.135 mmol) was added to a solution of complex **7b** (114 mg, 0.125 mmol) in thf (5 cm^3). The colour changed from orange to red. The solvent was removed under reduced pressure and the residue extracted with dichloromethane (5 cm^3) to eliminate KBF_4. The extract was evaporated to dryness and the residue washed with a diethyl ether–hexane (1:1 vol./vol.) mixture (two 2-cm^3 portions) to give complex **9** as a brick red solid (90 mg, 84%). Anal. Found: C, 38.1; H, 2.85; N, 3.2. Calc. for $C_{27}H_{23}N_2O_9PRu_3$: C, 38.0; H, 2.7; N, 3.3%.

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