

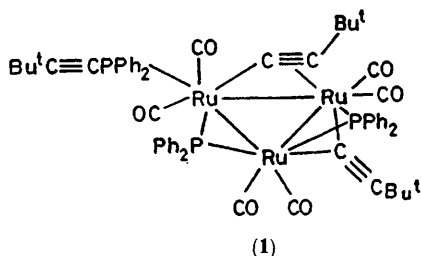
Synthesis and X-Ray Molecular Structure of $[\text{Ru}_3(\text{CO})_6(\mu_2\text{-C}_2\text{Bu}^t)(\mu_2\text{-}\eta^2\text{-C}_2\text{Bu}^t)\text{(PPh}_2)_2(\text{Ph}_2\text{PC}_2\text{Bu}^t)]$; a Cluster Containing Symmetrical and Unsymmetrical Edge Bridging Alkynyl Groups

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Summary Oxidative cleavage of the phosphinoalkyne $\text{Ph}_2\text{PC}\equiv\text{CBu}^t$ by $\text{Ru}_3(\text{CO})_{12}$ gives good yields of a carbonyl cluster $[\text{Ru}_3(\text{CO})_6(\mu_2\text{-C}_2\text{Bu}^t)(\mu_2\text{-}\eta^2\text{-C}_2\text{Bu}^t)(\text{PPh}_2)_2(\text{Ph}_2\text{PC}_2\text{Bu}^t)]\cdot\text{C}_6\text{H}_6$ which is shown by X-ray crystallography to contain both symmetrical (μ_2) and unsymmetrical ($\mu_2\text{-}\eta^2$) edge bridging $\text{-C}\equiv\text{CBu}^t$ groups.

CONSIDERABLE attention has recently focused on the structural chemistry and reactivity of bi- and tri-nuclear carbonyl complexes containing bridging vinyl and alkynyl ligands, not least because these hydrocarbyl groups are often highly activated towards nucleophilic reagents.¹⁻³ We now report the easy synthesis of an unusual triruthenium cluster $[\text{Ru}_3(\text{CO})_6(\mu_2\text{-C}_2\text{Bu}^t)_2(\text{PPh}_2)_2(\text{Ph}_2\text{PC}_2\text{Bu}^t)]$ (**1**) via oxidative cleavage of *t*-butylethynyldiphenylphosphine by $[\text{Ru}_3(\text{CO})_{12}]$. Compound (**1**) is the first example of a carbonyl cluster having a symmetrical μ_2 -bound ethynyl ligand. We also emphasise the potential of phosphinoacetylenes as precursors for stable carbonyl clusters with strong supporting bridging ligands (PPh_2) and unsaturated hydrocarbyl units.



The reaction of $[\text{Ru}_3(\text{CO})_{12}]$ (1 mmol) with $\text{Ph}_2\text{PC}\equiv\text{CBu}^t$ (3 mmol) in refluxing acetonitrile rapidly gives a dark red solution of the trisubstituted cluster $[\text{Ru}_3(\text{CO})_6(\text{Ph}_2\text{PC}\equiv\text{CBu}^t)_3][\nu(\text{CO})(\text{C}_6\text{H}_{12})$ 1991vs, 1977vs, and 1950 cm^{-1}]. Further refluxing (*ca.* 1 h) yields a pale yellow solution from which the yellow (**1**) (60%) and another yellow, as yet unidentified, complex (*ca.* 35%) were obtained *via* chromatography on Florisil. These reactions are clean and devoid of troublesome side reactions. The i.r. spectrum of (**1**) exhibited a weak $\nu(\text{C}\equiv\text{C})$ doublet at 2210 and 2170 cm^{-1} typical of a P-co-ordinated phosphino-alkyne and a complex pattern of bands in the $\nu(\text{CO})$ region (C_6H_{12} ; 2074m, 2058s, 2050s, 2012vs, 1994s, 1984s, 1970vs, 1949vs, and 1949w cm^{-1}) indicating probable retention of the cluster framework. Crystals of a toluene solvate of (**1**) are triclinic, space group $P\bar{1}$ with $a = 12.264(1)$, $b = 12.639(1)$, $c = 22.324(2)$ Å, $\alpha = 75.977(8)$, $\beta = 104.984(9)$, $\gamma = 93.590(9)^\circ$, $M = 1362.39$, $U = 3244.5$ Å³, $D_m = 1.41$, $D_c = 1.394$ g cm^{-3} ; $Z = 2$, $\mu(\text{Mo-K}\alpha) = 7.97$ cm^{-1} . The structure was solved by Patterson and Fourier methods using the intensities of 5336 observed [$I > 3\sigma(I)$] diffractometer (Syntex P2₁) measured reflections and refined by full matrix least squares

techniques to $R = 0.039$. All phenyl ring hydrogen atoms were located and refined. An ORTEP II plot of the molecular structure is shown (Figure). Each ruthenium atom in

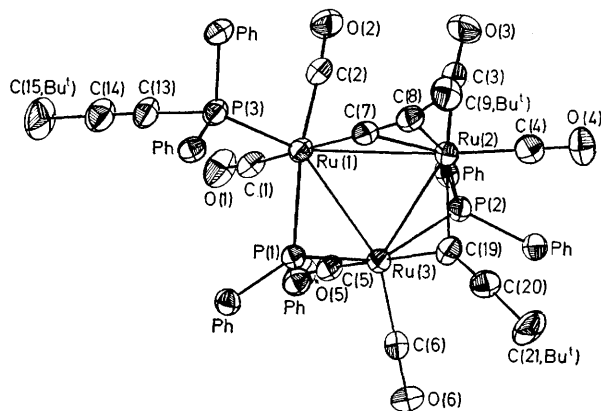


FIGURE. A perspective view of the molecular structure of $[\text{Ru}_3(\text{CO})_6(\mu_2\text{-C}_2\text{Bu}^t)(\mu_2\text{-}\eta^2\text{-C}_2\text{Bu}^t)(\text{PPh}_2)_2(\text{Ph}_2\text{PC}_2\text{Bu}^t)]\cdot\text{C}_6\text{H}_6$ (**1**) showing the atomic numbering. For clarity phenyl rings are labelled Ph and only one carbon atom of each ring is shown. Similarly only one carbon atom of each -Bu^t group is illustrated.

the triangular cluster has two terminally bound carbonyl groups. Two of the metal atoms [Ru(2)–Ru(3)] are bridged by a phosphido group and by a symmetrical μ_2 -*t*-butylethyne ligand [Ru(2)–C(19) 2.22(1) and Ru(3)–C(19) 2.185(9) Å]. Symmetrical μ_2 -bonding of alkynyl groups is rare. Indeed the only examples known to us are in the beryllium compound $[\{\text{MeBe}(\text{C}\equiv\text{CMe})\text{NMe}_2\}_2]$ ⁴ and the copper clusters $[\text{Cu}_n\text{R}_4(\text{C}\equiv\text{CR}')_2]$.⁵ A $\sigma\text{-}\pi$ -acetylide bridges the Ru(1)–Ru(2) edge and an intact phosphinoacetylene is coordinated to Ru(1) *via* phosphorus as a terminal ligand. Within the μ_2 -acetylide the C(19)–C(20) bond length [1.19(1) Å] is indistinguishable from the unco-ordinated triple bond length [C(14)–C(15), 1.20(2) Å] while the C(7)–C(8) distance in the $\mu_2\text{-}\eta^2$ -bridge is significantly longer [1.24(3) Å] and comparable to corresponding distances in binuclear iron $\sigma\text{-}\pi$ -acetylides $\{[\text{Fe}_2(\text{CO})_6(\text{C}_2\text{Ph})\text{PPh}_2]$ 1.23(1) Å; $[\text{Fe}_2(\text{CO})_5(\text{C}_2\text{Ph})(\text{PPh}_2)(\text{PPh}_3)]$ 1.225(6) Å).⁶ The μ_2 -acetylide is not significantly distorted from linearity [$\angle\text{C(19)–C(20)–C(21)}$ is 177.9(6)°] but for the $\mu_2\text{-}\eta^2$ -ligand, the η^2 interaction with Ru(2) results in 'bend back' angles of 20.2° at C(8) and 11.2° at C(7). Thus we consider the symmetrical μ_2 group to be a 1-electron donor and the $\mu_2\text{-}\eta^2$ -unit as a 3-electron ligand. The cluster as a whole is a 54-electron species. All three Ru–Ru distances are different, presumably reflecting the bridging characteristics of the $\text{-C}\equiv\text{CR}$ and PPh_2 ligands. The shortest Ru–Ru bond length [2.863(1) Å] is associated with the acute Ru(2)–C(19)–Ru(3) bond angle [81.1(0)°] subtended at the α -carbon of the symmetrical

μ_2 -acetylide. The Ru(1)–Ru(2) [3.139(1) Å] and Ru(1)–Ru(3) [3.05(1) Å] distances are amongst the longest yet reported for trinuclear clusters.^{7†}

Structural data for (1) confirm indications that $-\text{C}\equiv\text{CR}$ groups are the most versatile of bridging hydrocarbyl ligands; apart from μ_2 -bonding observed here, μ_2 - η^2 -modes are known for both transition^{1,3} and main group⁸ metals and μ_3 - η^2 -co-ordination is common in cluster chemistry.⁹

Finally, we point out that the presence of three differently bonded acetylides in (1) offers a unique opportunity to explore the influence of co-ordination mode on patterns of reactivity for these unsaturated hydrocarbyl ligands.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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