

Synthesis and X-Ray Structure of $[\text{RuCo}_3(\mu\text{-CO})_2(\text{CO})_7(\mu\text{-PPh}_2)(\mu_4\text{-}\eta^2\text{-Bu}^t\text{C}\equiv\text{CH})]$: a Novel Heteronuclear Butterfly Cluster *via* the Fragmentation of a Phosphinoalkyne

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The dehalogenation of $[\text{RuCl}_2(\text{Ph}_2\text{PC}\equiv\text{CBu}^t)(p\text{-cymene})]$ (**1**) by $\text{Co}_2(\text{CO})_8$ and subsequent protonation afford the mixed metal cluster $[\text{RuCo}_3(\mu_4\text{-}\eta^2\text{-Bu}^t\text{C}\equiv\text{CH})(\mu\text{-PPh}_2)(\text{CO})_9]$ (**2**) for which an X-ray structure determination has established the butterfly configuration of the RuCo_3 species.

Although a substantial number of mixed metal clusters have been characterised in recent years¹ compounds containing a single ruthenium atom within a cluster framework are rare, in part because of the lack of suitable mononuclear ruthenium precursors.

We describe herein the synthesis and characterisation of $[\text{RuCo}_3(\mu\text{-PPh}_2)(\mu_4\text{-}\eta^2\text{-Bu}^t\text{C}\equiv\text{CH})(\mu\text{-CO})_2(\text{CO})_7]$ (**2**), the first mixed cluster of the type $\text{RuCo}_3(\text{alkyne})$ *via* reaction of the (arene)(phosphinoalkyne)ruthenium(II) complex (**1**) with $\text{Co}_2(\text{CO})_8$. Novel features of this reaction are the facile dehalogenation of the ruthenium(II) complex (**1**) by $\text{Co}_2(\text{CO})_8$ and the cleavage of a phosphorus-carbon bond of the co-ordinated phosphinoacetylene to give a bridging phosphido-group and an $\eta^2\text{-}\mu_4$ -bound acetylene. Phosphinoacetylenes have recently attracted attention as sources of phosphido-bridges² but the synthesis of an acetylene *via* P-C bond cleavage appears to be unprecedented. X-Ray analysis has established that (**2**) is a new member of the interesting series of tetranuclear complexes with the butterfly configuration.

Complex (**1**) was prepared by the addition of 2 equiv. of $\text{Ph}_2\text{PC}\equiv\text{CBu}^t$ to $[\text{RuCl}_2(p\text{-cymene})]_2$.³ Treatment of complex (**1**) with 2 equiv. of $\text{Co}_2(\text{CO})_8$ in dry tetrahydrofuran (THF) at 25 °C afforded a brown-violet solution from which (**2**) was isolated *via* silica gel preparative thin layer chromatography and crystallisation in hexane [yield 30%, m.p. 145–148 °C; i.r. $\nu(\text{CO})$ (Nujol) 2060s, 2025s, 1995s, 1980s, 1965s, 1870s, and 1848s cm^{-1} ; ¹H n.m.r. (CD_2Cl_2) δ 1.14 (s, Bu^t), 7.55 (m, PPh_2), and 8.95 (s, $\text{C}\equiv\text{CH}$); mass spectrum, m/z 797.789 (calc. for M^+ , $\text{C}_{27}\text{H}_{20}\text{O}_9\text{PCo}_3^{102}\text{Ru}$, 797.788)]. The i.r. spectrum indicated the presence of terminal and bridging CO groups and a ³¹P n.m.r. spectrum [CDCl_3 , δ (w.r.t. 85% H_3PO_4) + 222.05 p.p.m.] consisted of a broad singlet at low field typical of a phosphido-bridge across a Co-Ru or Co-Co bond.²

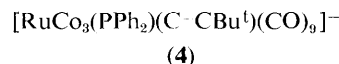
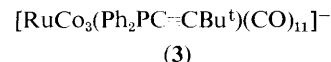
Crystal Data: $\text{C}_{27}\text{H}_{20}\text{O}_9\text{PCo}_3\text{Ru}$, (**2**), $M = 797.30$, monoclinic, space group $P2_1/c$, $a = 14.228(4)$, $b = 11.839(4)$, $c = 17.609(4)$ Å, $\beta = 94.42^\circ$, $U = 2957.3$ Å³, $Z = 4$, $F(000) = 1576$, $\mu(\text{Mo-K}\alpha) = 0.709$ cm^{-1} . The structure was solved by direct methods (Mulan) using the intensities of 3685 ($I > 2\sigma_I$) observed (5181 measured) reflections collected

on a Nonius CAD-4F diffractometer. Refinement by full-matrix least-squares methods with anisotropic thermal parameters for all non-hydrogen atoms gave R and R_w values of 0.029 and 0.035.†

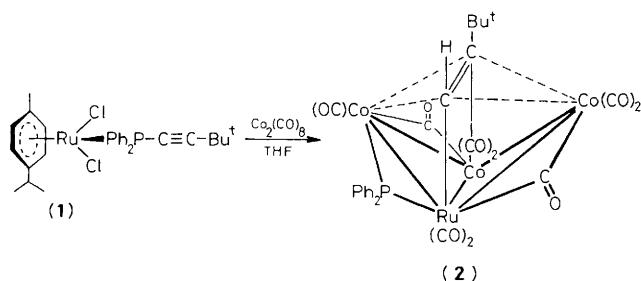
An ORTEP plot (Figure 1) shows that the metal framework and the two acetylenic carbon atoms C(10) and C(11) approximate to a *closo*-octahedron. The RuCo_3 skeleton has a butterfly configuration with Co(2) and Co(3) on the wing tips and with Ru and Co(1) as the hinge atoms. The dihedral angle between the wings is 64.8° and the non-bonding distance between the lateral atoms Co(2) and Co(3) is 3.517(2) Å. The alkyne is co-ordinated as a $\mu_4\text{-}\eta^2$ -ligand between the wings of the butterfly, forming an unsymmetrical metallo-

cycle $\text{Ru-Co(1)-C(11)-C(10)-Ru-C(10)}$ [Ru-C(10) 2.187(4), Co(1)-C(11) 2.009(4) Å] in which the C(10)-C(11) bond [1.424(5) Å] has double bond character. Although as a 60 electron butterfly the Co_3Ru cluster bears a strong structural resemblance to $[\text{Co}_4(\text{CO})_{10}(\text{EtC}_2\text{Et})]$,⁴ $[\text{Ru}_4(\text{CO})_{12}(\text{C}_2\text{Ph}_2)]$,⁵ and $[\text{Ru}_4(\text{CO})_{12}(\text{C}_3\text{Me}_2)]$,⁶ there is no plane of symmetry passing through the acetylenic atoms, Co(1) and Ru, since one edge of the cluster is bridged by a phosphido-group and two edges by asymmetric carbonyls C(3)-O(3) and C(8)-O(8). In addition the wing-tip atoms Co(2) and Co(3) have different co-ordination stereochemistries and the alkyne is somewhat displaced towards Co(2) [Co(2)-C(11) 2.086(4), Co(3)-C(11) 2.122(4) Å]. The RuCo_3 cluster is thus inherently chiral.

The formation of (**2**) can be understood in terms of the dehalogenation of (**1**), by $\text{Co}(\text{CO})_4^-$ generated from $\text{Co}_2(\text{CO})_8$, to afford successively the anions $[\text{RuCo}_3(\text{Ph}_2\text{PC}\equiv\text{CBu}^t)(\text{CO})_{11}]^-$ (**3**) and $[\text{RuCo}_3(\text{PPh}_2)(\text{C}\equiv\text{CBu}^t)(\text{CO})_9]^-$ (**4**), protonation of the latter during the extraction affording (**2**). In support of this hypothesis we showed that,



under similar conditions, $[\text{RuCl}_2\{\text{P}(\text{OMe})_3\}(\text{C}_6\text{H}_6)]^\ddagger$ and $\text{Co}_2(\text{CO})_8$ reacted to give the tetrahedral cluster $[\text{HRuCo}_3(\text{CO})_{11}\text{P}(\text{OMe})_3]$ (**5**) {yield 10%, m.p. 124–128 °C; ¹H n.m.r. (CDCl_3) δ 3.78 [d, $\text{P}(\text{OMe})_3$, ³ $J_{\text{P-H}}$ 11.0 Hz] and -18.37 (br. s, 1H)}. Moreover, the addition of an excess of D_2O to the (**1**) \rightarrow (**2**) reaction mixture led to the isolation of (**2**) containing only 30% of hydrogen at C(10) as indicated by



Scheme 1

† 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.

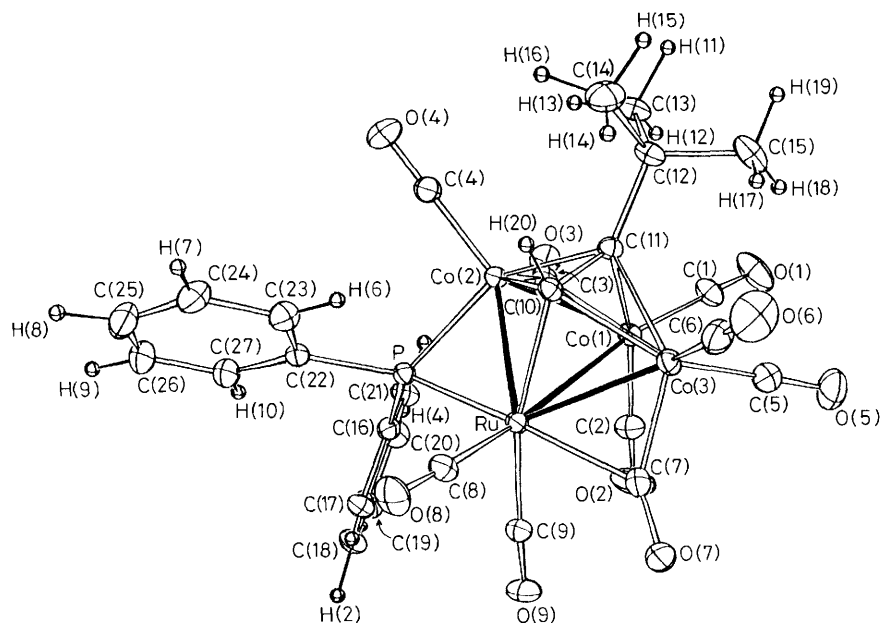


Figure 1. Molecular structure of $[\text{RuCo}_3(\mu\text{-CO})_2(\text{CO})_7(\mu\text{-PPh}_2)(\mu_4\text{-}\eta^3\text{-Bu}^4\text{C}\equiv\text{CH})]$. Important bond lengths (Å) are Ru-Co(1) 2.776(1), Ru-Co(2) 2.558(1), Ru-Co(3) 2.567(1), Co(1)-Co(2) 2.399(1), Co(1)-Co(3) 2.494(1), Co(1)-C(11) 2.009(4), Ru-C(10) 2.187(4), Ru-P 2.328(1), and Co(2)-P 2.131(1). Important bond angles ($^\circ$) are Ru-Co(2)-Co(1) 68.02(2), Ru-Co(3)-Co(1) 66.52(2), and Ru-P-Co(2) 69.88(3).

^1H n.m.r. spectroscopy. Therefore the butterfly configuration of the $\text{RuCo}_3(\text{alkyne})$ cluster (**2**) may result from the intramolecular interaction of the $\text{C}\equiv\text{C}$ bond of the phosphinoalkyne of (**3**) with the tetrahedral anionic RuCo_3 species.

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