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Preliminary communication

Phosphido-phosphinidene transformations. $Ru_3(CO)_6$-$[P(Ph)C(Ph)C(Ph)](\mu\text{-}PPh_2)_2$: a novel six vertex *nido*-pentagonal bipyramidal structure via reductive elimination and acetylene insertion at a triruthenium centre

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Abstract

The complex $Ru_3(CO)_6[P(Ph)C(Ph)C(Ph)](\mu\text{-}PPh_2)_2$ has been obtained by treating $(\mu\text{-}H)Ru_3(CO)_7(\mu\text{-}PPh_2)_3$ with C_2Ph_2 in aliphatic hydrocarbons and its structure has been determined by an X-ray diffraction study. The alkyne inserts into a Ru–P bond and there is reductive elimination of benzene, formed by coupling of a phenyl group of the $\mu\text{-}PPh_2$ ligand with the cluster μ-hydride.

The insertion of alkynes into metal–phosphinidene bonds in metal cluster compounds [1] generates new 4- or 5-membered ring systems $M_nP(R)C(R)C(R)$ ($n = 1, 2$) that have been described as metallacyclic 4π ligands [2] capable of η^4- or η^5-coordination to an appropriate metal fragment. Whatever the theoretical justification for this concept [3], it has the beauty of accomodating a diverse array of mixed main group-transition metal polynuclear compounds in a unified structural framework.

Although in principle the reaction of an alkyne with a μ_2-, μ_3- or μ_4-PR complex could provide a general route to the class of metallocarbon-phosphorus clusters, a limiting factor is the availability of phosphinidene precursors. In this communication we describe the direct synthesis of an $\overline{\mathrm{MMP(R)C(R)C}}\mathrm{(R)}$ system from a μ-diphenylphosphido group in high yield. This approach is potentially attractive since it opens up the possibility of obtaining metallocarbon-phosphorus clusters from the large and well studied group of μ-phosphido complexes. The structure of the compound $Ru_3(CO)_6[P(Ph)C(Ph)C(Ph)](\mu\text{-}PPh_2)_2$, which has been determined by X-ray diffraction, shows it to be the first triruthenium member of the *nido*-pentagonal bipyramidal M_3PC_2 cluster class.

Treatment of $(\mu\text{-}H)Ru_3(CO)_7(\mu\text{-}PPh_2)_3$ (**1**) [4] (0.21 g, 0.2 mmol) with diphenylacetylene (0.185 g, 1.04 mmol) in a mixture of toluene (10 ml) and heptane (150 ml) under N_2 for 24 h at reflux gave a bright-purple solution. Chromatography on preparative thin layer plates (Kieselgel Merck) with C_7H_{16}/ether (85/15) as eluent gave a yellow band of unchanged starting material (20.7 mg, 10%) and a purple band of the new product **2**. The latter was recrystallized from a mixture of n-heptane and $CHCl_3$ (124 mg, 60%). IR ν(CO) (C_6H_{12}): 2035 s, 2002 vs, 1984 s, 1966 s, 1950 m, 1942 m cm^{-1}. NMR ^1H ($CDCl_3$): δ 7.80–7.10 m (Ph); $^{31}P\{^1H\}$: δ 227.5 dd [P(1], 125.2 dd [P(2)], 75.1 dd [P(3)]. The ^{31}P NMR spectrum exhibited

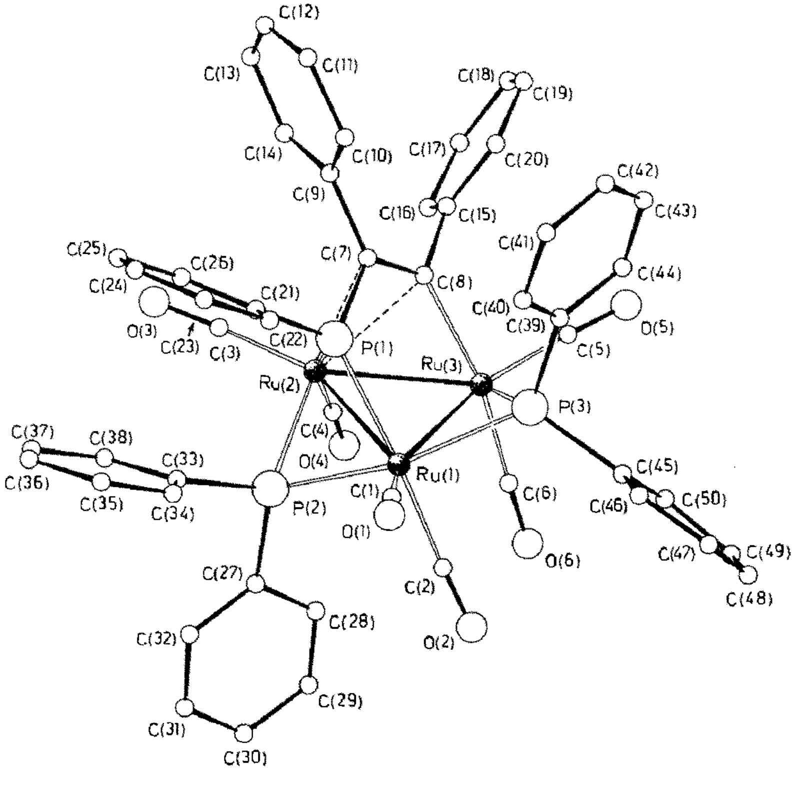
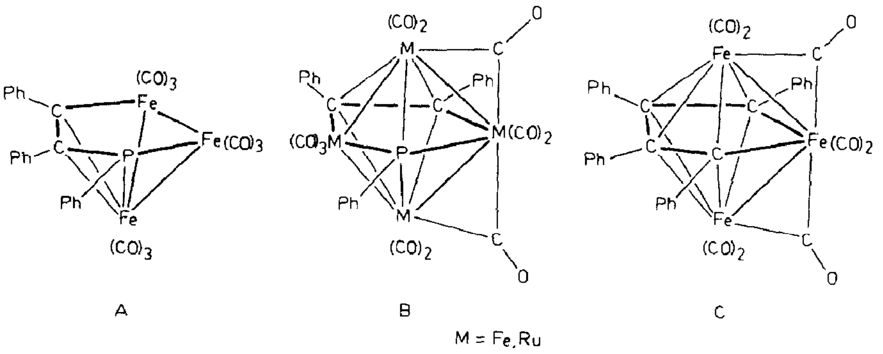


Fig. 1. View of the structure of the compound $Ru_3(CO)_6[P(Ph)C(Ph)C(Ph)](\mu\text{-}PPh_2)_2]$ with the atomic numbering scheme. Selected bond distances (Å) and angles (°): Ru(1)–Ru(2) 2.925(3), Ru(1)–Ru(3) 2.958(2), Ru(2)–Ru(3) 2.733(3), Ru(1)–P(1) 2.332(6), Ru(1)–P(2) 2.367(5), Ru(1)–P(3) 2.354(5), Ru(2)–P(1) 2.346(6), Ru(2)–P(2) 2.328(6), Ru(3)–P(3) 2.228(6), Ru(2)–C(7) 2.42(2), Ru(2)–C(8) 2.39(2), Ru(3)–C(8) 2.08(2), P(1)–C(7) 1.74(2), C(7)–C(8) 1.41(3); Ru(2)–Ru(1)–Ru(3) 55.4(1), Ru(1)–Ru(2)–Ru(3) 62.9(1), Ru(1)–Ru(3)–Ru(2) 61.7(1), Ru(1)–P(1)–Ru(2) 77.4(2), Ru(1)–P(2)–Ru(2) 77.1(2), Ru(1)–P(3)–Ru(3) 80.4(2), Ru(1)–P(1)–C(7) 119.6(7), P(1)–C(7)–C(8) 117(1), C(7)–C(8)–Ru(3) 129(1), C(8)–Ru(3)–Ru(1) 90.6(5), P(1)–Ru(1)–Ru(3) 82.6(2).

three distinct resonances, one at lower field than normal for μ-PPh$_2$ groups in Ru$_3$ clusters [5]. A single crystal X-ray analysis of **2** (Fig. 1) provided full details of the molecular structure [6*].

The core of the molecule consists of six atoms: three ruthenium atoms joined by one strong (Ru(2)–Ru(3) 2.733(3) Å) and two weaker (Ru(1)–Ru(2) 2.925(3) Å; Ru(1)–Ru(3) 2.958(2) Å) bonds, the phosphorus atom P(1) of a phenylphosphido group and two C(Ph) fragments of the diphenylacetylene molecule. The atoms $\overline{\text{Ru(1)Ru(3)C(8)C(7)P(1)}}$ are linked together in an almost planar five-membered ring (maximum deviation from the best least-squares plane through these atoms is $-0.17(2)$ Å for C(7)), and the third ruthenium atom Ru(2) is bound, albeit unsymmetrically, to all five of these atoms (Ru(2)–P(1) 2.346(6), Ru(2)–C(7) 2.42(2) and Ru(2)–C(8) 2.39(2) Å). The Ru(2) interactions with the alkyne carbon atoms C(7) and C(8) are weak but certainly not abnormally so [7]. Within the planar metallaphosphacarbacycle the P(1)–C(7) bond distance of 1.74(2) Å is slightly shorter than expected for a P–C$_{sp^2}$ linkage (for comparison the P(1)–C(21) (phenyl) distance to the same phosphorus atom is 1.79(2) Å), the C(7)–C(8) bond length (1.41(3) Å) is considerably longer than that for a triple bond (1.20 Å), and the Ru(3)–C(8) distance of 2.08(2) Å lies in the range found for ruthenium-carbene complexes (1.90–2.13 Å) [8]. Thus overall for this ring system there may be partial delocalization, supporting the view that the Ru(2) atom is η^5 bound to the 4π metallacycle.

Cluster **2** has a total count of 48 electrons, as expected for a closed trinuclear species. In terms of polyhedral skeletal electron pair theory [9] the molecule possesses eight skeletal pairs if the PPh and CPh moieties are considered as 4-electron phosphinidene and 3-electron alkylidyne fragments and the two μ-PPh$_2$ groups as edge bridging 3-electron ligands. Thus with 6-vertices the framework must be *nido* based on a 7-vertex polyhedron with one missing vertex, as is observed. Cluster **2** thus joins the small group of half-sandwich complexes having three metal atoms and including Fe(CO)$_9$[$\overline{\text{FeFeP(Ph)C(Ph)C}}$(Ph)] [1a,10]. These *nido* pentago-



Scheme 1.

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

nal bipyramidal species **A** (see Scheme 1) are also closely related to the corresponding *closo*-pentagonal bipyramidal species **B** derived from four metal atom phosphinidenes, $\mathrm{M_2(CO)_{11}[\overline{MP(Ph)MC(Ph)C}(Ph)]}$ (M = Fe [11], M = Ru [1b]) as well as to three-metal-atom four-carbon systems $\mathrm{M_2(CO)_8[\overline{MC(Ph)C(Ph)C(Ph)C}(Ph)]}$ **C** formed in reactions of acetylenes with metal carbonyls [12].

The formation of **2** from **1** in high yield requires the loss of a hydride from the cluster and a phenyl group from a diphenylphospido ligand, and the formal insertion of PhC≡CPh into the intermediate phosphinidene generated. Alternatively acetylene insertion into a phosphido bridge of **1** might precede reductive elimination of benzene. There are precedents for both reaction pathways [1a,7,10,11,13], and an example of P-phenyl activation on a μ-hydrido-μ-phosphidotriruthenium cluster has been described [14]. The high yield of the present reaction suggests that there is an unusual degree of selectivity in both steps of the mechanism, a fact which may augur well for the generation of these metallacycles from μ-$\mathrm{PPh_2}$ complexes. We are attempting to extend the scope of this synthetic route.

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6 $\mathrm{C_{50}H_{35}O_6P_3Ru_3 \cdot 2CHCl_3}$, $M = 1366.71$, monoclinic, space group $C2/c$, a 41.346(10), b 13.251(4), c 20.442(8) Å, β 96.04(2)°, $Z = 8$, V 11138(6) Å^3, D_{calcd} 1.630 g cm^{-3}, $F(000) = 5408$, $\mu(\mathrm{Cu}\text{-}K_\alpha)$ 106.1 cm^{-1}. A correction for absorption effects was applied (maximum and minimum transmission factor values were 1.237 and 0.853 respectively). Of 9577 independent reflections, measured on a Siemens AED diffractometer using the Ni-filtered Cu-K_α radiation with θ in the range 3–65°, 2933, having ($I > 2\sigma(I)$) were considered observed and used in the analysis. The structure was solved by direct and Fourier methods and refined by full matrix least squares to R and R_w values of 0.0688 and 0.0800, respectively, with anisotropic thermal parameters for the Ru and P atoms only. The $\mathrm{CHCl_3}$ molecules of solvation were found to be disordered and distributed over five different positions. All hydrogen atoms, except those of the solvent molecules, were placed at their geometrically calculated positions and introduced in the final structure factors calculations. Tables of atomic coordinates, and bond distances and angles, are available from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Requests must be accompanied by the full literature citation.

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