Reaction of Diphenyl(vinyl)phosphine with Carbonyls $[M_3(CO)_{12}]$ (M = Ru or Os); Oxidative Addition at $[Ru_3(CO)_{12}]$. Spectroscopic Characterization and Crystal Structure of $[Ru_3(\mu\text{-}H)(CO)_8(Ph_2PCH{=}CH_2)(\mu_3\text{-}Ph_2PCH{=}CH)]$†

Roberto Gobetto and Enrico Sappa*
Dipartimento di Chimica Inorganica, Chimica Fisica e Chimica dei Materiali, Università di Torino, Via Pietro Giuria 7, 10125 Torino, Italy
Antonio Tiripicchio* and Marisa Tiripicchio Camellini
Istituto di Chimica Generale ed Inorganica, Università di Parma, Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., Viale delle Scienze, 43100 Parma, Italy
Martin J. Mays
University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW

The reaction of $PPh_2(CH{=}CH_2)$ with $[Os_3(CO)_{12}]$ in aliphatic hydrocarbons gives the monosubstituted derivative $[Os_3(CO)_{11}(Ph_2PCH{=}CH_2)]$ in medium yield. By contrast $[Ru_3(CO)_{12}]$ gives, as the final product, $[Ru_3(\mu\text{-}H)(CO)_8(Ph_2PCH{=}CH_2)(\mu_3\text{-}Ph_2PCH{=}CH)]$ (**2**) in high yield; this reaction represents an example of oxidative addition of $PPh_2(CH{=}CH_2)$, occurring in two steps and presumably favoured by the t.l.c. support material used during purification. These compounds have been characterized by elemental analyses and spectroscopy, in particular ^1H, ^{13}C, and ^{31}P n.m.r. The structure of complex (**2**) has also been determined by *X*-ray diffraction methods. It crystallizes in the orthorhombic space group $P2_12_12_1$ with $Z = 4$ in a unit cell of dimensions a = 15.984(6), b = 22.441(7), and c = 10.327(4) Å. The structure has been solved from diffractometer data by direct and Fourier methods and refined by full-matrix least squares to R = 0.0430 for 1 634 observed reflections. The structure consists of a scalene triangle of Ru atoms [Ru(1)–Ru(2) 2.759(3), Ru(1)–Ru(3) 3.024(3) and Ru(2)–Ru(3) 2.862(3) Å] bound to eight terminal carbonyls. The $PPh_2(CH{=}CH_2)$ is σ-bound to one Ru atom through the P atom, while the $Ph_2PCH{=}CH$ ligand interacts with all three metals, being σ-bound to two Ru atoms (through the P and C atom) and π-bound to the third Ru atom through the double bond. This latter ligand is formed by stepwise oxidative addition of $PPh_2(CH{=}CH_2)$ to the cluster, with hydrogen transfer to give a hydride ligand bridging the longest edge of the cluster.

In recent years there has been considerable interest in the chemistry of phosphido- and phosphinidene-bridged metal clusters[1] with or without hydrocarbyl substituents; the former were initially obtained by thermal treatment of phosphine-substituted clusters characterized by strong metal–metal bonds, such as $[Os_3(CO)_{12-n}L_n]$ (L = phosphine).[2] In some instances P–C bond cleavage in the co-ordinated phosphines was preceded by hydrogen abstraction; isomerism between M–P–C bonded systems, such as $[Os_3H(CO)_9(Et_2PC{=}CH_2)]$, and phosphido-bridged, hydrocarbyl-substituted derivatives, such as $[Os_3H(CO)_9(CH{=}CH)(\mu\text{-}PEt_2)]$ was observed.[3] A more selective approach to phosphido-bridged, hydrocarbyl-substituted clusters is represented by P–C bond activation and cleavage of co-ordinated phosphinoalkynes; these reactions often occur under mild conditions.[4]

Very recently it has been shown that phosphinidene-bridged clusters (and, less easily, phosphido-bridged derivatives) may undergo insertion of alkynes into the M–P bonds under relatively mild conditions, forming a variety of systems with M–P–C bonds.[1b]

The P–C bond cleavage of co-ordinated phosphines may lead to undesired modification of phosphine-stabilized homogeneous catalysts;[5] on the other hand, insertion of small organic molecules into M–P bonds, with initial formation of M–P–C bonds, is a retrosynthetic pathway to phosphine-substituted complexes, and may lead to undesired modification of phosphido- or phosphinidene-substituted clusters during homogeneous catalytic processes.[6] The reactivities of P–C and M–P bonds are hence important in determining the occurrence of the above, catalytically relevant processes; however, little is known about the mechanism and energetics of such reactions.

As a qualitative contribution to knowledge in this field, we have examined the reactivity of diphenyl(vinyl)phosphine towards the carbonyls $[M_3(CO)_{12}]$ (M = Ru or Os). The compound $PPh_2(CH{=}CH_2)$ is a commercially available potential starting material for hydrocarbyl-substituted, phosphido-bridged clusters; it is expected to show intermediate reactivity between that of phosphinoalkynes (which undergo easy P–C cleavage) and alkylphosphines (which react with considerable difficulty).[2,3] We have found that it substitutes only a CO group in $[Os_3(CO)_{12}]$, whereas both substitution and oxidative addition occur in $[Ru_3(CO)_{12}]$; the latter, which occurs without P–C bond cleavage, is probably a two-step process, and is favoured by the t.l.c. material used during the purification of the reaction mixtures. The new product $[Ru_3(\mu\text{-}H)(CO)_8(Ph_2PCH{=}CH_2)(\mu_3\text{-}Ph_2PCH{=}CH)]$ has been characterized by spectroscopic techniques and its structure determined by *X*-ray diffraction methods.

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† 1,1,1,2,2,2,3,3-Octacarbonyl-μ_3-[2′-diphenylphosphinovinyl-$C^{1'}(Ru^{2,3})C^{2'}(Ru^2)P(Ru^1)$]-3-[diphenyl(vinyl)phosphine-*P*]-1,3-μ-hydrido-*triangulo*-triruthenium.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix-xxii.

Table 1. Proton and ^{31}P n.m.r. data for complex (**1**) (solvent $CDCl_3$, 22 °C)

Attribution	Chemical shift[a]	Coupling constants (Hz)
Ph	7.71 (m, 8)	
Ph	7.42 (m, 2)	
H^{1b}	7.04 (ddd, 1)	$J(H^1\text{-}P)$ 25.8, $J(H^1\text{-}H^{22})$ 17.7, $J(H^1\text{-}H^{21})$ 11.3
H^{21}	6.05 (ddd, 1)	$J(H^{21}\text{-}P)$ 40.6, $J(H^{21}\text{-}H^1)$ 11.3, $J(H^{21}\text{-}H^{22})$ 0.8
H^{22}	5.19 (ddd, 1)	$J(H^{22}\text{-}P)$ 21.0, $J(H^{22}\text{-}H^1)$ 17.7, $J(H^{22}\text{-}H^{21})$ 0.8
P^c	−9.29 (s)	

[a] Multiplicity and relative integrated intensities in parentheses. [b] H^1 on the carbon atom close to phosphorus; H^{21} and H^{22} on the other vinyl carbon, H^{21} *trans* to the phosphorus atom. [c] 85% H_3PO_4 as external standard.

Table 2. Proton, ^{31}P, and ^{13}C n.m.r. data for complex (**2**) [solvent $(CD_3)_2CO$, 22 °C]

Attribution	Chemical shift[a]	Coupling constants (Hz)
H^{10b}	8.27 (dd, 1)	$J(H^{10}\text{-}P^2)$ 46.2, $J(H^{10}\text{-}H^9)$ 9.6
Ph	7.93 (m, 2), 7.53 (m, 10), 7.44 (m, 2), 7.38 (m, 2), 7.22 (m, 2), 7.07 (m, 2)	
H^{11}	6.80 (ddd, 1)	$J(H^{11}\text{-}H^{121})$ 17.8, $J(H^{11}\text{-}H^{122})$ 11.9, $J(H^{11}\text{-}P^1)$ 22.4
H^{122c}	6.04 (ddd, 1)	$J(H^{122}\text{-}P^1)$ 40.3, $J(H^{122}\text{-}H^{11})$ 11.9
H^9	5.74 (ddd, 1)	$J(H^9\text{-}P^2)$ 11.2, $J(H^9\text{-}H^{10})$ 9.6, $J(H^9\text{-}H)$ 1.8
H^{121}	5.40 (dd, 1)	$J(H^{121}\text{-}P^1)$ 19.7, $J(H^{121}\text{-}H^{11})$ 17.8
H^d	−17.82 (ddd, 1)	$J(H\text{-}P^2)$ 19.2, $J(H\text{-}P^1)$ 10.1, $J(H\text{-}H^9)$ 1.8
P^e	+38.2 (d)	$J(P\text{-}P)$ 15.3
P	+27.3 (d)	$J(P\text{-}P)$ 15.3
CO^f	202.6 (dd, 1)	$J(C\text{-}P)$ 9.9, $J(C\text{-}P)$ 11.1
CO^g	201.5 (d, 1)	$J(C\text{-}P)$ 96.9
CO	197.0 (br, 3)	
CO	195.4 (d, 1)	$J(C\text{-}P)$ 11.0
CO	193.4 (d, 1)	$J(C\text{-}P)$ 7.7
CO	190.0 (d, 1)	$J(C\text{-}P)$ 6.6

[a] Multiplicity and relative integrated intensities in parentheses. [b] The hydrogen atoms are numbered as in the structure drawing. [c] Hydrogen *trans* to P^1. [d] Hydridic hydrogen. [e] Attribution uncertain; 85% H_3PO_4 as external reference. [f] Carbonyl region reported only; solvent $CDCl_3$, +22 °C. For attribution see text. [g] Probably C^8 as indicated by the high coupling constant with P; this is indeed the unique CO group *trans* to phosphorus.

Experimental

General Experimental Details.—The carbonyls $[M_3(CO)_{12}]$ and $PPh_2(CH{=}CH_2)$ were commercial products (Strem Chemicals) used as received, after purity checks. The reactions were performed in aliphatic hydrocarbons distilled over sodium, under a dry nitrogen atmosphere, in conventional three-necked flasks equipped with a gas inlet, cooler, and mercury valve. The reaction mixtures were reduced to small volume under reduced pressure and purified on preparative t.l.c. plates (Kieselgel P.F. Merck) with light petroleum (b.p. 40—70 °C) and diethyl ether (80:20) as the eluant. Elemental analyses were performed in F. Pascher Laboratories (Remagen, West Germany). I.r. spectra were recorded on a Perkin-Elmer 580 and ^1H, ^{13}C, and ^{31}P n.m.r. spectra on a JEOL JNM 270 GX FT instrument.

Synthesis of Complexes (**1**) *and* (**2**).—Treatment of $[Os_3(CO)_{12}]$ with a 2:1 molar excess of $PPh_2(CH{=}CH_2)$ in refluxing octane for 6 min gave a dark yellow solution; during cooling and concentration considerable amounts of $[Os_3(CO)_{12}]$ precipitated [these were reused for further reaction with $PPh_2(CH{=}CH_2)$]. T.l.c. purification afforded a broad yellow band of $[Os_3(CO)_{11}(Ph_2PCH{=}CH_2)]$ (**1**), 20% yield based on osmium) (Found: C, 29.4; Os, 50.5; P, 3.1. Calc.: C, 27.5; Os, 52.3; P, 2.85%). The analysis of hydrogen gave unreliable values because of the presence of osmium. I.r. [ν(CO), hexane–$CHCl_3$ (60:40)]: 2 104w, 2 064m, 2 050s, 2 026vs, 2 016vs, and 2000m cm^{-1}. N.m.r. data are given in Table 1.

Treatment of $[Ru_3(CO)_{12}]$ with a 1.5:1 molar excess of $PPh_2(CH{=}CH_2)$ in refluxing heptane for 2 min gave a dark red solution, which was reduced to small volume under reduced pressure; during deposition on the t.l.c. plates the colour became yellow and only one broad yellow band was observed after chromatography, together with a very small amount of $[Ru_3(CO)_{12}]$ and decomposition products. The yellow band was identified as $[Ru_3(\mu\text{-}H)(CO)_8(Ph_2PCH{=}CH_2)(\mu_3\text{-}Ph_2PCH{=}CH)]$ (**2**), 80–85% yield (Found: C, 44.6; H, 2.8; P, 6.4; Ru, 30.8. Calc.: C, 45.45; H, 2.75; P, 6.5; Ru, 32.0%). I.r. [ν(CO), hexane–$CHCl_3$ (60:40)]: 2 070vs, 2 032vs, 2 017vs, 1 998m, br, and 1 970m, br cm^{-1}. N.m.r. data are given in Table 2.

Crystal Structure Determination of Complex (**2**).—Crystals of complex (**2**) were obtained by slowly cooling an hexane–$CHCl_3$ (60:40) solution of the complex.

Crystal data. $C_{36}H_{26}O_8P_2Ru_3$, $M = 951.75$, orthorhombic, space group $P2_12_12_1$, $a = 15.984(6)$, $b = 22.441(7)$, $c = 10.327(4)$ Å, $U = 3\,704(2)$ Å^3 (by least-squares refinement of the θ values of 30 accurately measured reflections), $Z = 4$, $\lambda = 0.710\,73$ Å, $D_c = 1.707$ g cm^{-3}, $F(000) = 1\,872$, $\mu(\text{Mo-}K_\alpha) = 13.17$ cm^{-1}. A yellow crystal of approximate dimensions 0.21 × 0.23 × 0.30 mm was used for the data collection. No absorption correction was made.

Data collection and processing. Siemens AED diffractometer, θ—2θ scan mode, using niobium-filtered Mo-K_α radiation; all the reflections with θ in the range 3–25° were measured. Of 3 703 independent reflections, 1 634, having $I > 2\sigma(I)$, were considered observed and used in the analysis.

Structure solution and refinement. Direct and Fourier methods, full-matrix least squares with anisotropic thermal parameters in the last cycles for the Ru and P atoms only. In independent final cycles of refinement the co-ordinates $-x$, $-y$, $-z$ were used because of the acentric space group. No improvement in the R value was obtained [$R(x,y,z) = 0.0446$, $R(-x,-y,-z) = 0.0455$]. The former model was selected, and the reported data refer to this model. All the hydrogen atoms except for the hydride H(1) and those of the vinylene group, H(9) and H(10) (located in the final Fourier difference map), were placed at their geometrically calculated positions. All the hydrogen atoms were introduced in the final structure-factor calculation with fixed isotropic thermal parameters ($U = 0.9$ Å^2). The weighting scheme used in the last cycles of refinement was $w = K[\sigma^2(F_o) + gF_o^2]^{-1}$ with $K = 0.713$ and $g = 0.006$. Final R and R' values were 0.0430 and 0.0576 respectively.

The SHELX system of computer programs was used.[7] Atomic scattering factors, corrected for anomalous dispersion, were taken from ref. 8. All calculations were performed on the CRAY X-MP/12 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Bologna. Final atomic co-ordinates for the non-hydrogen atoms are given in Table 3.

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Table 3. Fractional co-ordinates (× 10^4) with estimated standard deviations (e.s.d.s) in parentheses for the non-hydrogen atoms of complex (**2**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Ru(1)	8 893(1)	3 798(1)	934(2)	C(13)	11 030(15)	3 489(9)	−3 076(22)
Ru(2)	8 891(1)	3 011(1)	−1 119(2)	C(14)	11 851(16)	3 449(10)	−2 976(25)
Ru(3)	10 469(1)	3 143(1)	157(2)	C(15)	12 333(15)	3 202(11)	−4 041(25)
P(1)	9 031(4)	4 733(2)	1 855(6)	C(16)	11 900(15)	3 035(11)	−5 096(25)
P(2)	10 469(4)	3 774(2)	−1 649(5)	C(17)	11 108(20)	3 071(13)	−5 223(30)
O(1)	7 035(12)	3 939(8)	891(18)	C(18)	10 590(17)	3 284(11)	−4 151(26)
O(2)	8 859(12)	3 206(8)	3 604(18)	C(19)	10 912(13)	4 525(9)	−1 513(20)
O(3)	8 346(12)	2 143(8)	950(19)	C(20)	10 924(15)	4 886(10)	−2 617(23)
O(4)	7 084(13)	2 996(8)	−1 882(19)	C(21)	11 197(17)	5 503(12)	−2 538(24)
O(5)	9 429(16)	2 103(10)	−3 175(25)	C(22)	11 504(15)	5 690(11)	−1 379(26)
O(6)	11 179(14)	2 136(9)	−1 487(20)	C(23)	11 482(14)	5 359(11)	−316(24)
O(7)	12 132(12)	3 503(8)	1 316(17)	C(24)	11 193(14)	4 756(9)	−359(21)
O(8)	10 074(11)	2 222(7)	2 254(16)	C(25)	8 729(12)	5 370(9)	833(21)
C(1)	7 751(14)	3 888(10)	951(23)	C(26)	9 097(14)	5 434(10)	−388(22)
C(2)	8 891(18)	3 436(11)	2 586(25)	C(27)	8 935(16)	5 927(10)	−1 143(24)
C(3)	8 601(14)	2 490(11)	221(25)	C(28)	8 332(17)	6 355(12)	−728(27)
C(4)	7 790(17)	3 021(11)	−1 665(24)	C(29)	7 937(16)	6 278(11)	437(23)
C(5)	9 236(18)	2 434(14)	−2 230(30)	C(30)	8 128(15)	5 798(10)	1 232(24)
C(6)	10 897(16)	2 529(12)	−893(27)	C(31)	10 045(14)	4 977(10)	2 529(21)
C(7)	11 510(14)	3 377(9)	882(23)	C(32)	10 247(15)	5 592(11)	2 607(25)
C(8)	10 230(14)	2 595(10)	1 466(22)	C(33)	11 006(16)	5 732(10)	3 231(24)
C(9)	9 374(12)	3 856(9)	−2 068(20)	C(34)	11 501(16)	5 344(12)	3 768(28)
C(10)	8 837(13)	4 002(8)	−980(21)	C(35)	11 290(16)	4 708(11)	3 694(26)
C(11)	8 314(15)	4 763(10)	3 284(23)	C(36)	10 547(15)	4 537(10)	3 091(22)
C(12)	8 591(15)	4 878(11)	4 492(26)				

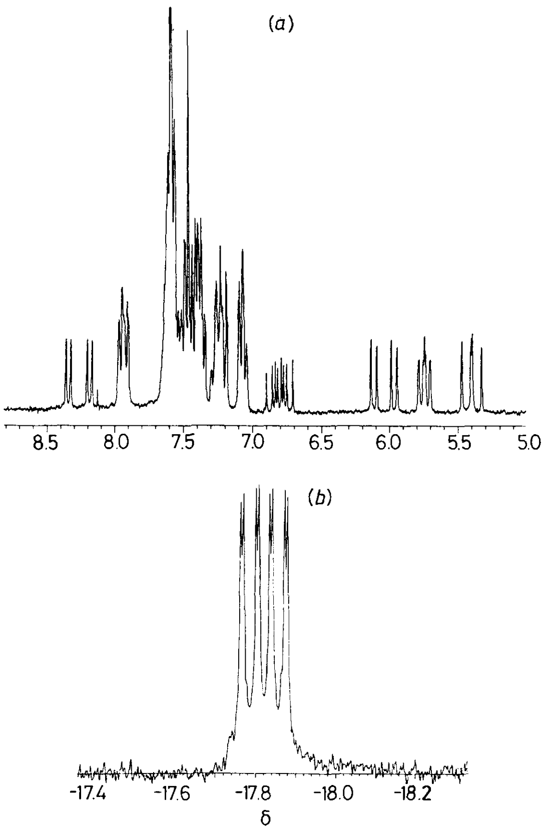

Figure 1. Proton n.m.r. spectrum of complex (**2**) (*a*) in the phenyl, vinyl, and vinylene regions, (*b*) in the bridging hydride region

tallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond distances and angles.

Results and Discussion

The reactions of $[Os_3(CO)_{12}]$ and $[Ru_3(CO)_{12}]$ with $PPh_2(CH{=}CH_2)$ give different final products; under the conditions adopted $[Os_3(CO)_{12}]$ gives only complex (**1**), in which one CO is substituted by a 'terminal' phosphine acting as a two-electron donor.

By contrast $[Ru_3(CO)_{12}]$, which is generally more reactive, presumably gives as a first product the disubstituted $[Ru_3(CO)_{10}(Ph_2PCH{=}CH_2)_2]$; this is transformed to complex (**2**) on the t.l.c. plates. Evidence for the formation of $[Ru_3(CO)_{10}(Ph_2PCH{=}CH_2)_2]$ in solution is provided by: (*i*) the red colour, as generally for $[Ru_3(CO)_{12-n}L_n]$ ($n = 2$) derivatives;[9,10] (*ii*) the i.r. spectrum of the heptane reaction solution, in which well resolved CO signals at 2 068vs, 2 058m(sh), 2 030vs, 2 016vs, 1 987s, br and 1 970s, br cm^{-1} were observed. These can be compared with those of the complexes reported in refs. 9 and 10. An alternative hypothesis could be formulated for the nature of the red compound; it could have a $PPh_2(CH{=}CH_2)$ ligand bridging two metals, by using the PPh_2 and the $CH{=}CH_2$ groups in a way comparable to that reported for some styrylphosphine triruthenium derivatives.[9b] This complex could also undergo stepwise oxidative addition as described below.

Spectroscopic Characterization of Complexes (**1**) *and* (**2**).— Complexes (**1**) and (**2**) have been identified by elemental analyses (see Experimental section), i.r. and n.m.r. spectra (see Tables 1 and 2). From these data and from the results of an *X*-ray structure determination,[11] complex (**1**) could be formulated as $[Os_3(CO)_{11}(Ph_2PCH{=}CH_2)]$. Figure 1 shows the very characteristic ^{1}H n.m.r. spectrum of (**2**) in deuteriated acetone at room temperature; an accurate examination of the peaks, together with double-resonance experiments, allows the assignment of the different multiplets according to Table 2 (the numbering of the hydrogen atoms is related to that of the carbon atoms to which they are bonded and given in the drawing of the structure). The hydride region of the ^{1}H n.m.r. spectrum consists of four pairs of closely spaced lines corresponding to two different coupling constants to the phosphorus atoms [J(H–P) = 19.2 and 10.1 Hz] and to a small coupling

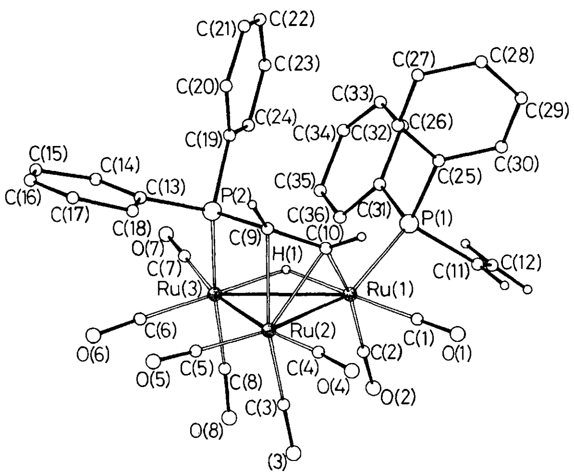

Figure 2. View of the structure of $[Ru_3(\mu\text{-}H)(CO)_8(Ph_2PCH{=}CH_2)(\mu_3\text{-}Ph_2PCH{=}CH)]$ (**2**) with the atomic numbering scheme

Table 4. Selected bond distances (Å) and angles (°) in complex (**2**)

Ru(1)–Ru(2)	2.759(3)	Ru(3)–C(7)	1.90(2)
Ru(1)–Ru(3)	3.024(3)	Ru(3)–C(8)	1.87(2)
Ru(2)–Ru(3)	2.862(3)	P(1)–C(11)	1.87(2)
Ru(1)–P(1)	2.315(6)	P(2)–C(9)	1.81(2)
Ru(3)–P(2)	2.340(6)	C(9)–C(10)	1.45(3)
Ru(1)–C(1)	1.84(2)	C(11)–C(12)	1.35(4)
Ru(1)–C(2)	1.89(3)	C(1)–O(1)	1.15(3)
Ru(1)–C(10)	2.03(2)	C(2)–O(2)	1.17(3)
Ru(2)–C(3)	1.87(3)	C(3)–O(3)	1.16(3)
Ru(2)–C(4)	1.85(3)	C(4)–O(4)	1.15(3)
Ru(2)–C(5)	1.91(3)	C(5)–O(5)	1.16(4)
Ru(2)–C(9)	2.27(2)	C(6)–O(6)	1.17(3)
Ru(2)–C(10)	2.23(2)	C(7)–O(7)	1.13(3)
Ru(3)–C(6)	1.88(3)	C(8)–O(8)	1.19(3)
Ru(2)–Ru(1)–Ru(3)	59.1(1)	P(2)–Ru(3)–Ru(2)	72.3(2)
Ru(1)–Ru(2)–Ru(3)	65.1(1)	P(2)–Ru(3)–C(6)	89.1(8)
Ru(1)–Ru(3)–Ru(2)	55.8(1)	P(2)–Ru(3)–C(7)	98.5(7)
P(1)–Ru(1)–C(1)	89.5(7)	C(6)–Ru(3)–Ru(2)	88.8(8)
P(1)–Ru(1)–C(2)	91.1(8)	C(6)–Ru(3)–C(7)	96.4(10)
P(1)–Ru(1)–C(10)	101.5(6)	C(6)–Ru(3)–C(8)	90.5(11)
P(1)–Ru(1)–Ru(3)	118.0(2)	C(7)–Ru(3)–Ru(1)	119.4(7)
C(1)–Ru(1)–Ru(2)	94.4(7)	C(7)–Ru(3)–C(8)	94.3(10)
C(1)–Ru(1)–C(2)	92.1(11)	C(8)–Ru(3)–Ru(1)	87.6(7)
C(1)–Ru(1)–C(10)	86.6(10)	C(8)–Ru(3)–Ru(2)	94.9(7)
C(2)–Ru(1)–Ru(2)	114.8(7)	Ru(1)–P(1)–C(11)	107.4(8)
C(2)–Ru(1)–Ru(3)	91.9(8)	Ru(3)–P(2)–C(9)	104.6(7)
C(10)–Ru(1)–Ru(2)	52.9(6)	P(2)–C(9)–C(10)	114.2(15)
C(10)–Ru(1)–Ru(3)	83.6(6)	P(1)–C(11)–C(12)	122.4(19)
C(3)–Ru(2)–Ru(1)	80.3(8)	Ru(1)–C(1)–O(1)	176(2)
C(3)–Ru(2)–Ru(3)	86.7(7)	Ru(1)–C(2)–O(2)	177(2)
C(3)–Ru(2)–C(4)	89.8(11)	Ru(2)–C(3)–O(3)	172(2)
C(3)–Ru(2)–C(5)	98.5(12)	Ru(2)–C(4)–O(4)	173(2)
C(4)–Ru(2)–Ru(1)	103.2(8)	Ru(2)–C(5)–O(5)	177(3)
C(4)–Ru(2)–C(5)	94.4(12)	Ru(3)–C(6)–O(6)	177(2)
C(5)–Ru(2)–Ru(3)	97.3(9)	Ru(3)–C(7)–O(7)	178(2)
P(2)–Ru(3)–Ru(1)	85.3(2)	Ru(3)–C(8)–O(8)	177(2)

constant to atom H^9 [J(H–H) = 1.8 Hz]. When the hydridic signal is saturated in a double-resonance experiment, the multiplet at δ 5.74 is reduced to a doublet of doublets with J(H–H) = 9.6 and J(H–P) = 11.2 Hz as expected for a *cis* disposition of the two hydrogen atoms H^9 and H^{10}.

The ^{13}C n.m.r. spectrum of complex (**2**) in the carbonyl region shows only five different resonances, all of them coupled to the phosphorus atoms; a very broad signal centred at 197 p.p.m. can be explained in terms of scrambling at 22 °C of the three carbonyls bound to Ru(3).

X-Ray Crystal Structure of Complex (**2**).—The structure of complex (**2**) is shown in Figure 2 together with the atomic numbering scheme; important bond distances and angles are given in Table 4. The structure consists of a scalene triangle of Ru atoms [Ru(1)–Ru(2) 2.759(3), Ru(1)–Ru(3) 3.024(3), and Ru(2)–Ru(3) 2.862(3) Å] bound to eight terminal carbonyl groups, three each on Ru(2) and Ru(3) and two on Ru(1), which also bears the terminal $Ph_2PCH{=}CH_2$ ligand [Ru(1)–P(1) 2.315(6) Å]. The hydride bridges the longest edge of the cluster [Ru(1)–H(1) 1.84 and Ru(3)–H(1) 1.76 Å] with the hydride bridge making a dihedral angle of 14.6(1)° with the metal triangle.

The $Ph_2PCH{=}CH$ ligand interacts with all three metals being σ bound to Ru(3) through the P(2) atom [Ru(3)–P(2) 2.340(6) Å] and to Ru(1) through C(10) [Ru(1)–C(10) 2.03(2) Å] and π bound to Ru(2) through the C(9)–C(10) double bond [Ru(2)–C(9) 2.27(2) and Ru(2)–C(10) 2.23(2) Å]. This ligand is formed by stepwise oxidative addition of $PPh_2(CH{=}CH_2)$ to the cluster, with hydrogen transfer. Noteworthy is the C(9)–C(10) bond 'activation',[12] 1.45(3) Å. The presence in (**2**) of an additional $PPh_2(CH{=}CH_2)$ ligand, co-ordinated as a two-electron donor, offers the possibility of evaluating the activation of the C=C double bond after oxidative addition [C(11)–C(12) 1.35(4) Å].

The $Ph_2PCH{=}CH$ ligand can be considered as being derived from insertion of acetylene into a M–P bond of a bridging PPh_2 ligand (a known reaction). Regarded in this way complex (**2**) is the first example, to our knowledge, of a product of the insertion of an unsubstituted acetylene into a M–P bond. An example of a ruthenium cluster with acetylene inserted into a bridging PPh_2 is $[Ru_3(CO)_6\{P(Ph)C(Ph)CPh\}(\mu\text{-}PPh_2)_2]$, even if reductive elimination of benzene also occurs [C–C 1.41(3) Å].[13]

The electron count for complex (**2**) is 48, as the $Ph_2PCH{=}CH$ ligand acts as a five-electron donor.

Some Comments on the Reactivity of $PPh_2(CH{=}CH_2)$ *towards* $[M_3(CO)_{12}]$ *Clusters.*—As pointed out above, $[Ru_3(CO)_{12}]$ is more reactive than its osmium analogue; this greater reactivity may probably be related to the ease with which the CO groups are released and hence free co-ordination sites formed.[14] The fact that the formation of complex (**2**) is favoured by the t.l.c. silica gel support is in accord with this hypothesis; it is known that CO groups bound to clusters can react with surface OH^- groups to give CO_2 and H_2 in processes related to the water gas shift reaction.[15] Such a process for (**2**) would leave free sites for the multi-site co-ordination of $PPh_2(CH{=}CH_2)$ and for the oxidative-addition process which results in hydrogen transfer to the cluster.

As expected, $PPh_2(CH{=}CH_2)$ is less reactive than comparable phosphinoalkynes; under comparable conditions the latter easily undergo P–C bond cleavage. To our knowledge, only complexes with terminally bound phosphinoalkynes or with ligands derived from P–C cleavage have been isolated; notable examples of ruthenium clusters of this type are $[Ru_3(CO)_6(\mu\text{-}C_2Bu^t)(\mu,\eta\text{-}C_2Bu^t)(Ph_2PC{\equiv}CBu^t)(\mu\text{-}PPh_2)_2]$[16] and $[Ru_4(CO)_8(\mu,\eta\text{-}C_2Bu^t)(\mu_3,\eta^2\text{-}C_2Bu^t)(Ph_2PC{\equiv}CBu^t)(\mu\text{-}PPh_2)_2]$.[17] By contrast $PPh_2(CH{=}CH_2)$ can oxidatively add to a triruthenium frame without P–C bond cleavage.

Bridging ligands with P–C bonds are now well established; many of these are formed by attack of carbenes at μ_3-PR bridges,[18] or by insertion of alkynes into μ_3-PR[19,20] or μ-PR_2 bridges.[13] More complex ligands may be obtained from the interaction of phosphinoalkynes with cluster-bound hydrocarbyls[14] or by rearrangement reactions.[21] To our knowledge, however, the $Ph_2PCH{=}CH$ bridging ligand in (**2**) is the first example of such a ligand obtained by simple oxidative addition. Thermolysis of complex (**2**) in hydrocarbons under N_2 gives small yields of seven complexes, which are presently under investigation.

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