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Synthesis and reactivity of triruthenium carbonyl clusters containing bis(diphenylphosphino)methane and the face-bridging ligand 2-amido-6-methylpyridine

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Abstract

The compounds $[Ru_3(\mu\text{-H})(\mu_3\text{-ampy})(CO)_9]$ (**1**) and $[Ru_3(\mu\text{-H})_2(\mu_3\text{-ampy})(CO)_9]BF_4$ (**2**) (Hampy = 2-amino-6-methylpyridine) react with bis(diphenylphosphino)methane (dppm) to give $[Ru_3(\mu\text{-H})(\mu_3\text{-ampy})(CO)_7(dppm)]$ (**3**) and $[Ru_3(\mu\text{-H})_2(\mu_3\text{-ampy})(CO)_7(dppm)]BF_4$ (**4**), respectively. In complex **3** the two P atoms of the dppm ligand are *cis* to both the hydride and the amido-fragment of the bridging ampy ligand, whereas in complex **4** each P atom is *trans* to a hydride. Protonation of complex **3** with $HBF_4 \cdot OEt_2$ affords $[Ru_3(\mu\text{-H})_2(\mu_3\text{-ampy})(CO)_7(dppm)]BF_4$ (**5**), which is an isomer of complex **4**; in fact, **5** can also be obtained by refluxing a solution of complex **4** in tetrahydrofuran. Complex **5** undergoes deprotonation upon reaction with potassium methoxide or triethylamine, giving **3**; however, the reaction of **4** with potassium methoxide produces the methoxycarbonyl derivative $[Ru_3(\mu\text{-H})_2(\mu_3\text{-ampy})(CO_2Me)(CO)_6(dppm)]$ (**6**), which contains the CO_2Me group in an equatorial position on the Ru atom bonded to the two hydrides.

Introduction

In previous papers [1–3] we have reported the use of monodentate phosphines in the carbonyl substitution reactions of the complexes $[Ru_3(\mu\text{-H})(\mu_3\text{-ampy})(CO)_9]$ (**1**) [4] and its protonated derivative $[Ru_3(\mu\text{-H})_2(\mu_3\text{-ampy})(CO)_9]BF$ (**2**) [1] (Hampy = 2-amino-6-methylpyridine). The products of these substitutions undergo a series of protonation and deprotonation reactions which has allowed the selective synthesis of isomeric clusters [1,2]. Throughout these reactions, the ampy ligand binds the three metal atoms very firmly, since we have not detected any cluster break-down, even at high temperatures.

We now report the synthesis and reactivity of bis(diphenylphosphino)methane (dppm) derivatives of clusters **1** and **2**. We undertook this study in view of the fact that the rigidity of the dppm ligand (which forces the two P atoms to coordinate to

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two adjacent metal centres [5]) would avoid rearrangement reactions which frequently take place when monodentate phosphines are used [2]. Very recently, it has been reported that the related cluster $[Ru_3(\mu\text{-H})(\mu_3\text{-anpy})(CO)_9]$ (Hanpy = 2-anilinopyridine), which is very similar to complex **1**, catalyses the hydrogenation of alkynes, and promotes the codimerization of alkynes and alkenes [6]. A small part of this work has been communicated in a preliminary form [7].

Results and discussion

The results are summarized in Scheme 1. The reaction of compound **1** at room temperature with dppm gave the complex $[Ru_3(\mu\text{-H})(\mu_3\text{-ampy})(CO)_7(dppm)]$ (**3**). Its IR spectrum in the ν(CO) region (see Experimental) was very similar to that of $[Ru_3(\mu\text{-H})(\mu_3\text{-ampy})(CO)_7(PPh_3)_2]$ [2], suggesting a similar structure. This was confirmed by its $^{31}P\{^1H\}$ NMR spectrum (Table 1), which showed equivalent P atoms, and by its ^1H NMR spectrum, which revealed a *cis*-coupling (13.4 Hz) [2,8] of the hydride to both P atoms as well as to the proton of the amido-group; however, the resonance of the NH proton was too broad to show any defined coupling.

The reaction of the cationic dihydrido-complex **2** with dppm gave $[Ru_3(\mu\text{-H})_2(\mu_3\text{-ampy})(CO)_7(dppm)]BF_4$ (**4**). Its ^1H NMR spectrum (Table 1) clearly showed that the two P atoms occupy equatorial positions on the Ru atoms bonded to only one hydride, since it displayed J_{trans}(P–hydride) couplings (24.7 and 24.8 Hz) [1,2]. It is noteworthy that the reactions leading to the clusters **3** and **4** take place at room temperature, whilst the incorporation of two PPh_3 ligands in complexes **1** and **2** requires high temperatures [2].

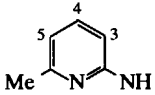
Protonation of complex **3** with $HBF_4 \cdot OEt_2$ in dichloromethane led to the cationic dihydrido-complex $[Ru_3(\mu\text{-H})_2(\mu_3\text{-ampy})(CO)_7(dppm)]BF_4$ (**5**), which is an isomer of cluster **4**. As expected, the IR spectrum of **5** showed ν(CO) absorptions shifted to higher wavenumbers than those of its neutral precursor. The comparison of the NMR spectra of clusters **4** and **5** (Table 1), indicates that they have different structures. Thus, in cluster **5** the hydrides H^A and H^B (see assignments in Fig. 1) are coupled to each other, $J(H^A\text{–}H^B) = 2.5$ Hz, and to both phosphorus atoms, $J(H^A\text{–}P^A) = 16.5$ Hz, $J(H^A\text{–}P^B) = 8.0$ Hz, $J(H^B\text{–}P^A) = 41.4$ Hz, $J(H^B\text{–}P^B) = 6.8$ Hz, and from the values of the coupling constants it is inferred that H^A is *cis* to both P^A and P^B, whereas H^B is *trans* to P^A. The off-resonance ^{31}P NMR spectrum (Fig. 1) is in complete agreement with the proton spectrum and both show a small coupling of P^A to the NH proton. These data definitely prove that the protonation has taken place at one hydride-unbridged Ru–Ru edge of cluster **3**. The structures of complexes **4** and **5** are quite different from those of related complexes containing two PPh_3 ligands instead of dppm [2].

It is interesting to note that complex **4** isomerizes into complex **5** in refluxing THF, but this was not observed when the solution contained dppm, indicating that the reaction takes place through a dissociative mechanism.

Cluster **5** underwent instantaneous deprotonation when treated with triethylamine in dichloromethane or with a solution of potassium methoxide in methanol, giving **3**. However, prolonged (24 h) treatment of the isomeric cluster **4** with an excess of triethylamine in dichloromethane led to a mixture of **4** and some other products which we were unable to separate. On the other hand, the reaction of

Table 1

NMR data [a]



Complex	$\delta(^1H)$							$\delta(^{31}P\{^1H\})$
	H^3	H^4	H^5	NH	Me	μ-H	Other	
3 [b]	6.64 (d)		5.29 (d)	3.20 (s,br)	2.73 (s)	−10.84 (td) [13.4]{4.5}	7.7–7.0 (m,P*Ph*$_2$), 4.53 (m, PC*H*P), 3.68 (m, PC*H*P)	2.6 (s)
4	6.47 (d)	6.74 (t)	6.18 (d)	6.40 (s,br)	2.78 (s)	−12.41 (ddd) [24.7][1.0]{2.5}, −14.12 (ddd) [24.8][1.0]{2.5}	7.8–6.8 (m, P*Ph*$_2$), 4.72 (m, PC*H*P), 3.75 (m, PC*H*P)	21.5 (d){36.4}, 14.9 (d){36.4}
5 [b]	7.10 (d)		6.91 (d)	4.94 (t) [2.5]{2.5}	2.73 (s)	−11.66 (ddt) [16.5][8.0]{2.5}, −12.76 (ddd) [41.4][6.8]{2.5}	7.7–7.2 (m, P*Ph*$_2$), 5.20 (m, PC*H*P), 3.96 (m, PC*H*P)	4.4 (d){32.8}, −0.4 (d){32.8}
6	6.34 (d)	6.61 (t)	5.31 (d)	4.75 (s,br)	1.93 (s)	−11.72 (d) [44.3], −13.82 (d) [58.3]	7.9–6.8 (m, P*Ph*$_2$), 4.56 (m, PC*H*P), 3.74 (m, PC*H*P), 3.65 (s, CO_2*Me*)	21.7 (d){61.0}, 17.6 (d){61.0}

[a] Spectra recorded in $CDCl_3$, at 300 MHz (^1H) or 121.7 MHz (^{31}P), 25°C; chemical shifts (δ) relative to $SiMe_4$ (internal, ^1H) or 85% H_3PO_4 (external, ^{31}P); multiplicities (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad) in parentheses; coupling constants, J/Hz, in parentheses (J(H–H)), square brackets [J(H–P)], or braces {J(P–P)}; coupling constants J(H–H) for H^3, H^4, and H^5 are of *ca.* 7 Hz in all cases. [b] The resonance of H^4 overlaps with those of the dppm phenyl hydrogen atoms.

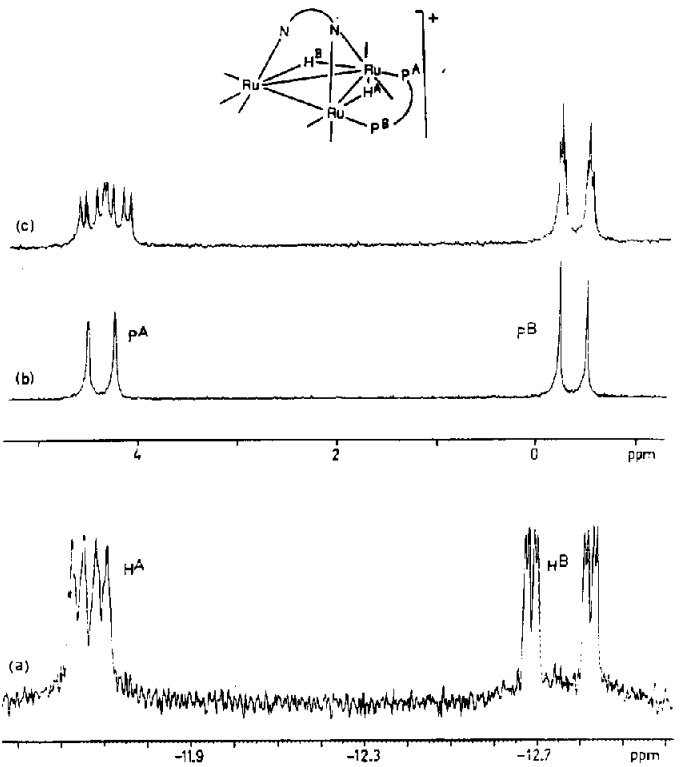
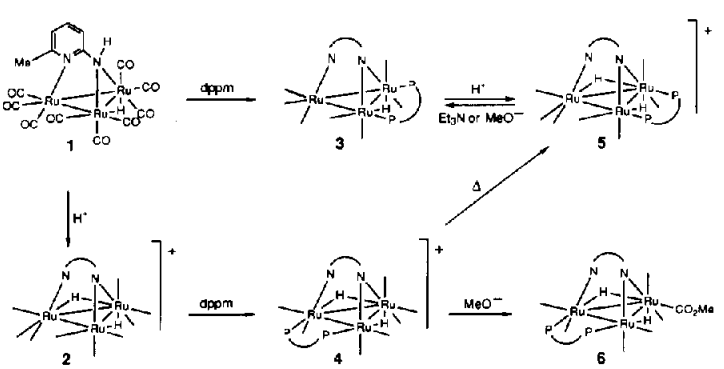


Fig. 1. NMR spectra of $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-ampy})(CO)_7(dppm)]BF_4$ (**5**): (a) ^1H ($CDCl_3$, 25°C, 300 MHz), (b) $^{31}P\{^1H\}$, and (c) off-resonance ^{31}P ($CDCl_3$, 25°C, 121.5 MHz).

cluster **4** with potassium methoxide afforded the neutral methoxycarbonyl derivative $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-ampy})(CO_2Me)(CO)_6(dppm)]$ (**6**). Its ^1H NMR spectrum showed the hydrides *trans* to the P atoms of the dppm ligand and confirmed the presence of the methoxycarbonyl group. Although the exact position of the CO_2Me group in the cluster could not be determined, we believe that it is in an equatorial position on the Ru atom bonded to the two hydrides, as depicted in



Scheme 1

Scheme 1; in fact, the presence of the basic phosphine coordinated to the other Ru atoms should decrease the electrophilic character of their carbonyl ligands, making them less susceptible to nucleophilic attack by the methoxide ion than the carbonyl ligands coordinated to the Ru atom bearing the two hydrides. A similar situation has been described for the complex $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-ampy})(CO_2Me)(CO)_7(PPh_3)]$ [1].

From these results, it is concluded that the rigidity imposed by the linking of the two P atoms of the dppm ligand through the methylene bridge has allowed an extension of the derivative chemistry of complex **1** [1–3]. The reactivity patterns described in this work differ considerably from those previously observed in clusters derived from **1** containing two triphenylphosphine ligands [2].

Experimental

Solvents were dried and distilled under dinitrogen prior to use. All reactions were carried out under dinitrogen, using standard Schlenk vacuum line techniques. The compounds **1** [4] and **2** [1] were prepared as described previously; all other reagents were obtained from Aldrich and used as received. ^1H and ^{31}P NMR spectra were recorded on a Bruker AC-300 instrument. IR spectra were recorded on a Perkin–Elmer FT 1720-X spectrophotometer. Microanalyses were obtained by the University of Oviedo Analytical Service.

$[Ru_3(\mu\text{-}H)(\mu_3\text{-ampy})(CO)_7(dppm)]$ (3)

Complex **1** (50 mg, 0.075 mmol) and bis(diphenylphosphino)methane (29 mg, 0.075 mmol) were stirred in dichloromethane (10 ml) for 2h. The solution was evaporated to dryness and the residue recrystallized from THF-hexane to give complex **3** as red-orange crystals (60 mg, 81%). Found: C, 46.2; H, 3.2; N, 2.7. $C_{38}H_{30}N_2O_7P_2Ru_3$ calc.: C, 46.0; H, 3.05; N, 2.8%. ν(CO) (THF): 2031s, 1988s, 1975w, 1955s, 1935w, 1926w cm^{-1}. ν(NH) (Nujol): 3309w cm^{-1}.

$[Ru_3(\mu\text{-}H)_2(\mu_3\text{-ampy})(CO)_7(dppm)]BF_4$ (isomer 4)

A solution of complex **2** (50 mg, 0.066 mmol) in THF (10 ml) was treated with bis(diphenylphosphino)methane (26 mg, 0.066 mmol). The colour changed from yellow to orange. After stirring for 2 h, the solution was evaporated to dryness and the residue washed with hexane (5 ml) to give complex **4** as an orange solid (59 mg, 83%). Found: C, 42.8; H, 3.0; N, 2.4. $C_{38}H_{31}BF_4N_2O_7P_2Ru_3$ calc.: C, 42.25; H, 2.85; N, 2.6%. ν(CO) (THF): 2125s, 2069m, 2045m, 2023m, 2000vs, 1967m, 1947m cm^{-1}. ν(NH) (Nujol): 3300m cm^{-1}.

$[Ru_3(\mu\text{-}H)_2(\mu_3\text{-ampy})(CO)_7(dppm)]BF_4$ (isomer 5)

An excess of $HBF_4 \cdot OEt_2$ (0.5 ml) was added to a solution of complex **3** (74 mg, 0.075 mmol) in dichloromethane (5 ml). The colour changed from red to deep-red and then to orange. The solvent was removed under reduced pressure and the oily residue washed with diethyl ether (4 × 5 ml) to give complex **5** as an orange solid (48 mg, 60%). Found: C, 42.95; H, 2.9; N, 2.45. $C_{38}H_{31}BF_4N_2O_7P_2Ru_3$ calc.: C, 42.25; H, 2.85; N, 2.6%. ν(CO) (THF): 2076s, 2058s, 2020s, 2010s, 1998m, 1963w cm^{-1}. ν(NH) (Nujol): 3311w cm^{-1}.

Isomerization of complex 4 into complex 5

A solution of complex **4** (50 mg) in THF (5 ml) was stirred at reflux temperature for 5 h and then evaporated to dryness. The solid residue was analysed by IR and ^{31}P NMR spectroscopies, showing the transformation of complex **4** into complex **5**.

Deprotonation of complex 5

A solution of KOH in methanol (0.54 ml, 0.1 M, 0.054 mmol) was added to a solution of complex **5** (55 mg, 0.051 mmol) in THF (5 ml). The solution was stirred for 1 h while the colour changed from yellow to red. The IR spectrum of the final solution showed only the presence of complex **3**. The same result was obtained when complex **5** was treated with an excess of triethylamine in dichloromethane.

$[Ru_3(\mu\text{-}H)_2(\mu_3\text{-}ampy)(CO_2Me)(CO)_6(dppm)]$ (6)

A solution of KOH in methanol (0.55 ml, 0.1 M, 0.055 mmol) was added to a solution of complex **4** (57 mg, 0.053 mmol) in THF (5 ml). The colour changed from orange to yellow. The solvent was removed under reduced pressure and the residue extracted with dichloromethane (2×5 ml) to remove the insoluble KBF_4. The combined extracts were evaporated to dryness and the residue washed with hexane (5 ml) to give complex **6** as a yellow solid (35 mg, 64%). Found: C, 45.6; H, 3.6; N, 2.4. $C_{39}H_{34}N_2O_8P_2Ru_3$ calc.: C, 45.75; H, 3.35; N, 2.74%. ν(CO) (THF): 2038s, 2006s, 1984s, 1971s, 1950m, 1931m cm^{-1}. $\nu(CO_2)$ (Nujol): 1603m cm^{-1}. ν(NH) (Nujol): 3310w cm^{-1}.

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