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Reactivity of unsaturated clusters. Phosphorus–carbon bond activation, hydrogen migration and acetylene interconversion in the reactions of 46-electron $(H)Ru_3(CO)_9(\mu\text{-}PPh_2)$ with $Ph_2PC{\equiv}CR$ (R = Ph, Bu^t, Pr^i). X-ray structure of $Ru_3(CO)_9(\mu\text{-}PPh_2)_2(\mu_3\text{-}\eta^2\text{-}HC{\equiv}CPh)$: a new type of 5-vertex, 7-skeletal pair cluster

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Abstract

Novel examples of P–C bond activation under mild conditions are reported. The reactions of phosphinoalkynes $Ph_2PC{\equiv}CR$ (R = Ph, Bu^t, Pr^i) with the formally 46-electron cluster $HRu_3(CO)_9(\mu\text{-}PPh_2)$ result in P–C bond cleavage, transfer of a phosphido group onto the cluster, and transfer of hydride to the acetylide. The new species $Ru_3(CO)_7(\mu\text{-}PPh_2)_2(\mu_3\text{-}\eta^2\text{-}HC{\equiv}CR)$, of which the derivative with R = Ph has been studied by X-ray diffraction, are representatives of a new class of $\mu_3\text{-}\eta^2\text{-}\|$ acetylene clusters with NIDO 5-vertex structures.

Among the many phosphido- and phosphinidene-bridged transition metal clusters [1] which have been synthesized in recent years are a relatively small number of compounds which appear to be electronically and coordinatively unsaturated. Typical examples are $Fe_4(CO)_{11}(\mu_4\text{-}PR)_2$ [2], which reacts reversibly with donor ligands, and $(\mu\text{-}H)Ru_3(CO)_9(\mu\text{-}PPh_2)$ [3] in which one phenyl group of a μ_2-phosphido bridge blocks an axial site on the unique ruthenium atom. The cluster

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(μ-H)$Ru_3(CO)_9$(μ-PPh_2) (**1**) is also an avid acceptor, reacting rapidly with Lewis bases to produce adducts (μ-H)$Ru_3(CO)_9$(μ-PPh_2)(L) [3,4].

Another class of reactive clusters are those which, while formally electron precise and saturated, add donor ligands by virtue of the facility with which they undergo M–M bond cleavage [1,5]. We have previously shown that the 46-electron cluster **1** reacts with diphenyl-acetylene via 4-electron addition without CO loss but with Ru–Ru bond cleavage, to afford the adduct (μ-H)$Ru_3(CO)_9$(μ-PPh_2)(μ_3-η^2-PhC≡CPh) [6], which has an *arachno*-pentagonal bipyramidal structure if the C(Ph) units are considered skeletal.

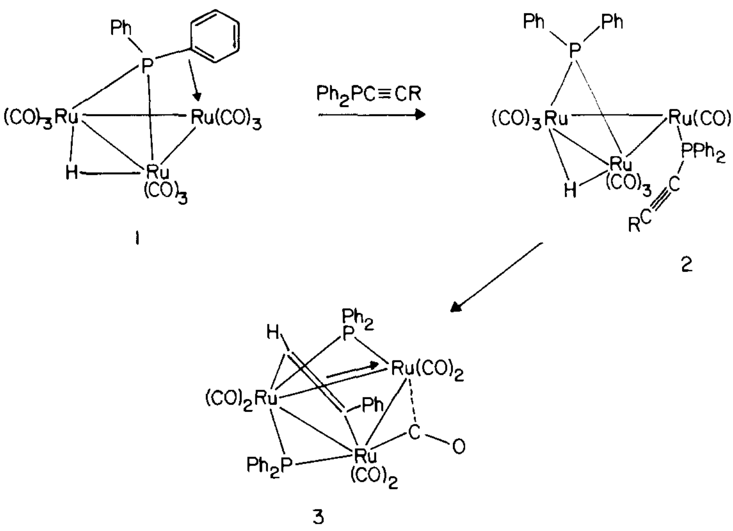
In view of the rapid reactions of **1** with phosphines to give adducts (μ-H)$Ru_3(CO)_9$(μ-PPh_2)(PR_3) [3] and with PhC≡CPh to give **2**, the behaviour of **1** towards phosphinoacetylenes $Ph_2PC{\equiv}CR$ was explored. These molecules can behave as simple P-donors [7] or as 4-electron (P + 2π) [8] or 6-electron (P + 4π) [9] systems, but also undergo oxidative P–C cleavage reactions with metal carbonyls, serving as a useful source of multi-site bound acetylides and phosphido bridges [10].

In this paper we describe the activation of the P–C bond of $Ph_2PC{\equiv}CR$ (R = Ph, Bu^t, Pr^i) by **1** which results in a net exchange of phosphido group for hydrogen at the alkyne and μ-hydride for μ-phosphide on the cluster. Although acetylene metathesis is well established [11], very few examples of R-C_{sp} activation of alkynes leading to exchange of R for a metal-derived ligand have been reported [12].

Cluster **1** (R = Ph) (277 mg, 0.37 mmol) was dissolved in benzene (20 ml) with vigorous stirring and a solution of $Ph_2PC{\equiv}CPh$ (107 mg, 0.37 mmol) in benzene (10 ml) was slowly syringed into the solution which rapidly turned deep red. After 5 minutes the solvent was removed on a rotary evaporator until precipitation began. A few ml of heptane were added and further concentration afforded a red crystalline mass (347 mg, 90%). ^{31}P and IR spectroscopy of the reaction mixture and solid (^{31}P {H} NMR ($CDCl_3$): δ 133.4s, (*P*Ph_2), 7.7s (*P*$Ph_2C{\equiv}CPh$) ppm; ^1H NMR ($CDCl_3$): δ 7.4 m (30 H, Ph) −15.3 d ppm (*H*) *J*(P–H) 29.7 Hz; IR (C_6H_6) ν(CO): 2071 m, 2047 m, sh, 2039 vs, 2023s, 2001 vs, 1984 m, 1978 m, sh, 1965 w, sh cm^{-1}) suggested that the red compound was **2** (R = Ph) with the phosphinoalkyne occupying a site on the unique ruthenium atom previously blocked by the lightly coordinated Ph–P group of the μ-PPh_2 ligand. The analogues of **2** (R = Bu^t, Pr^i) were obtained similarly in yields of 87.6 and 85.9% respectively (**2**, R = Bu^t, IR ν(CO) (C_6H_6) 2071 m, 2047 w, sh, 2038 vs, 2023 s, 2001 vs, 1986 s, 1977 m, sh, 1963 w, sh cm^{-1}; ^{31}P {H} NMR ($CDCl_3$): δ 133.4 s (*P*Ph_2), 5.4 s (*P*$Ph_2C{\equiv}CBu^t$) ppm; **2**, R = Pr^i, IR ν(CO) (C_6H_6): 2072 m, 2047 sh, 2039 s, 2023 s, 2001 s, 1987 s, 1972 m, 1963 w cm^{-1}; ^{31}P {H} NMR ($CDCl_3$): δ 134.2 s (*P*Ph_2), 9.5 s (*P*$Ph_2C{\equiv}CPr^i$).

Warming a solution of **2** (R = Ph) (105 mg, 0.1 mmol) in benzene (50 ml) at 60 °C for 5½ h, followed by addition of n-heptane and cooling to −15 °C for 24 h afforded dark red crystals of **3** (87 mg, 87.6%) (IR ν(CO) (C_6H_6): 2056, 2019 s, 2006 vs, 2000 s, 1965 s, 1948 w cm^{-1}; ^{31}P {H} NMR (C_7H_8) 223 K: 272.2 d, 223.4 d ppm (^2J(P–P) 181 Hz); ^1H NMR ($CDCl_3$): 7.6–7.0 m (30 H, Ph), 6.7 t ppm (^3J(P–H) 8.3 Hz, 1 H, *H*C≡). Subsequent experiments showed that **3** (R = Ph) was formed essentially quantitatively from **2** when a slow stream of N_2 was passed through the solution for 15 d. The corresponding derivatives **3** (R = Bu^t, Pr^i) were similarly identified as products of P–C bond cleavage of **2**. The reactions leading from **1** to **3** are given in Scheme 1.

The ^{31}P and ^1H NMR data for **3** suggested the presence of two different



Scheme 1

phosphido groups and a terminal alkyne. Precise details of the molecular structure were provided by an X-ray diffraction study of the benzene solvate of **3** (R = Ph) * (Fig. 1). The complex consists of a triangular array of ruthenium atoms with two phosphido bridges spanning the longer edges (Ru(1)–Ru(2) 2.773 (2), Ru(1)–Ru(3) 2.872(2)Å). One of the μ-PPh$_2$ groups (P(1)) lies approximately in the Ru$_3$ plane (dihedral angle between planes P(1)–Ru(1)–Ru(2), Ru(1)–Ru(2)–Ru(3) 165.56(8)°) the other is tipped slightly towards the alkyne (dihedral angle between planes P(2)–Ru(1)–Ru(3), Ru(1)–Ru(2)–Ru(3) is 25.1(1)°). There are two terminal CO's per metal and a semi-bridging carbonyl along the shortest Ru–Ru vector (Ru(2)–Ru(3) 2.689(2), Ru(3)–C(5) 1.94(1); Ru(2)–C(5) 2.51(1)Å; Ru(3)–C(5)–O(5) 161(1)°). The alkyne, phenylacetylene, formed by P–C cleavage and transfer of the bridging hydride of **1** onto the acetylide is bonded to Ru(1) and Ru(3) via σ-interactions and to Ru(2) in π-fashion. The acetylene–metal bonding is thus of the μ_3-η^2-$\|$ type [13] with the C–C(alkyne) bond distance (1.37(1) Å) lying within the range of values normally associated with trimetallic alkyne complexes of this type [13b]. The molecule is a closed shell 48-electron cluster, but a skeletal electron count

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* *Crystal data*: C$_{39}$H$_{26}$O$_7$P$_2$Ru$_3$·$\frac{1}{2}$C$_6$H$_6$, M = 1010.84 triclinic crystals, space groups $P\bar{1}$, a 12.545(6), b 13.256(6), c 12.289(7)Å, α 91.23(2), β 97.52(2), γ 107.06(3)°, Z = 2, V 1933(2) Å^3, D_{calc} 1.737 g cm^{-3}, μ(Mo-K_α) 12.65 cm^{-1}. The structural analysis was based on 3795 observed ($I \geq 2\sigma(I)$) (5966 measured) reflections collected with a Siemens AED diffractometer using Mo-K_α (λ 0.71069 Å) radiation with θ in the range 3–24°. The structure was solved by direct and Fourier methods and refined by full-matrix least-squares to R and R_w values of 0.047 and 0.059, respectively. All non hydrogen atoms, except those of the solvent, were refined anisotropically. The hydrogen atoms were located in the final ΔF map and introduced in the final calculations, but not refined. The atomic coordinates, and a list of bond distances and angles are available from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Lists of thermal parameters and observed and calculated structure factors are available from one of the Authors (A.T.).

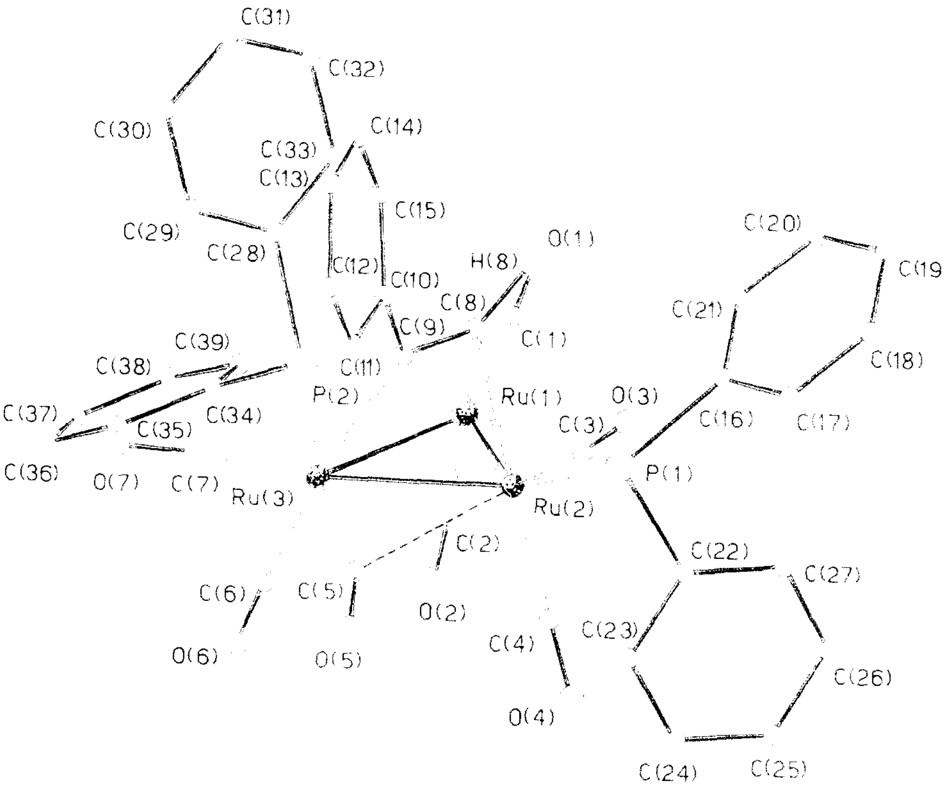
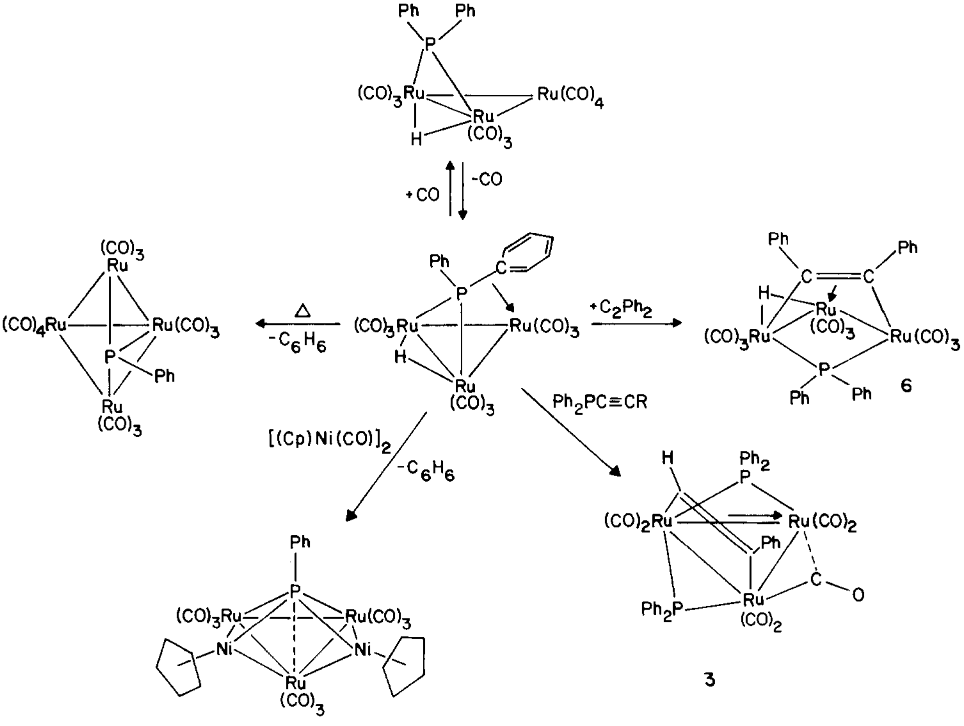


Fig. 1. A view of the molecular structure of $Ru_3(CO)_7(\mu\text{-}PPh_2)_2(\mu_3\text{-}\eta^2\text{-}HC{\equiv}CPh)$ drawn to illustrate the alkyne-metal interactions. Important internuclear distances (Å) and angles (°) are: Ru(1)–Ru(2) 2.773(2), Ru(1)–Ru(3) 2.872(2), Ru(2)–Ru(3) 2.689(2), Ru(1)–P(1) 2.307 (3), Ru(2)–P(1) 2.269(3), Ru(3)–P(2) 2.339(3), Ru(1)–P(2) 2.314(3), Ru(1)–C(8) 2.106 (12), Ru(3)–C(9) 2.134(11), Ru(2)–C(8) 2.284(9), Ru(2)–C(9) 2.286(9), C(8)–C(9) 1.37(1); Ru(1)–P(1)–Ru(2) 74.6(1), Ru(1)–P(2)–Ru(3) 76.2(1), C(8)–C(9)–C(10) 121(1), C(9)–C(8)–H(8) 123.

with the alkyne carbon atoms as part of the framework gives a 7-electron pair, 5 vertex, *nido*-structure as observed with the base of the square pyramid consisting of Ru(1), Ru(3), C(8) and C(9). Complexes **3** are the first examples of the class of bis-phosphido bridged M_3-alkyne complexes $M_3(CO)_x(\mu\text{-}PPh_2)_2(RC{\equiv}CR')$ (M = Fe, Ru, Os) ($x = 6$ *closo*, $x = 7$, *nido*, $x = 8$, *arachno*). Interestingly, addition of PhC_2Ph to **1** affords the *arachno* member of the monophosphido series $HM_3(CO)_y(\mu\text{-}PPh_2)(RC{\equiv}CR')$ ($y = 7$, *closo*, $y = 8$, *nido*, $y = 9$, *arachno*). We are currently attempting to complete both series from **3** and **2** via electron pair addition or removal.

The formation of **3** from **1** at ambient temperature is a remarkable example of a P–C bond activation proceeding via phosphorus coordination of $Ph_2PC{\equiv}CR$ in the intermediates **2**. Although P–C cleavage is now an established phenomenon [10,14], thermal activation at room temperature is rare. Conversion of the adducts **2** to **3** can be envisaged as proceeding by formation of phosphido and acetylide ligands from an activated phosphinoalkyne followed by coupling of μ-hydrido and acetylide to give the μ_3-η^2-acetylene in **3**.



Scheme 2

The effectively unsaturated cluster **1** has now been shown to exhibit a number of reaction pathways. As illustrated in Scheme 2 these are as follows: (i) facile addition of ligands without M–M bond cleavage to form adducts $HRu_3(CO)_9(\mu\text{-}PPh_2)(L)$ ($L = CO, PR_3$); (ii) addition of PhC≡CPh without CO loss but with M–M cleavage: (iii) reductive elimination of benzene, via P–C bond cleavage in the PPh_2 ligand, coupling of one phenyl with the cluster bound hydride and formation of $Ru_4(CO)_{13}(\mu_3\text{-}Ph)$ upon thermal treatment [3] or of $(\eta^5\text{-}C_5H_5)_2Ni_2Ru_3(CO)_9(\mu_5\text{-}PPh)$ [15] by reaction with $(\eta^5\text{-}C_5H_5)_2Ni_2(CO)_2$.

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