Chemistry of Multi-site Bound Unsaturated Ligands on Metal Carbonyl Clusters. Intramolecular Reductive Coupling in the Conversion of $[Ru_3(\mu\text{-}H)(CO)_9(\mu_3,\eta^2\text{-}C{\equiv}CBu^t)]$ to the Butadienyl Cluster $[Ru_3(CO)_8\{\mu_3,\eta^4\text{-}C(Bu^t)CC(H)C(Ph)(PPh_2)\}]$, and its Crystal Structure.* An Example of Ligand Isomerism on Metal Clusters

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The hydride $[Ru_3(\mu\text{-}H)(CO)_9(\mu_3,\eta^2\text{-}C{\equiv}CBu^t)]$ (**1**) reacts with $PPh_2C{\equiv}CPh$, in the presence of Me_3NO, forming the monosubstituted cluster $[Ru_3(\mu\text{-}H)(CO)_8(PPh_2C{\equiv}CPh)(\mu_3,\eta^2\text{-}C{\equiv}CBu^t)]$ (**2**), which has been characterized spectroscopically. Upon thermal treatment (**2**) gives the isomeric derivative $[Ru_3(CO)_8\{\mu_3,\eta^4\text{-}C(Bu^t)CC(H)C(Ph)(PPh_2)\}]$ (**3**), whose structure has been determined by *X*-ray diffraction methods. Crystals of (**3**) are triclinic, space group $P\bar{1}$, with $Z = 2$ in a unit cell of dimensions $a = 12.351(5)$, $b = 15.530(6)$, $c = 10.558(5)$ Å, $\alpha = 91.27(2)$, $\beta = 110.87(3)$, and $\gamma = 106.94(3)°$. The structure has been solved by direct and Fourier methods and refined by blocked-matrix least squares to $R = 0.0472$ for 4 109 observed reflections. The triangular cluster of Ru atoms is bound to eight carbonyl groups, of which seven are terminal and one is semibridging, and to a substituted butadienyl ligand, interacting with all three metal atoms, through a σ bond to Ru(3) and through extensive η bonding to Ru(1) and Ru(2). This organic ligand is obtained by tail-to-tail coupling of the cluster-bound C_2Bu^t of (**2**) with the phenylacetylide derived from the terminally bound phosphinoalkyne with shift of a phenyl group. A mechanism of formation of (**3**) from (**2**) is proposed and discussed.

A major problem related to the use of transition-metal clusters in homogeneous catalysis is that of their stability under the reaction conditions usually required, for example, in hydroformylation or Fischer–Tropsch reactions.[1] A well known approach to the stabilization of clusters consists in the use of bridging or capping ligands.[2] Phosphido and phosphinidene bridges[3] are widely used for this purpose, because of their flexibility, which allows reversible metal–metal bond formation and cleavage in the presence of donor ligands;[4] these bridges are also inert to several reactions typical of clusters, at least under mild conditions. However, under more drastic conditions, the phosphorus-containing ligands show reactivity and in particular: (*i*) insertion of small molecules into M–P bonds, resulting in the formation of new P–C bonds;[5] (*ii*) M–P hydrogenolysis to give terminally bound phosphines;[6] and (*iii*) P–C bond cleavage between phosphorus and its organic substituents, resulting in the formation of μ_3- or μ_4-PR ligands starting from μ-PR_2 bridges.[7]

Reverse reactions allow the synthesis of phosphido- and phosphinidene-bridged clusters; thus, thermal treatment of phosphine-substituted complexes[8] or reactions of free or co-ordinated phosphines PR_2H or PRH_2 with loss of hydrogen[9] are widely used for synthetic purposes. Also of interest is the P–C bond cleavage in phosphinoalkynes co-ordinated as two-electron donor ligands; this has proven a remarkably successful method for the synthesis of phosphido-bridged, hydrocarbyl-substituted clusters.[10] At present there is, however, little or no knowledge on the coupling of μ-PR_2 bridges with multisite bound hydrocarbyls, resulting in the formation of new P–C bonds.

Here we report an example of such a reaction, that is the co-ordination and P–C cleavage of a $PPh_2C{\equiv}CPh$ molecule, followed by formation of a new P–C bond under mild conditions; the overall process leads to the formation of two new isomeric clusters, characterized by very different co-ordinated ligands. We have found that the hydride $[Ru_3(\mu\text{-}H)(CO)_9(\mu_3,\eta^2\text{-}C{\equiv}CBu^t)]$ (**1**)[11] reacts with $PPh_2C{\equiv}CPh$, in the presence of Me_3NO, forming the monosubstituted derivative $[Ru_3(\mu\text{-}H)(CO)_8(PPh_2C{\equiv}CPh)(\mu_3,\eta^2\text{-}C{\equiv}CBu^t)]$ (**2**), which has been characterized spectroscopically; upon thermal treatment (**2**) gives the isomeric derivative $[Ru_3(CO)_8\{\mu_3,\eta^4\text{-}C(Bu^t)CC(H)C(Ph)(PPh_2)\}]$ (**3**) whose structure has been fully elucidated by an *X*-ray analysis. The synthesis, structure, and reactivity of both compounds (**2**) and (**3**) are discussed.

Experimental

General Procedures and Materials, Analysis of the Products.—The compound $[Ru_3(CO)_{12}]$ was obtained from Strem Chemicals, and 3,3-dimethylbut-1-yne from Fluka. Anhydrous Me_3NO was obtained upon sublimation *in vacuo* of commercial $Me_3NO{\cdot}2H_2O$; the phosphinoalkyne[12] and the hydride $[Ru_3H(CO)_9(C_2Bu^t)]$[13] were obtained by well established procedures. All the reactions were performed in three-necked flasks with a gas inlet, reflux condenser, and mercury check valve, using solvents distilled over sodium and under an atmosphere of dry nitrogen. Kieselgel P.F. (Merck) was used for t.l.c. purifications (eluants were mixtures of light petroleum, b.p. 40—70 °C, and diethyl ether).

Elemental analyses were performed with a F & M 165 C,H,N Analyzer; metal and phosphorus analyses were by F. Pascher

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* 1,1,1,2,2,2,3,3-Octacarbonyl-μ_3-[6-diphenylphosphino-2,2-dimethyl-6-phenylhexa-3,5-diene-3,4-diyl-$C^3(Ru^{2,3})C^4(Ru^{1,3})C^{5,6}(Ru^1)$-$P(Ru^3)$]-*triangulo*-triruthenium.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

(Bonn, W. Germany). Infrared spectra were recorded on a Perkin-Elmer 580 instrument, ^1H and ^{31}P n.m.r. spectra on a JEOL JNM GX 270 FT instrument. Shifts are reported relative to external $SiMe_4$ (^1H) or 85% H_3PO_4 (^{31}P). Compounds (**2**) and (**3**) decomposed in the inlet system of the mass spectrometer [Kratos MS-50, electron-impact (e.i.) technique, 70 eV (*ca.* 1.12×10^{-17} J)].

Synthesis of Compounds (**2**) *and* (**3**).—The compound $[Ru_3H(CO)_9(C_2Bu^t)]$ (**1**) (0.32 g, *ca.* 0.5 mmol) was dissolved in heptane and $PPh_2C{\equiv}CPh$ (0.28 g, *ca.* 1 mmol) and Me_3NO (30 mg) were added; after reflux for 15 min the dark yellow suspension was reduced to small volume *in vacuo* and chromatographed on t.l.c. preparative plates. Three bands were observed; the first, light yellow band was unchanged (**1**); the second yellow band was (**2**) (60% yield calculated on ruthenium); the third, dark yellow band, is under investigation.

Compound (**2**) (Found: C, 46.0; H, 3.1; P, 3.6; Ru 34.4. $C_{34}H_{25}O_8PRu_3$ requires C, 45.55; H, 2.9; P, 3.45; Ru, 33.8%): i.r., $\nu_{CO}(C_6H_{14})$ 2 063vs, 2 057s(sh), 2 026vs(sh), 2 018vs, 1 997vs(br), 1 988s(sh), 1 966m(br), and 1 945m(br) cm^{-1}; ^1H n.m.r. ($CDCl_3$, 298 K), δ 7.92 (m), 7.38 (m, 15 H, Ph), 1.41 (s, 9 H, Bu^t), and −21.0 (s, 1 H, hydride); ^{31}P n.m.r. ($CDCl_3$, 298 K), δ +24.04 (s) p.p.m.

Reflux of compound (**2**) in heptane, under an atmosphere of dry N_2 for 15—20 min, gave a cherry-red solution, which was evaporated *in vacuo* and the residue, redissolved in CH_3Cl (10 cm^3), was chromatographed on t.l.c. plates. One major product (**3**) (about 35% yield) was obtained, besides (**2**) (15% yield), together with five, uninvestigated, trace products. Compound (**3**) (Found: C, 45.3; H, 3.0; P, 3.5; Ru, 34.6. $C_{34}H_{25}O_8PRu_3$ requires C, 45.5; H, 2.9; P, 3.45; Ru, 33.8%): i.r., $\nu_{CO}(C_6H_{14})$ 2 067vs, 2 042vs, 2 007vs, 1 997vs, and 1 958m cm^{-1}; ^1H n.m.r. ($CDCl_3$, 298 K), δ 7.39 (m), 7.0 (m, Ph), 3.46 (d, C–H), and 1.19 (t, Bu^t); ^{31}P n.m.r. ($CDCl_3$, 298 K), δ +44.96 (s), and +45.09 (s) p.p.m. (intensity 2 : 1).

Crystals of compound (**3**), suitable for *X*-ray analysis, were obtained by cooling at −15 °C heptane–$CHCl_3$ solutions of (**3**) under N_2; two kinds of crystals, dark red and pink, were deposited; the dark red ones were chosen for the crystallographic work.

Crystal Structure Determination of Compound (**3**).—*Crystal data.* $C_{34}H_{25}O_8PRu_3{\cdot}0.5CHCl_3$, M = 955.44, triclinic, space group $P\bar{1}$, a = 12.351(5), b = 15.530(6), c = 10.558(5) Å, α = 91.27(2), β = 110.87(3), γ = 106.94(3)°, U = 1 792(1) Å^3 (by least-squares refinement of the θ values of 30 accurately measured reflections), Z = 2, λ = 0.710 69 Å, D_c = 1.771 g cm^{-3}, $F(000)$ = 938, $\mu(Mo\text{-}K_\alpha)$ = 14.29 cm^{-1}.

A crystal of approximate dimensions 0.15 × 0.30 × 0.30 mm was used for the structure analysis. No correction for absorption effects was made because of the low absorbance of the sample.

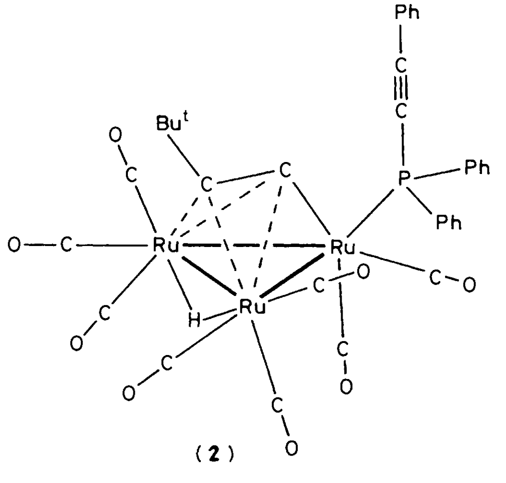
Data collection and processing. Siemens AED diffractometer, θ–2θ mode, using niobium-filtered $Mo\text{-}K_\alpha$ radiation; all the reflections with θ in the range 3—25° were measured. Of 5 937 independent reflections, 4 109 having $I > 2\sigma(I)$ were considered observed and used in the analysis.

Structure solution and refinement. Direct and Fourier methods, blocked-matrix least-squares refinement with anisotropic thermal parameters in the last cycles for all non-hydrogen atom except those of the $CHCl_3$ molecule. This solvent molecule was found disordered and distributed in two centrosymmetric positions. All hydrogen atoms were placed at their geometrically calculated positions, except for H(10) clearly localized in the final Fourier difference map, and introduced in the final structure factor calculation with fixed isotropic thermal parameters. A weighting scheme $w = [\sigma^2(F_o) + gF_c^2]^{-1}$ was used in the last cycles of refinement, with k = 0.6512 and g = 0.0109 at convergence. Final R and R' values were 0.0472 and 0.0721 respectively. The SHELX system of computer programs was used.[14] Atomic scattering factors, corrected for anomalous dispersion, were taken from ref. 15. All calculations were carried out on the CRAY X-MP/12 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Bologna, with financial support from the University of Parma. Final atomic co-ordinates for the non-hydrogen atoms are given in Table 1.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond distances and angles.

Results and Discussion

We have found that the hydridic complex (**1**), in the presence of Me_3NO, reacts with $PPh_2C{\equiv}CPh$ giving high yields of the monosubstituted complex $[Ru_3(\mu\text{-}H)(CO)_8(PPh_2C{\equiv}CPh)(\mu_3,\eta^2\text{-}C_2Bu^t)]$ (**2**), which has been characterized spectroscopically. The ^1H n.m.r. spectrum confirms the presence of one hydridic hydrogen, and a singlet at +24.04 p.p.m. in the ^{31}P n.m.r. spectrum indicates the presence of a terminally bound phosphinoalkyne. The i.r. spectrum shows the presence of all terminal carbonyl groups and is closely comparable to that of other phosphine derivatives of (**1**), such as $[Ru_3H(CO)_8(PPh_3)(C_2Bu^t)]$[16] and $[Ru_3H(CO)_8\{PPh_2(OEt)\}(C_2Bu^t)]$.[17] Finally the elemental analysis agrees with the proposed formulation. On the basis of these results, the structure shown below is proposed.



(**2**)

Indeed, all the known examples of monosubstituted phosphine derivatives of (**1**) show the phosphine on the ruthenium atom σ-interacting with the acetylide C(α).[16,17]

From the thermal reaction of compound (**2**) in heptane, two other processes are expected, namely the coupling of the cluster-bound hydride with the C≡CPh acetylide, obtained upon cleavage of $PPh_2C{\equiv}CPh$,[18] to form an acetylene, or the coupling of C≡CPh with the co-ordinated $\mu_3,\eta^2\text{-}C_2Bu^t$ to form a four-carbon ligand.[19] In both processes, the formation of a phosphido bridge was also expected.

Instead compound (**3**) is apparently formed upon insertion of the phosphinoalkyne into the Ru–C(α) bond of (**2**). No hydridic signals were detected in the ^1H n.m.r. spectrum of (**3**). Its structure, determined by *X*-ray diffraction methods, is presented in the Figure together with the atomic numbering scheme. Selected bond distances and angles are given in Table 2.

The triangular metal cluster shows all the three edges of different length [Ru(1)–Ru(2) 2.792(2), Ru(1)–Ru(3) 2.963(2),

Table 1. Fractional atomic co-ordinates (× 10^4) with estimated standard deviations (e.s.d.s) in parentheses for the non-hydrogen atoms of complex (**3**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Ru(1)	−100(1)	1 020(1)	2 261(1)	C(14)	3 062(11)	4 293(7)	3 393(11)
Ru(2)	−634(1)	2 592(1)	2 754(1)	C(15)	3 709(11)	5 192(8)	3 461(13)
Ru(3)	−2 397(1)	1 378(1)	647(1)	C(16)	3 715(12)	5 839(9)	4 298(13)
P	1 400(2)	2 877(2)	4 050(2)	C(17)	3 008(12)	5 617(8)	5 128(15)
O(1)	−1 809(7)	−470(5)	−54(8)	C(18)	2 326(12)	4 714(8)	5 038(13)
O(2)	1 161(7)	−427(5)	2 461(9)	C(19)	2 010(7)	2 666(6)	5 787(8)
O(3)	−1 147(7)	352(5)	4 426(8)	C(20)	3 295(9)	2 953(8)	6 487(10)
O(4)	−1 949(8)	2 139(8)	4 699(8)	C(21)	3 784(10)	2 728(9)	7 800(11)
O(5)	−671(10)	4 507(7)	2 996(11)	C(22)	3 054(12)	2 255(9)	8 439(11)
O(6)	−3 957(9)	2 530(8)	734(10)	C(23)	1 778(11)	1 995(8)	7 775(11)
O(7)	−3 711(7)	594(7)	−2 383(8)	C(24)	1 271(9)	2 208(8)	6 450(10)
O(8)	−3 884(8)	−74(8)	1 783(12)	C(25)	2 900(8)	1 864(6)	3 572(9)
C(1)	−1 368(8)	160(7)	697(9)	C(26)	3 143(9)	1 338(8)	4 601(11)
C(2)	728(9)	116(6)	2 418(10)	C(27)	4 213(9)	1 115(8)	5 075(12)
C(3)	−735(9)	640(7)	3 637(10)	C(28)	5 074(9)	1 430(8)	4 477(12)
C(4)	−1 429(9)	2 318(9)	3 974(9)	C(29)	4 839(8)	1 924(7)	3 431(12)
C(5)	−654(11)	3 783(9)	2 889(11)	C(30)	3 770(9)	2 161(7)	2 916(10)
C(6)	−3 355(10)	2 091(9)	696(12)	C(31)	−964(10)	3 128(7)	−527(9)
C(7)	−3 207(8)	875(7)	−1 257(11)	C(32)	334(11)	3 903(7)	109(12)
C(8)	−3 351(9)	469(8)	1 360(12)	C(33)	−1 966(11)	3 568(8)	−773(12)
C(9)	1 745(7)	2 102(6)	3 047(8)	C(34)	−1 047(13)	2 669(8)	−1 889(11)
C(10)	1 131(8)	2 073(5)	1 610(9)	C(35)	5 431(21)	5 299(20)	654(27)
C(11)	1(8)	2 255(5)	1 276(8)	Cl(1)	5 042(9)	4 337(7)	1 306(10)
C(12)	−1 000(8)	2 414(6)	435(8)	Cl(2)	6 707(9)	5 277(7)	424(10)
C(13)	2 354(9)	4 042(6)	4 158(9)	Cl(3)	4 367(10)	5 331(8)	−708(11)

Table 2. Selected bond distances (Å) and angles (°) for complex (**3**)

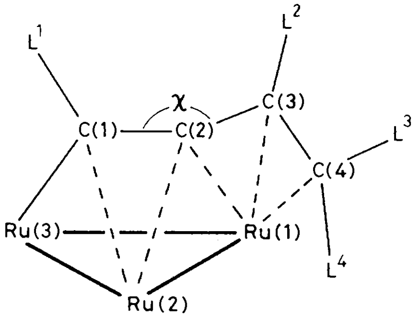
Ru(1)–Ru(2)	2.792(2)	Ru(1)–C(11)	2.195(8)	Ru(3)–C(12)	2.071(9)	C(1)–O(1)	1.109(12)
Ru(1)–Ru(3)	2.963(2)	Ru(2)–C(4)	1.867(12)	P–C(9)	1.821(11)	C(2)–O(2)	1.116(15)
Ru(2)–Ru(3)	2.686(2)	Ru(2)–C(5)	1.860(15)	P–C(13)	1.824(9)	C(3)–O(3)	1.157(15)
Ru(2)–P	2.292(3)	Ru(2)–C(11)	2.097(11)	P–C(19)	1.796(8)	C(4)–O(4)	1.154(16)
Ru(1)–C(1)	1.950(8)	Ru(2)–C(12)	2.320(9)	C(9)–C(10)	1.427(11)	C(5)–O(5)	1.135(19)
Ru(1)–C(2)	1.942(11)	Ru(3)–C(6)	1.853(15)	C(10)–C(11)	1.427(14)	C(6)–O(6)	1.155(20)
Ru(1)–C(3)	1.912(12)	Ru(3)–C(7)	1.922(10)	C(11)–C(12)	1.335(13)	C(7)–O(7)	1.133(13)
Ru(1)–C(9)	2.250(7)	Ru(3)–C(8)	1.912(12)	C(12)–C(31)	1.522(14)	C(8)–O(8)	1.117(17)
Ru(1)–C(10)	2.192(9)						
Ru(2)–Ru(1)–Ru(3)	55.6(1)	P–Ru(2)–C(4)	105.3(3)	C(7)–Ru(3)–C(8)	98.4(5)	C(10)–C(11)–C(12)	154.6(9)
Ru(1)–Ru(2)–Ru(3)	65.5(1)	P–Ru(2)–C(5)	97.7(4)	C(7)–Ru(3)–C(12)	96.5(4)	C(11)–C(12)–C(31)	123.1(9)
Ru(1)–Ru(3)–Ru(2)	59.0(1)	P–Ru(2)–C(11)	78.8(3)	C(7)–Ru(3)–Ru(1)	118.3(3)	C(11)–C(12)–Ru(3)	102.6(6)
C(1)–Ru(1)–C(2)	83.9(4)	P–Ru(2)–Ru(1)	73.8(1)	C(8)–Ru(3)–Ru(1)	92.9(4)	C(31) – C(12)–Ru(3)	133.7(7)
C(1)–Ru(1)–C(3)	99.1(5)	C(4)–Ru(2)–C(5)	90.7(6)	C(8)–Ru(3)–Ru(2)	108.4(4)	Ru(1)–C(1)–O(1)	156.8(9)
C(2)–Ru(1)–C(3)	94.8(4)	C(4)–Ru(2)–Ru(1)	104.6(4)	C(12)–Ru(3)–Ru(1)	74.1(3)	Ru(3)–C(1)–O(1)	122.3(8)
C(1)–Ru(1)–Ru(2)	114.1(3)	C(4)–Ru(2)–Ru(3)	95.5(4)	C(12)–Ru(3)–Ru(2)	56.6(3)	Ru(1)–C(1)–Ru(3)	80.9(3)
C(1)–Ru(1)–Ru(3)	58.6(3)	C(5)–Ru(2)–C(11)	114.6(4)	Ru(2)–P–C(13)	114.1(3)	Ru(1)–C(2)–O(2)	177.0(9)
C(3)–Ru(1)–Ru(2)	82.6(3)	C(5)–Ru(2)–Ru(3)	118.7(4)	Ru(2)–P–C(9)	99.7(3)	Ru(1)–C(3)–O(3)	175.5(9)
C(3)–Ru(1)–Ru(3)	89.9(4)	C(11)–Ru(2)–Ru(1)	51.0(2)	C(19)–P–Ru(2)	125.4(3)	Ru(2)–C(4)–O(4)	178.2(9)
C(9)–Ru(1)–C(11)	64.6(3)	C(11)–Ru(2)–Ru(3)	67.4(2)	P–C(9)–Ru(1)	97.6(4)	Ru(2)–C(5)–O(5)	178.6(11)
C(9)–Ru(1)–Ru(2)	76.7(2)	C(6)–Ru(3)–C(7)	98.2(5)	C(25)–C(9)–P	122.8(6)	Ru(3)–C(6)–O(6)	179.3(12)
C(10)–Ru(1)–Ru(2)	76.4(2)	C(6)–Ru(3)–C(8)	88.6(6)	C(10)–C(9)–P	112.2(7)	Ru(3)–C(7)–O(7)	177.7(10)
C(10)–Ru(1)–Ru(3)	97.3(2)	C(6)–Ru(3)–C(12)	95.9(5)	C(9)–C(10)–C(11)	112.7(8)	Ru(3)–C(8)–O(8)	178.0(12)
C(11)–Ru(1)–Ru(3)	60.9(2)	C(6)–Ru(3)–Ru(2)	85.2(4)				

and Ru(2)–Ru(3) 2.686(2) Å]. Of the eight carbonyl groups, seven are terminally bound to the Ru atoms [two to each of Ru(1) and Ru(2), three to Ru(3)] and one is semibridging between Ru(1) and Ru(3) [Ru(1)–C(1) 1.950(8) and Ru(3)–C(1) 2.560(12) Å, Ru(1)–C(1)–O(1) 156.8(9)°]. Application of the effective atomic number (e.a.n.) rule leads to a 17-electron count for the sterically less hindered Ru(3); this situation is relieved partially by the semibridging carbonyl.

The organic moiety is a substituted butadienylphosphine, interacting with all three metal atoms, as an eight-electron donor, through a σ bond to Ru(3) [Ru(3)–C(12) 2.071(9) Å], an olefinic bond to Ru(2) [Ru(2)–C(11) 2.097(11) and Ru(2)–C(12) 2.320(9) Å], and an allylic bond to Ru(1) [Ru(1)–C(9) 2.250(7), Ru(1)–C(10) 2.192(9), and Ru(1)–C(11) 2.195(8) Å]. The P atom is attached to Ru(2) [Ru(2)–P 2.292(3) Å]. Noteworthy in this C_4 chain is the very large angle at C(11) [C(10)–C(11)–C(12) 154.6(9)°], which bridges two Ru atoms.

This organic ligand is formed by tail-to-tail coupling of the C_2Bu^t unit to a rearranged PhC_2PPh_2 ligand with incorporation of the cluster-bound H atom. As already pointed out, the formation of the new C–C bond involves the C(α) of the cluster-bound acetylide.[19,20] This way of coupling seems favoured;[21] the possibility of head-to-tail coupling leading to a substitution isomer cannot be ruled out, especially in the light of the n.m.r. data. In the ^1H and ^{31}P n.m.r. spectra more signals than those expected were observed, so that there is the possibility of the

Table 3. Comparison of dimensions in the substituted butadienyl ligand bound to triangular ruthenium cluster



Bond distances (Å) and angles (°)	$[Ru_3(CO)_6(C_{12}H_{20})(C_{13}H_{20}O)]$ L^1 = Buᵗ; L^2 = Buᵗ, L^3 = H; L^4 = H	$[Ru_3(CO)_5(C_{12}H_{20})(C_{19}H_{30}O)]$ L^1 = Buᵗ; L^2 = Buᵗ, L^3 = H; L^4 = H	$[Ru_3(CO)_7(C_2Bu^t)\{PhC_2(H)Ph\}(C_2Ph_2)]$ L^1 = Buᵗ; L^2 = H L^3 = Ph; L^4 = H	$[Ru_3(CO)_8\{C(Bu^t)C_2(H)C(Ph)(PPh_2)\}]$ L^1 = Buᵗ; L^2 = H L^3 = Ph; L^4 = PPh_2
C(1)–C(2)	1.380(9)	1.40(3)	1.37(2)	1.335(13)
C(2)–C(3)	1.444(10)	1.40(3)	1.45(2)	1.427(14)
C(3)–C(4)	1.414(10)	1.41(4)	1.41(2)	1.427(11)
Ru(3)–C(1)	2.058(6)	2.05(2)	2.04(1)	2.071(9)
Ru(2)–C(1)	2.287(6)	2.16(2)	2.27(2)	2.320(9)
Ru(2)–C(2)	2.188(7)	2.10(2)	2.14(1)	2.097(11)
Ru(1)–C(2)	2.163(7)	2.19(2)	2.12(1)	2.195(8)
Ru(1)–C(3)	2.228(7)	2.22(2)	2.24(1)	2.192(9)
Ru(1)–C(4)	2.253(7)	2.19(3)	2.32(1)	2.250(7)
χ	151.8(8)	157(2)	146(1)	154.6(9)
Ref.	19*a*	19*b*	19*c*	This work

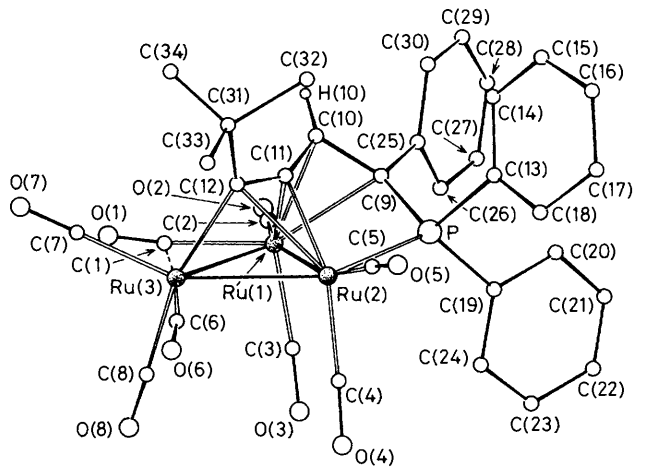
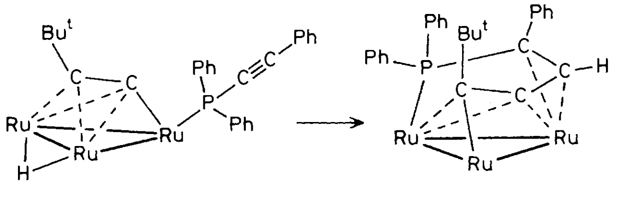


Figure. View of the structure of the complex $[Ru_3(CO)_8\{\mu_3,\eta^4\text{-}C(Bu^t)CC(H)C(Ph)(PPh_2)\}]$ with the atomic numbering scheme

existence of isomers in solution, which could originate from head-to-tail or tail-to-tail coupling of the acetylides.[19,21]

The formation of a butadienyl moiety in compound (**3**) *via* acetylide–acetylide coupling is supported by the close similarities of its four-carbon chain (and its bonding to the metals) with those found in the complexes $[Ru_3(CO)_6(C_{12}H_{20})(C_{13}H_{20}O)]$,[19a] $[Ru_3(CO)_5(C_{12}H_{20})(C_{19}H_{30}O)]$,[19b] and $[Ru_3(CO)_7(C_2Bu^t)\{PhC_2(H)Ph\}(C_2Ph_2)]$,[19c] some of which obtained as two substitution isomers. The C_4 chains in the above mentioned complexes are compared in Table 3 and in the annexed scheme.

The isomerization of compound (**2**) to (**3**) is shown in the scheme below. These processes could be explained with a



formation mechanism for (**3**) based on a multi-step reaction sequence. Phosphorus–carbon bond cleavage in the phosphinoalkyne co-ordinated to (**2**) could occur to form a μ-PPh_2 bridge. The phenylacetylide could then condense tail-to-tail with the cluster-bound t-butylacetylide as discussed above; finally insertion of the C_4 chain into a M–P bond and migration of the cluster-bound hydride on C(10) would lead to complex (**3**), the overall process being the isomerization of (**2**) to (**3**). All the proposed reaction steps have been previously observed. Easy P–C bond cleavage in co-ordinated phosphinoalkynes has been reported,[10] acetylide–acetylide condensations have been discussed above, and insertion of small molecules into M–P bonds is known.[5] Finally the formation of a diphenylphosphido vinylidene ligand upon isomerization of a PPh_2-bridged acetylide cluster, in a process closely comparable with that reported here, has been observed by Carty and co-workers.[22]

Some Comments on the Reactivity of Terminally Co-ordinated Phosphinoalkynes.—Phosphorus–carbon bond cleavage of terminally bound phosphinoalkynes occurs to different extents apparently depending on the nature of the co-ordinating cluster. It occurs under mild conditions for $[Ru_3(CO)_{11}(PPh_2C_2R)]$ (R = Prⁱ, Buᵗ, or Ph),[10] is more difficult for (**2**), and becomes nearly impossible for $[NiOs_3H_3(\eta\text{-}C_5H_5)(CO)_8(PPh_2C_2R)]$,[23,24] which at reflux disproportionates to $[NiOs_3H_3(\eta\text{-}C_5H_5)(CO)_9]$ and $[NiOs_3H_3(\eta\text{-}C_5H_5)(CO)_7(PPh_2C_2R)_2]$.[25] This behaviour could be related to the ease with which CO release and/or formation of free co-ordination sites occurs on the clusters.

The formation of compound (**3**) is indeed unexpected, in the light of current knowledge on the reactivity of phosphinoalkynes. The reactions reported here represent a new example of the many possibilities intrinsic to phosphinoalkyne-substituted clusters and show that considerable work is still to be done for a satisfactory knowledge of the reactivity patterns of these derivatives.

Acknowledgements

Financial support from Ministero della Pubblica Istruzione and C.N.R., Rome is acknowledged. We thank also Johnson-Matthey for a loan of $RuCl_3$. An International Scientific Exchange Award (to E. S.) from the National Research and Engineering Council (Canada) allowed useful discussion with Professor A. J. Carty (University of Waterloo, Ontario).

References

1 R. Whyman, 'Transition Metal Clusters,' ed. B. F. G. Johnson, Wiley, New York, 1981; J. Zwart and R. Snel, *J. Mol. Catal.*, 1985, **30**, 305.
2 C. Masters, *Adv. Organomet. Chem.*, 1979, **17**, 61; H. Verkade, *ibid.*, 1984, **22**, 169.
3 A. J. Carty, S. A. MacLaughlin, and D. Nucciarone, in Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis; Organic Compounds and Metal Complexes, eds. J. G. Veikampte and L. D. Quinn, V.H.C., New York, 1987, ch. 16, p. 559; E. Sappa, A. Tiripicchio, and P. Braunstein, *Coord. Chem. Rev.*, 1985, **65**, 219 and refs. therein.
4 G. Huttner, G. Mohr, and A. Frank, *Angew. Chem., Int. Ed. Engl.*, 1976, **15**, 682; K. Knoll, G. Huttner, L. Zsolnai, I. Jibril, and M. Wasiucionek, *J. Organomet. Chem.*, 1985, **294**, 91 and refs. therein; R. Bender, P. Braunstein, A. Tiripicchio, and M. Tiripicchio Camellini, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 861; J. S. Field, R. J. Haines, D. N. Smit, K. Natarajan, O. Scheidsteger, and G. Huttner, *J. Organomet. Chem.*, 1982, **240**, C23.
5 A. Knoll and G. Huttner, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 743; J. Lunniss, S. A. MacLaughlin, N. J. Taylor, A. J. Carty, and E. Sappa, *Organometallics*, 1985, **4**, 2066.
6 G. L. Geoffroy, S. Rosenberg, P. M. Schulman, and R. R. Whittle, *J. Am. Chem. Soc.*, 1984, **106**, 1519. A. D. Harley, G. J. Guskey, and G. L. Geoffroy, *Organometallics*, 1983, **2**, 53; A. Ceriotti, L. Garlaschelli, G. Longoni, C. Malatesta, and D. Strumolo, *J. Mol. Catal.*, 1984, **24**, 309; S. G. Shyu and A. Woicicki, *Organometallics*, 1985, **4**, 1457.
7 S. A. MacLaughlin, A. J. Carty, and N. J. Taylor, *Can. J. Chem.*, 1982, **60**, 87; S. A. MacLaughlin, N. J. Taylor, and A. J. Carty, *Organometallics*, 1984, **3**, 392; M. Lanfranchi, A. Tiripicchio, E. Sappa, and A. J. Carty, *J. Chem. Soc., Dalton Trans.*, 1986, 2737.
8 P. E. Garrou, *Chem. Rev.*, 1985, **85**, 171 and refs. therein.
9 R. P. Rosen, G. L. Geoffroy, C. Bueno, M. R. Churchill, and R. B. Ortega, *J. Organomet. Chem.*, 1983, **254**, 89.
10 A. J. Carty, *Adv. Chem. Ser.*, 1982, **196**, 163; *Pure Appl. Chem.*, 1982, **54**, 113.
11 M. Catti, G. Gervasio, and S. A. Mason, *J. Chem. Soc., Dalton Trans.*, 1977, 2260.
12 A. J. Carty, N. K. Hota, H. A. Patel, T. J. O'Connor, and T. W. Ng, *Can. J. Chem.*, 1971, **49**, 2706.
13 E. Sappa, O. Gambino, L. Milone, and G. Cetini, *J. Organomet. Chem.*, 1972, **39**, 169.
14 G. M. Sheldrick, SHELX Program for crystal structure determination, University of Cambridge, 1976.
15 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.
16 C. Jangala, E. Rosenberg, D. Skinner, S. Aime, L. Milone, and E. Sappa, *Inorg. Chem.*, 1980, **19**, 1571.
17 A. J. Carty, S. A. MacLaughlin, N. J. Taylor, and E. Sappa, *Inorg. Chem.*, 1981, **20**, 4437.
18 F. Van Gastel, S. A. MacLaughlin, M. Lynch, A. J. Carty, E. Sappa, A. Tiripicchio, and M. Tiripicchio Camellini, *J. Organomet. Chem.*, 1987, **326**, C 65.
19 (*a*) S. Aime, G. Gervasio, L. Milone, E. Sappa, and M. Franchini Angela, *Inorg. Chim. Acta*, 1978, **27**, 145; (*b*) G. Gervasio, E. Sappa, A. M. Manotti Lanfredi, and A. Tiripicchio, *ibid.*, 1983, **68**, 171 and refs. therein; (*c*) E. Sappa, A. M. Manotti Lanfredi, G. Predieri, and A. Tiripicchio, *Inorg. Chim. Acta*, 1982, **61**, 217.
20 S. A. MacLaughlin, J. P. Johnson, N. J. Taylor, A. J. Carty, and E. Sappa, *Organometallics*, 1983, **2**, 352.
21 E. Sappa, L. Milone, and A. Tiripicchio, *J. Chem. Soc., Dalton Trans.*, 1976, 1843; E. Sappa, L. Milone, and G. D. Andreetti, *Inorg. Chim. Acta*, 1975, **13**, 67; E. Sappa, A. Tiripicchio, and P. Braunstein, *Chem. Rev.*, 1983, **83**, 203 and refs. therein.
22 S. A. MacLaughlin, N. J. Taylor, and A. J. Carty, unpublished work; S. A. McLaughlin, Ph.D. Thesis, University of Waterloo, Ontario, 1982.
23 E. Sappa, M. Valle, G. Predieri, and A. Tiripicchio, *Inorg. Chim. Acta*, 1984, **88**, L 23.
24 E. Sappa, G. Predieri, A. Tiripicchio, and M. Tiripicchio Camellini, *J. Organomet. Chem.*, 1985, **297**, 103.
25 E. Sappa, M. L. Nanni Marchino, G. Predieri, A. Tiripicchio, and M. Tiripicchio Camellini, *J. Organomet. Chem.*, 1986, **307**, 97.

Received 20*th March* 1988; *Paper* 8/01265B