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Diphenylphosphine and diphenylphosphido derivatives of $[Ru_3(\mu\text{-}H)(\mu_3\text{-ampy})(CO)_9]$ (Hampy = 2-amino-6-methylpyridine)

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Abstract

The reactions of $[Ru_3(\mu\text{-}H)(\mu\text{-ampy})(CO)_9]$ (**1**) (Hampy = 2-amino-6-methylpyridine) with one or two equivalents of PPh_2H lead to the complexes $[Ru_3(\mu\text{-}H)(\mu_3\text{-ampy})(CO)_8(PPh_2H)]$ (**2**) or $[Ru_3(\mu\text{-}H)(\mu_3\text{-ampy})(CO)_7(PPh_2H)_2]$ (**3**), in which the PPh_2H ligands are *cis* to the bridging NH fragment and *cis* to the hydride. Complex **2** can be transformed in refluxing THF into the phosphido-bridged derivative $[Ru_3(\mu_3\text{-ampy})(\mu\text{-}PPh_2)(\mu\text{-}CO)_2(CO)_6]$ (**4**), which contains the PPh_2 ligand spanning one of the two Ru–Ru edges unbridged by the amido moiety, and presents an extremely high ^{31}P chemical shift of 386.9 ppm. Under similar conditions, complex **3** gives a 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 (**5**) has a plane of symmetry, whereas the minor one (**6**) is asymmetric.

In the last few years there has been an increasing interest in phosphido-bridged ruthenium clusters [1–7]. The activity has been related to the search for polynuclear catalytic systems containing bridging ligands that avoid cluster fragmentation and also to the very interesting structural aspects presented by many of these complexes. However, the thermal reaction of $[Ru_3(CO)_{12}]$ with PPh_2H gives many products, the nuclearity of which ranges from the binuclear $[Ru_2(\mu\text{-}PPh_2)_2(CO)_6]$ to the octanuclear $[Ru_8(\mu_8\text{-}P)(\mu\text{-}\eta^1,\eta^6\text{-}CH_2Ph)(\mu\text{-}CO)_2(CO)_{17}]$ [6], and the thermal and photochemical transformations of ruthenium carbonyl clusters containing PPh_2H ligands also afford mixtures of phosphido-bridged derivatives [1,2]. Interestingly, the complexes $[Ru_2(\mu\text{-}PPh_2)_2(CO)_6]$, $[Ru_3(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_{10}]$, $[Ru_3(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_9]$, $[Ru_3(\mu\text{-}H)_2(\mu\text{-}PPh_2)_2(CO)_8]$ and $[Ru_3(\mu\text{-}H)(\mu\text{-}PPh_2)_3(CO)_7]$ are active hydrogenation catalyst precursors, but they all rearrange to mixtures of other complexes under catalytic conditions [8].

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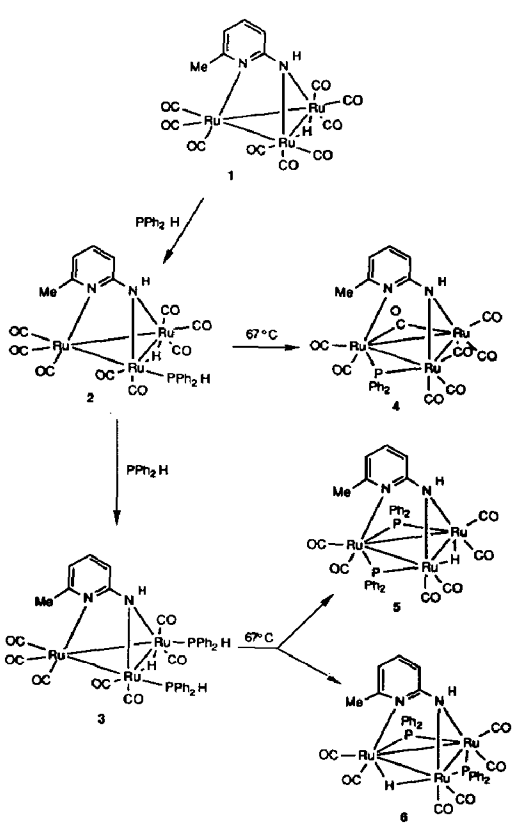

Scheme 1.

In this context, we now report the high-yield syntheses of some phosphido-bridged triruthenium clusters, derived from the complex $[Ru_3(\mu\text{-}H)(\mu_3\text{-ampy})(CO)_9]$ (1) (Hampy = 2-amino-6-methylpyridine) [9]. The trinuclear framework of complex **1** and of many of its derivatives has already been shown to be extremely stable towards fragmentation at high temperatures [10,11], probably due to the presence of the triply bridging ampy ligand.

Complex **1** reacted readily with one or two equivalents of PPh_2H in THF solution to give the substituted compounds $[Ru_3(\mu - H)(\mu_3\text{-ampy})(CO)_8(PPh_2H)]$ (**2**) and $[Ru_3(\mu\text{-}H)(\mu_3\text{-ampy})(CO)_7(PPh_2H)_2]$ (**3**), respectively (Scheme 1) [12]. In both cases, the displaced CO ligands were those *cis* to the NH fragment and *cis* to the hydride, as inferred from the values of the J(P–hydride) coupling constants (Table 1) [10,11]. In both cases, small couplings of the hydrides to the P*H* hydrogens were observed (ca. 3 Hz).

The phosphido-bridged derivative $[Ru_3(\mu_3\text{-ampy})(\mu\text{-}PPh_2)(\mu\text{-}CO)_2(CO)_6]$ (**4**) was obtained quantitatively by refluxing a solution of complex **2** in THF for two hours. Its IR spectrum [12*] showed the presence of bridging carbonyls (1878w, 1819m cm^{-1}) and the absence of ν(PH) absorptions. Its ^1H NMR spectrum only contained the resonances of the ampy and PPh_2 ligands, in a 1 : 1 ratio. As expected, the $^{31}P\{^1H\}$ NMR spectrum was a singlet, but at a very high chemical shift, 386.9 ppm.

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

Table 1

Selected NMR data [a]

Complex	δ(hydride)	δ(P*H*)	$\delta(^{31}P\{^1H\})$
2	-11.15 (dd, 11.9 [b], 3.1 [c])	6.81 (dd, 346.5 [b], 3.1 [c])	2.0 (s)
3	-10.98 (tt, 11.7 [b], 2.7 [c])	6.06 (dd, 326.5 [b], 2.7 [c])	0.9 (s)
4			386.9 (s)
5	-7.97 (t, 29.1 [b])		246.2 (s)
6	-8.40 (dd, 31.2 [b], 29.8 [b])		251.2 (d, 156.9 [d]) 226.3 (d, 156.9 [d])

[a] Spectra recorded at 22°C, in $CDCl_3$, on a Bruker AC-300 instrument; δ (ppm) referred to internal $SiMe_4$ (^1H) or external 85% H_3PO_4 (^{31}P); multiplicity and coupling constants (Hz) in parentheses. [b] P–H coupling. [c] H–H coupling. [d] P–P coupling.

As far as we are aware, this is the highest chemical shift ever reported for a bridging PPh_2 ligand, which in most other cases appear below 200 ppm [7–11,13]. The position of the PPh_2 ligand in the complex was established from a $^{13}C\{^1H\}$ NMR spectrum of a sample made with ca. 30% ^{13}CO-enriched $[Ru_3(CO)_{12}]$ as starting material (Fig. 1) [14*], which showed two bridging (δ 240.2 and 226.9 ppm) and six terminal carbonyls (as expected for the structure depicted in Scheme 1), ruling out the possibility that the PPh_2 ligand spanned the same edge as the NH fragment, since in this case only five CO resonances should be observed.

The thermal transformation of the bis(diphenylphosphine) complex $[Ru_3(\mu\text{-}H)(\mu_3\text{-ampy})(CO)_7(PPh_2H)_2]$ in refluxing THF (2 h) gave a mixture of two isomers of $[Ru_3(\mu\text{-}H)(\mu_3\text{-ampy})(\mu\text{-}PPh_2)_2(CO)_6]$ (**5** and **6**), in a 5 : 1 ratio; this mixture was separated by thin layer chromatography. The IR spectra [12*] of **5** and **6** displayed only terminal CO ligands, and their NMR spectra (Table 1) [14*] clearly indicated that the major product (**5**) bears the PPh_2 ligands symmetrically arranged on the amido-unbridged Ru–Ru edges {δ(P) singlet, δ(hydride) triplet}, whereas the minor one (**6**) is asymmetric, as shown in Scheme 1.

The phosphido-bridged complexes **4–6** were unchanged after several hours of refluxing of their THF solutions, and are indefinitely air-stable. We expect that the thermal stability of these complexes and the presence of the triply bridging ampy ligand (which anchors the Ru_3 triangle and has a high *cis*-labilizing effect [10]) will lead to a variety of ruthenium clusters that will undergo a range of chemical

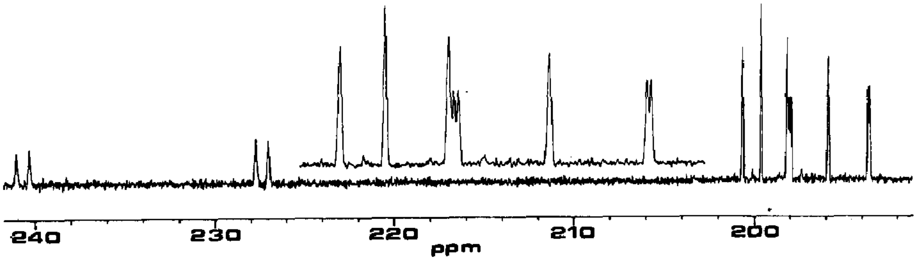

Fig. 1. A part of the $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$, 22°C, 75.4 MHz) of $[Ru_3(\mu_3\text{-ampy})(\mu\text{-}PPh_2)(\mu\text{-}CO)_2(CO)_6]$ (**4**) (ca. 30% enriched in ^{13}CO) showing the CO resonances. The central fragment is an expansion of the 202–192 ppm region.

(substitutions, oxidative additions, etc.) and catalytic reactions. We are now investigating these possibilities.

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12 All compounds gave satisfactory microanalyses (C, H, N) and were obtained in quantitative yields. IR data (cm^{-1}): ν(NH) (nujol mull): **2**: 3303m; **3**: 3298w; **4**: 3319w; **5**: 3318w; **6**: 3312w. ν(PH) (nujol mull): **2**: 2304m; **3**: 2321w, 2294w. ν(CO): **2** (THF): 2058m, 2021vs, 1993s, 1979s, 1957m, 1940m; **3** (CH_2Cl_2): 2033s, 1994vs, 1978w, 1957s, 1944w, 1927w; **4** (THF): 2050s, 2014vs, 2006vs, 1976m, 1957m, 1878w, 1819m; **5** (THF): 2028vs, 1997s, 1990s, 1950m, 1935s; **6** (THF): 2026m, 2001s, 1987m, 1960m, 1940m, 1925m.

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14 Selected $^{13}C\{^1H\}$ NMR data: δ(CO) ($CDCl_3$, 22°C, 75.4 MHz): **4**: 240.2 (d, $J = 55.2$ Hz), 226.9 (d, $J = 53.4$ Hz), 200.3 (2), 199.2 (s), 197.8 (s), 197.6 (d, $J = 8.1$ Hz), 195.5 (s), 193.2 (d, $J = 7.0$ Hz); **5**: 203.9 (m, 2C), 199.3 (s, 2C), 195.7 (d, 2C, $J = 6.0$ Hz); **6**: 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.