

The oxidative addition of a vinylic C–H bond of divinyldiphenyl phosphine at $M_3(CO)_2$ carbonyls ($M = Ru, Os$).

Stepwise formation and crystal structure of $[(\mu-H)Ru_3(CO)_8(PPh(CH=CH_2)_2)\{\mu_3-PPh(CH=CH_2)(CH=CH)\}]$

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Abstract

The metal carbonyls $M_3(CO)_2$ ($M = Ru, Os$) react with diphenylvinylphosphine ($PPh_2CH=CH_2$) and divinyldiphenylphosphine ($PPh(CH=CH_2)_2$) in *n*-octane or toluene giving carbonyl substitution products of formulae $M_3(CO)_2L$ ($L = PPh_2CH=CH_2$ or $PPh(CH=CH_2)_2$). When $M = Os$ the reactions stop at this stage. When $M = Ru$ oxidative addition of the vinylic C–H bond of one of the phosphinic ligands of complexes **3** occurs to form $[(\mu-H)Ru_3(CO)_8(PPh_2CH=CH_2)\{\mu_3-PPh(CH=CH_2)\}]$ (**4a**) and $[(\mu-H)Ru_3(CO)_8(PPh(CH=CH_2)_2)\{\mu_3-PPh(CH=CH_2)(CH=CH)\}]$ (**4b**), starting from $PPh_2CH=CH_2$ and $PPh(CH=CH_2)_2$ respectively; this process is favoured by the TLC material and is faster for $PPh_2CH=CH_2$ than for $PPh(CH=CH_2)_2$. The structure of **4b**, determined by X-ray diffraction methods, consists of a triangle of Ru atoms bound to eight terminal carbonyls. The $PPh(CH=CH_2)_2$ ligand is σ -bound to one of the Ru atoms through the P atom, whilst the $PPh(CH=CH_2)(CH=CH)$ moiety interacts with all of the three metals, being σ -bound to two Ru atoms through the P and C atoms and π -bound to the third Ru atom through the double bond. © 1997 Elsevier Science S.A.

Keywords: Ruthenium; Reactions with vinylphosphines; X-ray structures

1. Introduction

The reactions of alkynes with phosphido- and phosphinidene-bridged metal clusters are well known [1,2], giving facile insertions of acetylenes into the M–P bonds in μ_3 -phosphinidene derivatives [3,4] and less easily in μ_2 -phosphido complexes ². Sometimes, the latter reactions are accompanied by reductive elimina-

tion [8]; hence the synthesis of complexes characterized by M–P(RR')–C–C–M metallacycles is generally a difficult task. Some of them, however, were isolated and characterized during the homogeneous hydrogenation of alkynes in the presence of phosphido-bridged ruthenium clusters [9,10].

Therefore, we were interested in gaining a better knowledge of the synthetic methods and in having a deeper insight into the reactivity of this type of complexes. A possible route to M–P(RR')–C–C–M systems could be the reaction of vinylphosphines with $M_3(CO)_2$ ($M = Ru, Os$) carbonyls. Indeed, we have found that $Ru_3(CO)_2$ reacts with diphenylvinylphosphine ($PPh_2CH=CH_2$) to form the disubstituted complex $[Ru_3(CO)_8(PPh_2CH=CH_2)_2]$ (**3a**), which undergoes oxidative addition on the TLC plates affording

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² Examples of ruthenium and osmium clusters with apparent insertion of hydrocarbyls into M–P(RR') bonds are given in Refs. [5,6]. A discussion is given in Ref. [7].

$[(\mu\text{-H})\text{Ru}_3(\text{CO})_8(\text{PPh}_2\text{CH}=\text{CH}_2)\{\mu_3\text{-PPh}(\text{CH}=\text{CH})\}]$ (**4a**) [11]³.

In a recent paper [12] Johnson et al. described the ruthenium and osmium carbonyl clusters obtained by the same phosphine $\text{PPh}_2\text{CH}=\text{CH}_2$ under different reaction conditions.

This paper deals chiefly with the reactions of divinylphenylphosphine, $\text{PPh}(\text{CH}=\text{CH}_2)_2$, with the same carbonyls: $\text{Os}_3(\text{CO})_{12}$ gives only CO substitution products and, in particular, $[\text{Os}_3(\text{CO})_{11}(\text{PPh}(\text{CH}=\text{CH}_2)_2)]$ (**1'a**), whereas $\text{Ru}_3(\text{CO})_{12}$ gives the disubstituted product $[\text{Ru}_3(\text{CO})_{10}(\text{PPh}(\text{CH}=\text{CH}_2)_2)]$ (**3b**) and then, in a slow process occurring on the TLC plates, $[(\mu\text{-H})\text{Ru}_3(\text{CO})_8(\text{PPh}(\text{CH}=\text{CH}_2)_2)\{\mu_3\text{-PPh}(\text{CH}=\text{CH}_2)(\text{CH}=\text{CH})\}]$ (**4b**), whose structure has been determined by X-ray diffraction study.

2. Experimental

2.1. General experimental details

The carbonyls $\text{M}_3(\text{CO})_{12}$ ($\text{M} = \text{Ru}$ or Os) and the vinylphosphines $\text{PPh}_2\text{CH}=\text{CH}_2$ and $\text{PPh}(\text{CH}=\text{CH}_2)_2$ were commercial products (Strem) used as received after purity tests. The reactions were performed in dry *n*-hexane or toluene, under dry nitrogen, in conventional three necked flasks equipped with gas inlet, cooler and mercury valve. The reaction mixtures, filtered under nitrogen, were brought to small volume under reduced pressure and purified on preparative TLC plates using Kieselgel (P.F. Merck) as stationary phase and mixtures of light petroleum (40–70°C) and diethylether (75:25 v/v, unless otherwise specified) as eluents.

Elemental analyses were carried out by the F. Pascher Laboratories (Remagen, Germany). IR spectra were recorded on a Perkin Elmer 580 spectrometer (KBr cells) and ¹H, ¹³C and ³¹P NMR spectra on a JEOL JNM 270 GX FT instrument.

2.2. Reactions of $\text{Ru}_3(\text{CO})_{12}$ with $\text{PPh}_2\text{CH}=\text{CH}_2$

The reactions leading to $\text{Ru}_3(\text{CO})_{10}(\text{PPh}_2\text{CH}=\text{CH}_2)_2$ (**3a**) and to complex **4a** has already been reported [11,12]. The same reaction was carried out in the presence of $[(\text{C}_5\text{H}_5)_2\text{Ni}(\text{CO})_2]$. A 2:1 molar excess of $\text{PPh}_2\text{CH}=\text{CH}_2$ was added to a suspension of $[(\text{C}_5\text{H}_5)_2\text{Ni}(\text{CO})_2]$ in toluene which was heated till incipient reflux; a suspension of $\text{Ru}_3(\text{CO})_{12}$ in toluene was then added and reflux was allowed for 10 min. The solution was filtered off (considerable amounts of metal

powder were separated) and purified by TLC: small amounts of the unreacted species, **4a** (40% ca.) and an unidentified yellow product were obtained.

2.3. Reactions of $\text{Os}_3(\text{CO})_{12}$ with $\text{PPh}_2\text{CH}=\text{CH}_2$

Heating $\text{Os}_3(\text{CO})_{12}$ at reflux with a 2:1 molar excess of $\text{PPh}_2\text{CH}=\text{CH}_2$ in toluene for 20 min leads to $[\text{Os}_3(\text{CO})_{11}(\text{PPh}_2\text{CH}=\text{CH}_2)]$ (**1'a**) (10%), $[\text{Os}_3(\text{CO})_{10}(\text{PPh}_2\text{CH}=\text{CH}_2)_2]$ (**3'a**) (20%) and to an orange product not eluted on the TLC plates [11]. An alternative route to **1'a** consists in adding a 2:1 molar excess of $\text{PPh}_2\text{CH}=\text{CH}_2$ to a suspension of $[(\text{C}_5\text{H}_5)_2\text{Ni}(\text{CO})_2]$ in toluene and warming till incipient reflux, then adding a suspension of $\text{Os}_3(\text{CO})_{12}$ in toluene; after 20 min at reflux, the suspension was filtered off (considerable amounts of osmium and nickel powders were separated) and the resulting solution was purified by TLC to give unreacted $\text{Os}_3(\text{CO})_{12}$, **1'a** (15%) and two isomers of $\text{Os}_3(\text{CO})_{10}(\text{PPh}_2\text{CH}=\text{CH}_2)_2$ (**2'a**, **2'a₁₁**). Complexes **1'a** [11,12] and **3'a** [12] have been already described. Complex **2'a**: C% 26.9 (27.1), H% 1.3 (1.2), P% 2.8 (2.9). IR (ν_{CO} , heptane) 2088m, 2032vs(br), 2004vs, 1973ms(br), cm^{-1} . ¹H NMR (CDCl_3 , RT): δ 7.50 m (10H, Ph), 6.74 ddd, 5.75 ddd, 5.07 ddd, J(H–H) 0.5, 10, 19 Hz, J(H–P) 6, 6, 12 Hz (3H, $\text{CH}=\text{CH}_2$). ³¹P{¹H} NMR (CDCl_3 , RT, 85% H_3PO_4): –12.26 s. Complex **2'a₁₁**: C% 27.3, H% 1.1, P% 2.6. IR: 2032 s, 2005vs, 1985vs(b), 1944m(b), cm^{-1} . ¹H NMR: δ 7.50 m (10H, Ph), 6.81 ddd, 5.53 ddd, 4.96 ddd J(H–H) 0.7, 11, 17 Hz, J(H–P) 6, 7, 14 Hz (3H, $\text{CH}=\text{CH}_2$). ³¹P NMR: –10.0 br.

2.4. Reactions of $\text{Ru}_3(\text{CO})_{12}$ with $\text{PPh}(\text{CH}=\text{CH}_2)_2$

The reaction of $\text{Ru}_3(\text{CO})_{12}$ with a 1.5:1 molar excess of $\text{PPh}(\text{CH}=\text{CH}_2)_2$ in toluene under N_2 for 3 min at reflux gave a deep red clear solution, which was brought to small volume under reduced pressure and analyzed on TLC plates: its elution resulted in the formation of a continuous band from bottom to top of the plates. The colour was yellow on top and still somewhat red where the solution had been deposited. The top yellow fraction contained pure **4b**, which was then crystallized from heptane- CHCl_3 solutions kept under nitrogen and cooled at –20°C for several days. Complex **4b**: C% 38.8 (39.5), H% 2.7 (2.6), P% 7.3 (7.3). IR (ν_{CO} , heptane): 2078vs, 2060 ms(sh), 2034vs, 2019vs, 2003s(sh), 1973s(b), cm^{-1} . ¹H NMR (CDCl_3 , RT): 7.94–7.09 mm (10H, Ph), 6.70–5.33 very complex series of multiplets (11 H, vinyl and $\text{CH}=\text{CH}$ groups), –18.2 m (hydride). ³¹P{¹H} NMR (CDCl_3 , H_3PO_4): +30.45 d, +22.61 d (intensity 1:1, J(P,P) = 15.2 Hz). ¹³C{¹H} NMR: see discussion.

The (bottom) red fraction gave an oily material which was likely to contain **3b**. IR: 2074vs, 2058m(sh), 2030vs, 2017vs, 2001–1990s(vb), 1972s(b), cm^{-1} .

³The Ru complexes are labelled with a number; the Os ones with a number marked with an apostrophe; the letters a and b indicate complexes with $\text{PPh}_2\text{CH}=\text{CH}_2$ and $\text{PPh}(\text{CH}=\text{CH}_2)_2$ as ligands, respectively.

$^3\text{P}\{^1\text{H}\}$ NMR: +31.1 d, +24.5 d (intensity 1:1, J(P–P) = 15.3 Hz). A sharp signal at +15.9 and a very broad resonance at +15.1 ppm were also observed.

2.5. Reactions of $\text{Os}_3(\text{CO})_{12}$ with $\text{PPh}(\text{CH}=\text{CH}_2)_2$

The reaction of $\text{Os}_3(\text{CO})_{12}$ with a 1.2:1 molar excess of $\text{PPh}(\text{CH}=\text{CH}_2)_2$ in toluene, under N_2 for 10 min at reflux, gives a dark yellow solution; after cooling unreacted $\text{Os}_3(\text{CO})_{12}$ (about 50% of the initial amount) is deposited. TLC purification affords a yellow band of $[\text{Os}_3(\text{CO})_{11}(\text{PPh}(\text{CH}=\text{CH}_2)_2)]$ (I' b, 20%) and an unidentified orange band that is not eluted. Complex I' b: C% 23.4 (24.2), H% 1.2 (1.1), P% 2.9 (3.0). IR (ν_{CO} , heptane): 2111s, 2057vs, 2037vs(sh), 2022vs, 2003s(sh), 1992vs, 1977s(br) cm^{-1} . $^3\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , RT): –19.06 s.

2.6. Crystal structure determination of complex 4b

A crystal of approximate dimensions $0.22 \times 0.25 \times 0.30$ mm was used for the X-ray analysis.

Crystal data. $\text{C}_{28}\text{H}_{22}\text{O}_8\text{P}_2\text{Ru}_3$, $M = 851.63$, triclinic, space group $P1$, $a = 15.633(7)$, $b = 10.518(5)$, $c = 10.066(6)$ Å, $\alpha = 107.73(2)$, $\beta = 96.52(2)$, $\gamma = 97.13(2)^\circ$, $V = 1544(1)$ Å³ (by least-squares refinement from the θ values of 30 accurately measured reflections with θ in the range 13.1 – 18.7° , $\lambda = 0.71073$ Å, $Z = 2$, $D_c = 1.832$ g cm^{-3} , $F(000) = 832$, $\mu(\text{Mo-K}\alpha) = 15.68$ cm^{-1} .

Data were collected at room temperature on a Siemens AED single-crystal diffractometer using the niobium-filtered Mo-K α radiation and the $\theta/2\theta$ scan mode. All reflections with θ in the range 3 – 27° were measured; out of 6776 independent reflections, 4764, having $I > 2\sigma(I)$, were considered observed and used in the analysis. The individual profiles were analyzed according to Lehmann and Larsen [13]. The intensity of one standard reflection was measured after 100 reflections as a general check on crystal and instrument stability. No significant change in the measured intensities was observed during the data collection. No correction for the absorption effects was applied.

The structure was solved by Patterson and Fourier methods, and refined by full-matrix least-squares first with isotropic and then with anisotropic thermal parameters in the last cycles for all of the non-hydrogen atoms. All hydrogen atoms were clearly localized in the final ΔF map and refined isotropically. A weighting scheme $w = [\sigma^2(F_o) + gF_o^2]^{-1}$ was used in the last refinement cycles; at convergence the g value was 0.0026. Final R and R_w values were 0.0334 and 0.0429. The SHELX-76 and SHELXS-86 systems of computer programs were used [14]. Atomic scattering factors, corrected for anomalous dispersion, were taken from Ref. [15]. Final atomic coordinates for the non-hydrogen

Table 1

Fractional atomic coordinates ($\times 10^4$) with Esd.s in parentheses for the non-hydrogen atoms of the complex 4b

	x/a	y/b	z/c
Ru(1)	1584(1)	–295(1)	3185(1)
Ru(2)	2627(1)	2145(1)	4805(1)
Ru(3)	2700(1)	1379(1)	1838(1)
P(1)	1434(1)	–2578(1)	1984(1)
P(2)	3871(1)	710(1)	2952(2)
O(1)	706(3)	–813(6)	5509(5)
O(2)	–94(3)	105(5)	1574(5)
O(3)	932(3)	3183(5)	4316(6)
O(4)	2471(4)	2515(6)	7876(5)
O(5)	3903(3)	4784(5)	5587(7)
O(6)	3786(4)	4071(5)	2070(7)
O(7)	2829(4)	–36(6)	–1269(5)
O(8)	1084(3)	2539(5)	1078(6)
C(1)	1005(4)	–618(6)	4599(6)
C(2)	528(4)	–48(5)	2150(6)
C(3)	1555(4)	2736(6)	4447(6)
C(4)	2526(4)	2368(6)	6720(7)
C(5)	3431(4)	3778(6)	5260(7)
C(6)	3370(4)	3067(6)	2016(7)
C(7)	2787(4)	461(6)	–1157(7)
C(8)	1654(4)	2072(6)	1386(7)
C(9)	3559(4)	602(5)	4549(6)
C(10)	2719(3)	–25(5)	4583(5)
C(11)	4885(4)	1909(6)	3510(7)
C(12)	5663(4)	1647(7)	3274(8)
C(13)	4251(3)	–870(5)	2100(6)
C(14)	4423(4)	–1166(6)	731(7)
C(15)	4818(5)	–2271(7)	139(9)
C(16)	5018(4)	–3108(7)	906(9)
C(17)	4812(5)	–2868(7)	2240(9)
C(18)	4436(4)	–1736(6)	2839(7)
C(19)	2142(6)	–3435(7)	2821(8)
C(20)	2012(10)	–4131(11)	3554(10)
C(21)	389(5)	–3617(8)	1751(7)
C(22)	–297(5)	–3298(10)	2096(12)
C(23)	1672(4)	–3025(5)	184(5)
C(24)	2375(4)	–3622(7)	–221(7)
C(25)	2516(6)	–3919(8)	–1591(9)
C(26)	1990(7)	–3619(9)	–2569(8)
C(27)	1281(6)	–3020(9)	–2172(7)
C(28)	1126(5)	–2727(7)	–808(7)

atoms are listed in Table 1. All calculations were carried out on the GOULD POWERNODE 6040 and ENCORE 91 computers of the Centro di Studio per la Strutturistica Diffraattometrica del CNR, Parma, Italy.

Additional data available from the Cambridge Crystallographic Data Centre or from the authors comprise H-atom coordinates and thermal parameters.

3. Results and discussion

3.1. Synthesis and spectroscopic characterization of the products

The reactions of the phosphorus ligands $\text{PPh}_2\text{CH}=\text{CH}_2$ and $\text{PPh}(\text{CH}=\text{CH}_2)_2$ with the metal

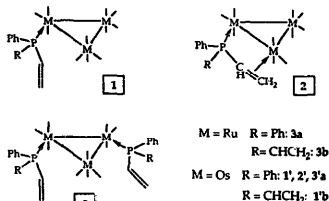
carbonyls $M_3(CO)_{12}$ appear to follow the same pathways, albeit the latter does react more slowly. The use of $[(C_5H_5)Ni(CO)_2]$ modified the reaction pathway of $PPh_2(CH=CH_2)$ with osmium carbonyl, presumably acting via a radical mechanism as observed for $[(C_5H_5)Fe(CO)_2]_2$ [16–18]. The products obtained were characterized by means of elemental analyses and spectroscopic techniques.

Complexes $M_3(CO)_{11}L$ are monosubstituted derivatives, and show comparable IR (and NMR) spectra. In particular, complex **1b** was also obtained from $Os_3(CO)_{11}(NCMe)$ and structurally characterized [12]. Complexes **1a** and **1b** show 1H NMR patterns closely comparable in the vinyl region: however, for **1a** the chemical shifts span a 2 ppm range, whilst for **1b** the signals fall within a 1 ppm range, thus reflecting the differences between the $PPh_2CH=CH_2$ and $PPh(CH=CH_2)_2$ ligands.

Complexes **2'**, obtained using $[(C_5H_5)Ni(CO)_2]$, were identified as $Os_3(CO)_{10}L$ derivatives, in which one vinyl group interacts π with one of the cluster metal atoms. Their identification is based on analytical data and on the 1H NMR spectra showing resonances in the 6–4 ppm region, different from the ones observed for complex **1'**. Complex **2'a** apparently exists as two isomers (**2'a₁** and **2'a₁₁**), presumably because of the orientation of the vinyl and phenyl groups bound to phosphorus or of the axial–equatorial coordination isomerism.

Complexes **3** have been characterized, by means of analytical and spectroscopic data, as $M_3(CO)_{10}L_2$ bisubstituted complexes with the ligands on adjacent metal centers [12,19,20]. The proposed structure is indirectly confirmed also by the intermediacy of the species **3** in the formation of complexes **4**, as discussed below.

The ^{13}C NMR of **4b** in the CO region shows five sharp signals at 202.1 (s,br), 200.7 (s,br), 196.0 (d, J(C–P) 10 Hz), 193.6 (d, J(C–P) 8 Hz), 190.4 (s,br), with intensity 1:1:1:1:1, and a broad hump between 197 and 202 ppm attributable to three fluxional CO's; a comparable situation was found for **4a** [11]. Worthy of note is the presence in both spectra, of a doublet at about 167 ppm (J(C–P) 31.9 for **4b** and 35.3 Hz for **4a**)



Scheme 1.

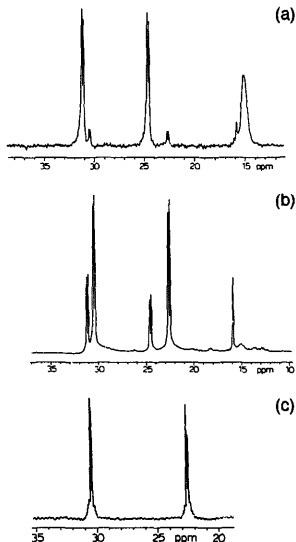


Fig. 1. ^{31}P NMR spectra of different fractions collected after TLC elution of the mixture of the reaction between $Ru_3(CO)_{12}$ and $PPh_2(CH=CH_2)_2$. (a) Bottom (red) band containing mostly **3b** and a broad extra signal; (b) lower intermediate band (reddish) containing **3b**, **4b** and a sharp extra band; (c) top band (yellow) containing only **4b**.

attributable to the vinylic carbon [C(9)] close to the phosphorus atom.

The structures proposed for complexes **1–3** are envisaged in Scheme 1.

3.2. Some comments on the formation of complexes **4a** and **4b**

$Ru_3(CO)_{12}$ reacts with $PPh_2CH=CH_2$ or $PPh(CH=CH_2)_2$ giving mainly the disubstituted complexes **3**; in their turn, they undergo oxidative addition on the TLC plates to form complexes **4**. This process is particularly slow for $PPh_2(CH=CH_2)_2$, so that the elution of the reaction solutions of $Ru_3(CO)_{12}$ with this ligand (containing nearly 100% of red **3b**) results in the formation of a continuous band on the plates. The colour was yellow on top and deep red at the bottom: differently coloured samples could be scraped from the plates and the solutions obtained were analyzed by ^{31}P NMR. They showed the gradual formation of **4b** and disappearance of **3b** going from the bottom to the top of the TLC plates: ^{31}P NMR are shown in Fig. 1.

Possible intermediates of this transformation could be complexes with vinyl groups interacting with metals (and gradually displacing CO) [21]. Indeed, in the ^{31}P NMR of the bottom red band an unexpected broad signal, which then sharpened and disappeared, was observed too. Evidence for the role of the TLC silica comes from the following observations: (i) on 2 mm thick plates (instead of the usual 1 mm) the rate of formation of **4b** increases; (ii) elution of smaller amounts of material results in an increase of the formation rate; (iii) the use of eluant mixtures with 50% diethyl ether increases the transformation rate; (iv) leaving the plates after elution for 60 min under moist air results in the total transformation to **4b**.

Different hypotheses could account for the formation of complexes **4**: one might be the formation of anionic triruthenium hydrides (with release of CO), in a sort of water–gas shift reaction involving the silanol groups or water. Recent examples of "surface organometallic chemistry" [22–25] involving water on silica have been reported: in some instances, splitting of water into its component atoms was observed [26–28]. This process could be accompanied by nucleophilic attack of $=\text{CH}_2$ to cluster bound CO's and stepwise transfer of hydrogen onto the cluster, as recently observed for the reaction of $\text{R}_3\text{P}=\text{CH}_2$ with $\text{Ru}_3(\text{CO})_{12}$ [29].

Trinuclear complexes comparable to **4a** or **4b**, but containing vinylidene ligands inserted into M–P(Ph) bonds, have been obtained by reductive elimination and coupling of phosphino-alkynes with $[\text{HFe}_2(\text{CO})_4]$ [30]; the "butadienyl" species $\text{Ru}_3(\text{CO})_9[\mu_3, \eta^3\text{-C}(\text{Bu}^t)\text{CC}(\text{H})\text{C}(\text{Ph})\text{P}(\text{Ph})_2]$ have been obtained from $\text{HRu}_3(\text{CO})_9(\text{PPh}_2\text{C}=\text{CPh})(\text{C}=\text{CBu}^t)$ via intramolecular reductive coupling of the cluster hydride with the acetylide ligand [5]. These reactions are just the reverse of the oxidative addition discussed in this paper. Another cluster with an alkyne inserted into a M–PRR' system is $\text{Ru}_3(\text{CO})_9[\text{PPh}_2\text{C}=\text{C}(\text{Pr}^+)]$, obtained by slow and spontaneous isomerization of the acetylide cluster $(\text{PPh}_2)_2\text{Ru}_3(\text{CO})_9(\text{C}\equiv\text{Pr}^+)$ in solution [31].

3.3. Crystal structure of complex **4b**

The structure of complex **4b** is shown in Fig. 2, together with the atomic numbering scheme; important distances and angles are reported in Table 2. The structure consists of a triangle of Ru atoms [Ru(1)–Ru(2) = 2.776(1), Ru(1)–Ru(3) = 3.035(1) and Ru(2)–Ru(3) = 2.866(2) Å] bound to eight terminal carbonyls, three on each of the Ru(2) and Ru(3) atoms and two on Ru(1), which also bears the terminal $\text{PhPCH}=\text{CH}_2$ ligand [Ru(1)–P(1) = 2.305(2) Å]. The hydride bridges the longest edge of the metal triangle [Ru(1)–H(1) = 1.68, Ru(3)–H(1) = 1.79 Å] with the hydride bridge making a dihedral angle of 37.8° with it. The $\text{PhCH}_2=\text{CH}(\text{P}(\text{CH}=\text{CH}))$ ligand interacts with all of

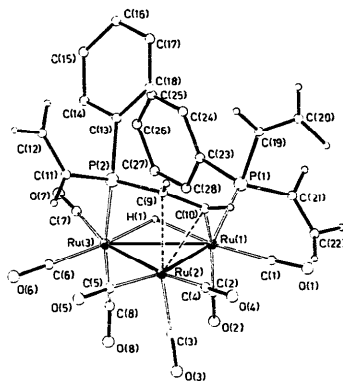


Fig. 2. View of the structure of the complex **4b** with the atomic numbering scheme.

the three metals, via σ bonds between Ru(3) and P(2) [Ru(3)–P(2) = 2.332(2) Å] and between Ru(1) and C(10) [Ru(1)–C(10) = 2.068(5) Å] and via a π bond between Ru(2) and the C(9)–C(10) bond [Ru(2)–C(9) = 2.290(6), Ru(2)–C(10) = 2.248(5) Å]. As expected, the "activation" of the C(9)–C(10) double bond results in its elongation [1.404(8) Å]. This distance is shorter

Table 2
Selected bond distances (Å) and angles ($^\circ$)

Ru(1)–Ru(2)	2.776(1)	Ru(2)–C(4)	1.897(7)
Ru(1)–Ru(3)	3.035(1)	Ru(2)–C(5)	1.897(6)
Ru(2)–Ru(3)	2.866(2)	Ru(2)–C(9)	2.290(6)
Ru(1)–P(1)	2.305(2)	Ru(2)–C(10)	2.248(5)
Ru(3)–P(2)	2.332(2)	Ru(3)–C(6)	1.892(6)
Ru(1)–C(1)	1.864(7)	Ru(3)–C(7)	1.937(6)
Ru(1)–C(2)	1.939(6)	Ru(3)–C(8)	1.935(7)
Ru(1)–C(10)	2.068(5)	P(2)–C(9)	1.760(6)
Ru(2)–C(3)	1.893(7)	C(9)–C(10)	1.404(8)
Ru(2)–Ru(1)–Ru(3)	58.9(1)	C(3)–Ru(2)–C(4)	93.2(3)
Ru(1)–Ru(2)–Ru(3)	65.0(1)	C(3)–Ru(2)–C(5)	101.3(3)
Ru(1)–Ru(3)–Ru(2)	56.0(1)	C(4)–Ru(2)–C(5)	93.5(3)
Ru(2)–Ru(1)–C(1)	97.9(2)	Ru(1)–Ru(3)–P(2)	84.7(1)
Ru(2)–Ru(1)–C(2)	112.6(2)	Ru(1)–Ru(3)–C(7)	114.6(2)
Ru(2)–Ru(1)–C(10)	52.9(2)	Ru(1)–Ru(3)–C(8)	86.4(2)
Ru(3)–Ru(1)–P(1)	111.5(1)	Ru(1)–Ru(3)–P(2)	71.3(1)
Ru(3)–Ru(1)–C(2)	90.9(2)	Ru(2)–Ru(3)–C(6)	92.6(2)
Ru(3)–Ru(1)–C(10)	84.5(2)	Ru(2)–Ru(3)–C(8)	94.3(2)
P(1)–Ru(1)–C(1)	91.9(2)	P(2)–Ru(3)–C(6)	92.4(2)
P(1)–Ru(1)–C(2)	94.9(2)	P(2)–Ru(3)–C(7)	99.6(2)
P(1)–Ru(1)–C(10)	100.3(2)	C(6)–Ru(3)–C(7)	97.5(3)
C(1)–Ru(1)–C(2)	92.8(3)	C(6)–Ru(3)–C(8)	89.1(3)
C(1)–Ru(1)–C(10)	85.7(2)	C(7)–Ru(3)–C(8)	94.5(3)
Ru(3)–Ru(2)–C(3)	88.7(2)	P(2)–C(11)–C(12)	126.5(6)
Ru(3)–Ru(2)–C(5)	94.3(2)	P(2)–C(9)–C(10)	121.1(4)
Ru(1)–Ru(2)–C(3)	79.4(2)	C(9)–P(2)–C(11)	104.0(3)
Ru(1)–Ru(2)–C(4)	107.0(2)		

than that found in **4a** [1.45(3) Å]. Only slight differences can be observed by comparing the other important structural features of **4a** and **4b**, in agreement with recent results on a large series of phosphine-substituted triruthenium clusters which suggested only minor changes in intracluster distances upon phosphine substitution [19,20].

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