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A NEW BOW-TIE: SYNTHESIS AND X-RAY STRUCTURE OF $Co_2Ru_3(\mu_5\text{-}\eta^2\eta^2\text{-}PhC_2C_2Ph)(CO)_{14}$, WHICH SHOWS A REMARKABLE AND UNUSUAL ASYMMETRY IN THE SOLID STATE*†

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Abstract—The reaction between $Ru_3(\mu_3\text{-}\eta^2\text{-}PhC_2C_2Ph)(\mu\text{-}CO)(CO)_9$ and $Co_2(CO)_8$ affords the pentametal cluster $Co_2Ru_3(\mu_5\text{-}\eta^2,\eta^2\text{-}PhC_2C_2Ph)(CO)_{14}$ in quantitative yield. The X-ray determined molecular structure consists of a Co_2Ru_3 bow-tie cluster which is straddled by the PhC_2C_2Ph ligand, interacting with all five metal atoms via the two C≡C triple bonds, each of which is attached in the $2\sigma(2Ru),\pi(Co)$ bonding mode. Of the 14 CO groups, one bridges one Co-central Ru bond in one half of the molecule, while two are found semi-bridging the central Ru—Co and —Ru vectors in the other half of the molecule. In the solid state, there is thus a curious and remarkable asymmetry between the two halves of the molecule, although in solution at room temperature the molecule appears to be symmetrical.

Reactions of alkynes with ruthenium carbonyls, particularly $Ru_3(CO)_{12}$ and $Ru_3(\mu\text{-dppm})(CO)_{10}$, are well known and many examples have been described.[2] However, there have been few studies carried out with diynes. In the case of $Os_3(CO)_{12}$, an unusual C—C bond cleavage reaction of the initially formed $Os_3(\mu_3\text{-}\eta^2\text{-}PhC_2C_2Ph)(\mu\text{-}CO)(CO)_9$ (**1**; Scheme 1) has been described which resulted in the formation of an Os_3 cluster containing both μ- and $\mu_3\text{-}C_2Ph$ moieties.[3] Carty and co-workers[4] have described the reactions of diynes on the PRu_3 cluster face of $Ru_4(\mu_3\text{-}PPh)(CO)_{13}$ (Scheme 2), which give firstly complexes containing the diynes attached to P and one Ru by σ-bonds and to a second Ru by a π-bond. On heating, rearrangement to clusters containing a $\mu_4\text{-}\eta^2$-diyne capping a square Ru_4 face occurs; prolonged reaction gives derivatives in which the diyne utilizes all four acetylenic carbons to bond to the square face. A similar reaction with PhC_2C_2Ph also afforded an unusual diyne trimer attached to an Ru_4 array via eight of the 12 acetylenic carbons.[5] In an earlier study, a $\mu_4\text{-}\eta^4\text{-}Bu^tC_2C_2Bu^t$ ligand was formed by coupling of a cluster-bound C_2Bu^t ligand to one of the C_2Bu^t groups from a coordinated $P(C_2Bu^t)_2$ ligand.[6]

We have commenced a study of simpler ruthenium systems and have found that reactions with activated ruthenium carbonyls give a plethora of complexes which will be described elsewhere. The present paper describes the highly unusual reaction

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* Dedicated to Eddie Abel, valued friend and colleague, on his retirement, in recognition of his splendid contributions to organometallic and inorganic chemistry and in gratitude for his advice and support.

† See ref. 1.

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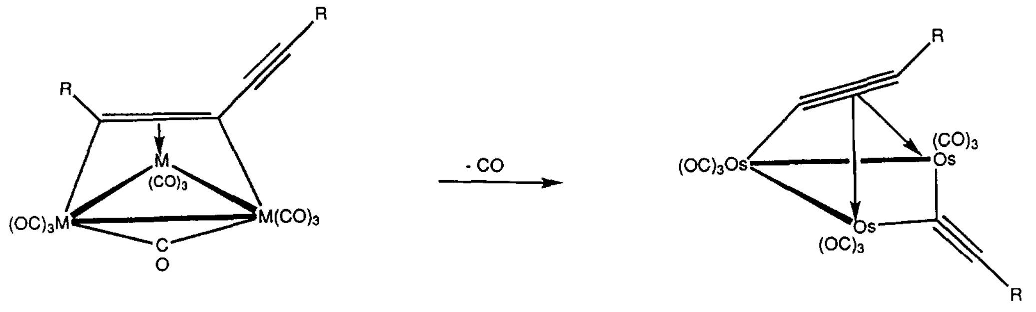
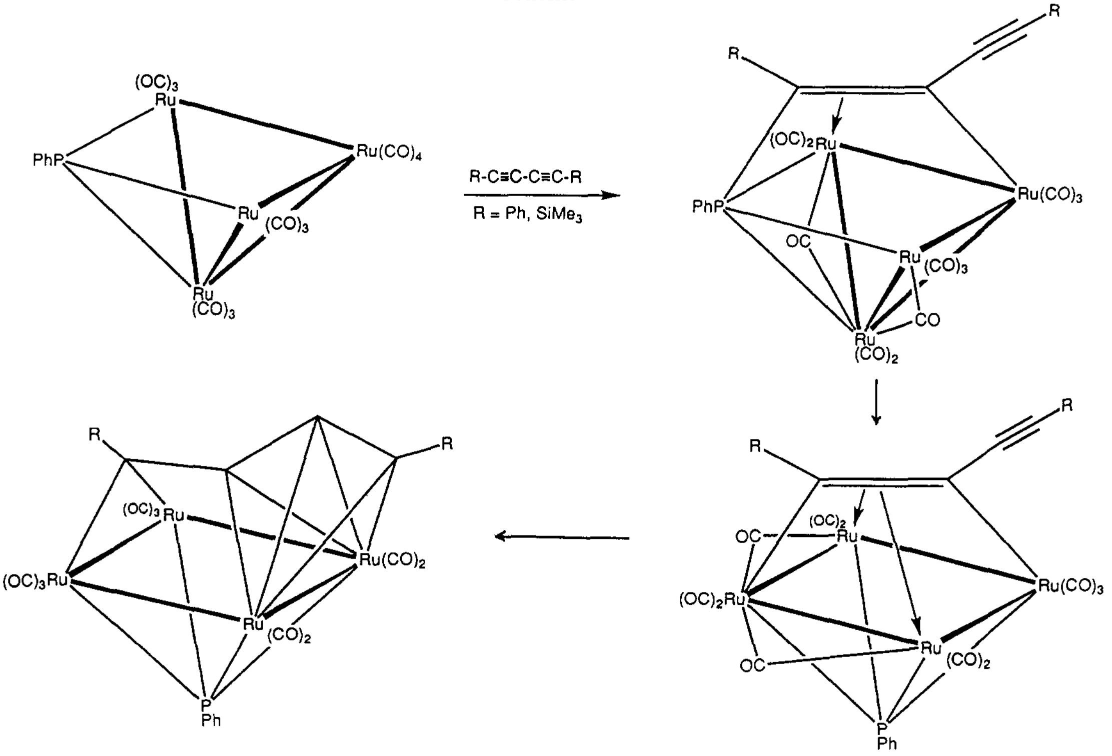


(**1**) M = Os, R = Ph, Bu^t, SiMe$_3$
(**2**) M = Ru, R = Ph

Scheme 1.

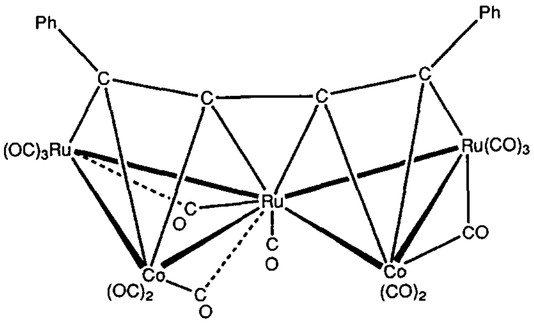


Scheme 2.

which ensues when one of these complexes, Ru$_3$(μ_3-η^2-PhC$_2$C$_2$Ph)(μ-CO)(CO)$_9$ (**2**), is treated with Co$_2$(CO)$_8$.

RESULTS AND DISCUSSION

The ready availability[7] of several complexes containing the diyne PhC$_2$C$_2$Ph attached to metal systems by only one of the C≡C triple bonds naturally raised the question of the complexing ability of the second uncoordinated C≡C triple bond, for example, in reactions with Co$_2$(CO)$_8$. We have found that a quantitative yield of a novel pentanuclear complex is obtained from the reaction between Ru$_3$(μ_3-η^2-PhC$_2$C$_2$Ph)(μ-CO)(CO)$_9$ (**2**) and Co$_2$(CO)$_8$ in hexane under mild conditions. Analytical and mass spectral data establish the formula as Co$_2$Ru$_3$(μ_5-η^2,η^2-PhC$_2$C$_2$Ph)(CO)$_{14}$ (**3**), the IR ν(CO) spectrum containing several bands in the terminal CO region, together with two weak



(**3**)

absorptions at 1900 and 1886 cm^{-1}, assigned to μ-CO groups. The mass spectrum contained a parent M^+ ion together with ions formed by successive loss of between 2 and 14 CO groups. The ^{13}C NMR spectrum contained two weak absorptions at δ 124.2 and 143.1, assigned to the acetylenic C atoms, and five CO resonances. Of the latter, three with relative intensities 2 : 1 : 2 between δ 190.2 and 192.2 are assigned to the *Ru*—CO ligands, while the other two, at δ 200.8 and 204.9, are assigned to the *Co*—CO groups. The molecular structure of **3** was determined by a single-crystal X-ray structural study.

Molecular structure of $Co_2Ru_3(\mu_5\text{-}\eta^2,\eta^2\text{-}PhC_2C_2Ph)(CO)_{14}$ (3)

A plot of a molecule of $Co_2Ru_3(\mu_5\text{-}\eta^2,\eta^2\text{-}PhC_2Ph)(CO)_{14}$ is shown in Fig. 1 and important structural parameters are collected in Table 1. It can be seen that a pentanuclear cluster consisting of two Co and three Ru atoms adopts a bow-tie configuration with a central Ru(1) atom. Metal–metal bond lengths [Co(4)—Ru(1,3) 2.643(1), 2.587(1); Co(5)—Ru(1,2) 2.730(1), 2.598(1); Ru(1)—Ru(2,3) 2.8712(9), 2.8243(9)Å] are similar to those found in $Co_2Ru(\mu_3\text{-}RC_2R')(\mu\text{-}CO)(CO)_8$ [Ru—Co (CO-bridged) 2.591(2), 2.568(1); Ru—Co (non bridged) 2.699(1), 2.690(6) Å for R, R′ = H, Bu^t and Ph, Ph, respectively],[8] for example; the Co(1)...Co(2) distance [3.997(1) Å] is too long for there to be any significant bonding interaction. The array Ru(2,3)Co(4,5) is approximately planar [δ 0.067(1), −0.067(1), 0.087(1), −0.087(1) Å, respectively] with Ru(1) deviant by 0.754(1) Å; the dihedral angle between the two $CoRu_2$ planes is 35.61(4)°.

The diyne unit is attached to all five metal atoms, being σ-bonded to the ruthenium atoms [Ru(1)—C(2,3) 2.191(5), 2.150(5); Ru(2)—C(4) 2.078(5); Ru(3)—C(1) 2.161(5) Å] and π-bonded to the cobalt atoms [Co(4)—C(1,2) 2.035(6), 2.089(6); Co(5)—C(3,4) 2.007(6), 2.136(6) Å]. These distances are similar to those encountered before, e.g. 2.132(4) and 2.078(5) Å for the σ-bonded carbons in **2**,[7] and Co—C 1.96(1), 2.00(1); Ru—C 2.11(1), 2.12(1) Å for the two Co_2Ru complexes mentioned above,[8] and Co—C (π-bonded) 2.02(1)–2.09(1) Å in the Co_2Ru complexes[8] and 1.948–2.022(10) Å in $Co_2(\mu\text{-}\eta^2\text{-}PhC_2Ph)(CO)_6$.[9] The phenyl groups are bent away strongly from the two metal planes, with angles at C(1) and C(4) being 125.2(5) and 123.1(4)°, respectively. Conversely, the bending at the inner carbons [C(1)—C(2)—C(3) 160.1(6), C(2)—C(3)—C(4) 155.4(6)°] is considerably less than that normally found for mono-η^2-alkyne complexes [cf. 140(1)° in $Co_2(\mu\text{-}C_2Ph_2)(CO)_6$][9], although the average bending at each carbon (141°) is similar. Within the diyne, the C(1)—C(2) and C(3)—C(4) separations have lengthened to 1.346(7) and 1.367(7) Å, respectively, which may be compared with the value of 1.395(6) Å found for the coordinated C≡C triple bond in **2**;[7] the central C(2)—C(3) bond [1.358(7) Å] is considerably shorter than that found in **2** [1.447(7) Å].[7]

Coordination about the five metal atoms in **3** is completed by 14 CO ligands. The Co(5)—Ru(1) and Ru(1)—Ru(2) vectors are semi-bridged by CO(53) and CO(12), respectively, while CO(4)—Ru(3) is spanned by the CO(43) ligand in the conventional bridging mode [Co(4)—C(43) 1.866(6), Ru(3)—C(43) 2.142(7) Å; O(43)—C(43)—Co(4) and —Ru(3) 141.9(6), 137.8(5)°, respectively]. The remaining 11 CO groups are terminal.

The most striking feature of the solid-state structure of **3** is its asymmetry, presumably a consequence of minimization of putative inter-carbonyl interactions. Formal electron accounting would give each metal atom an 18-electron configuration in the symmetrical structure: in the solid state, Ru(2) and Co(5) have 17- and 19-electron counts, the imbalance being relieved by semi-bridging of one each of the CO ligands attached to Ru(1) and to Co(5). The asymmetry is also reflected in the bond lengths of the two $CoRu_2$ triangles, with the semi-bridged M—M vectors in the Ru(1)Ru(2)Co(5) triangle being significantly longer than the corresponding bonds in the Ru(1)Ru(3)Co(4) triangle. It is interesting to note that the fully bridged Co(4)—Ru(3) separation in the latter is essentially the same as found for the non-bridged Co(5)—Ru(2) bond, while the two semi-bridged vectors [Ru(1)—Co(5), —Ru(2)] are, respectively, 0.08_7 and 0.04_7 Å longer than the non-bridged Ru(1)—Co(4), —Ru(3) vectors. Similarly, the attachment of the C(3)—C(4) moiety to its Ru_2Co triangle is considerably more unsymmetrical than that of the C(1)—C(2) moiety in the other half of the cluster. A strong σ-interaction between C(4) and Ru(2) results in a weak π-interaction of this carbon with Co(5). The reasons for these effects are not clear; perhaps attachment of the now-conjugated C_4 chain to the cluster induces the observed steric distortion.

In solution, the complex appears to be symmetrical insofar as only seven separate CO resonances are found in the ^{13}C NMR spectrum (see Experimental). This indicates that either the CO groups are symmetrically disposed in the solution structure or that some fluxional process gives the

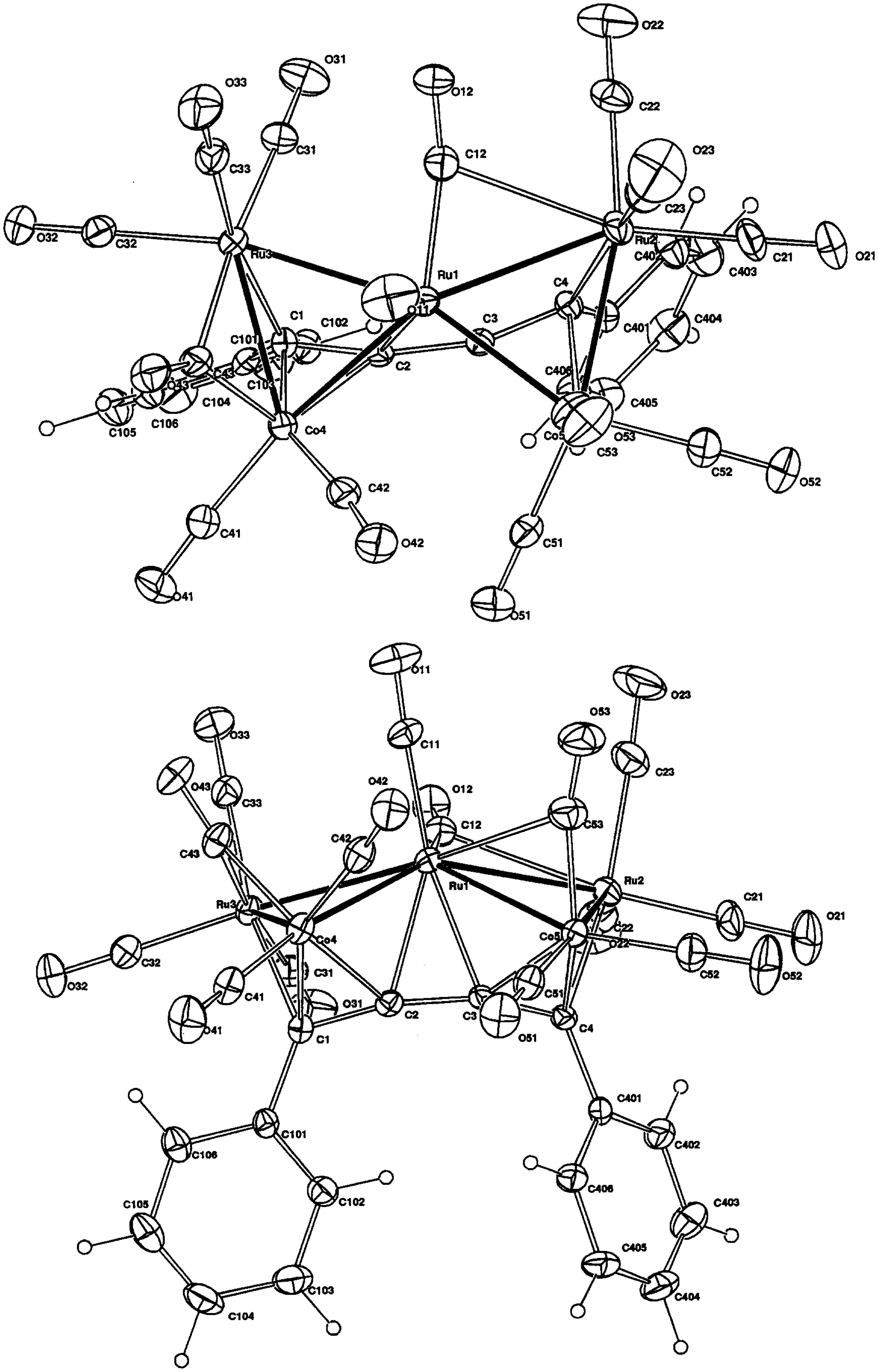


Fig. 1. Plots of a molecule of Co$_2$Ru$_3$(μ_5-η^2,η^2-PhC$_2$C$_2$Ph)(CO)$_{14}$(**3**) (a) on to the Ru(2,3)Co(4,5) plane and (b) side on, showing atom numbering system. Non-hydrogen atoms are shown as 20% thermal ellipsoids; hydrogen atoms have arbitrary radii of 0.1 Å.

Table 1. Some significant bond lengths (Å) and angles (°) for $Co_2Ru_3(\mu_5\text{-}\eta^2,\eta^2\text{-}PhC_2C_2Ph)(CO)_{14}$ (**3**)

Ru(1)—Ru(2)	2.8712(9)	Ru(1)—Ru(3)	2.8243(9)
Ru(1)—Co(5)	2.730 (1)	Ru(1)—Co(4)	2.643 (1)
Ru(2)—Co(5)	2.598 (1)	Ru(3)—Co(4)	2.587 (1)
Ru(1)—C(3)	2.150 (5)	Ru(1)—C(2)	2.191 (5)
Ru(2)—C(4)	2.078 (5)	Ru(3)—C(1)	2.161 (5)
Co(5)—C(3)	2.007 (6)	Co(4)—C(2)	2.089 (6)
Co(5)—C(4)	2.136 (6)	Co(4)—C(1)	2.035 (6)
C(3)—C(4)	1.367 (7)	C(1)—C(2)	1.346 (7)
C(2)—C(3)	1.358 (7)		
C(4)—C(401)	1.485 (7)	C(1)—C(101)	1.480 (7)

Ru(2)—Ru(1)—Ru(3)	131.69(3)		
Ru(1)—Ru(2)—Co(5)	59.63(2)	Ru(1)—Ru(3)—Co(4)	58.27(2)
Ru(1)—Co(5)—Ru(2)	65.16(3)	Ru(1)—Co(4)—Ru(3)	65.37(3)
Ru(2)—Ru(1)—Co(5)	55.21(2)	Ru(3)—Ru(1)—Co(4)	56.36(3)
Co(4)—Ru(1)—Co(5)	96.12(3)		
C(2)—C(3)—C(4)	155.4(6)	C(1)—C(2)—C(3)	160.1(6)
C(3)—C(4)—C(401)	123.1(4)	C(2)—C(1)—C(101)	125.2(5)
Ru(1)—C(12)—O(12)	166.6(5)		
Ru(2)—C(12)—O(12)	116.7(4)		

same result; we have not been able to resolve this point.

The formation of a pentanuclear complex as the only product under the extremely mild conditions used is unprecedented. It is known that $Co_2(CO)_8$ reacts readily with alkynes to give $Co_2(\mu\text{-}\eta^2\text{-}alkyne)(CO)_6$; indeed, the osmium analogue $Os_3(\mu_3\text{-}HC_2C_2SiMe_3)(CO)_{10}$ affords a complex containing a $Co_2(CO)_6$ unit attached to the formerly uncoordinated C≡C bond of the precursor as the only product; however, the X-ray structure of this derivative shows that the Co atoms are as far as possible from the Os_3 cluster and we have not succeeded in obtaining a complex analogous to **3**, either thermally or by chemical means.[10]

An alternative reaction pathway involving prior insertion of Co into the Ru_3 cluster is attractive. However, although this reaction is well known with unsubstituted ruthenium carbonyls, it generally requires an anionic reagent (Co or Ru) to proceed efficiently.[11] In the present case, with the η^2-diyne holding the Ru cluster together, insertion of Co into one Ru—Ru bond, followed by Co—Co bond cleavage and coordination of the second C≡C triple bond results in the diyne being able to straddle both halves of the newly formed cluster.

In principle, this complex could be made from a reaction between $Co_2(\mu\text{-}\eta^2\text{-}PhC_2C_2Ph)(CO)_6$ and $Ru_3(CO)_{10}(NCMe)_2$. In fact, the only isolable complexes from this reaction were the disproportionation products $\{Co_2(CO)_6\}_2(\mu,\mu\text{-}\eta^2:\eta^2\text{-}PhC_2C_2Ph)$[12] and $Ru_3(\mu_3\text{-}\eta^2\text{-}PhC_2C_2Ph)(\mu\text{-}CO)(CO)_9$. Further studies of related reactions, including those with Co or Ru precursors containing dppm-bridged Co—Co or Ru—Ru bonds, are in progress.

EXPERIMENTAL

All reactions were carried out under dry nitrogen using standard Schlenk techniques. General instrumental facilities were the same as those described in Ref. 13. The complex $Ru_3(\mu_3\text{-}\eta^2\text{-}PhC_2C_2Ph)(\mu\text{-}CO)(CO)_9$ was obtained from PhC_2C_2Ph and $Ru_3(CO)_{10}(NCMe)_2$.[7]

Preparation of $Co_2Ru_3(\mu_5\text{-}\eta^2,\eta^2\text{-}PhC_2C_2Ph)(CO)_{14}$

A solution of $Co_2(CO)_8$ (23 mg, 0.066 mmol) in hexane (5 cm^3) was added to one of $Ru_3(\mu_3\text{-}\eta^2\text{-}PhC_2C_2Ph)(\mu\text{-}CO)(CO)_9$ (50 mg, 0.064 mmol) in the same solvent (10 cm^3). The colour gradually changed from dark red to brown–green with the formation of a dark coloured precipitate after 1 h. After 2 h at room temperature, the Ru_3 precursor was no longer present (TLC). Removal of hexane under reduced pressure and recrystallization of the residue (C_6H_6) gave dark red crystals of $Co_2Ru_3(\mu_5\text{-}\eta^2,\eta^2\text{-}PhC_2C_2Ph)(CO)_{14}$ (**3**) (62 mg, 95%), dec. 245°C. Analysis: Found: C, 35.49; H, 0.99 calc. for $C_{30}H_{10}Co_2O_{14}Ru_3$: 35.47; H, 0.98%. IR (cyclohexane): $\nu(CO)$ 2099 m, 2080 s, 2058 vs, 2041 s, 2026 m, 2020 m, 2012 w, 2001 w, 1988 (sh), 1900 w (br), 1886 w (br) cm^{-1}. ^{13}C NMR ($CDCl_3$): δ

124.20, 143.10 (s, 2 × C≡), 128.22, 128.71, 128.92 (3 × s, *o*, *p*, *m* C of Ph), 145.8 (s, *ipso* C of Ph), 190.24, 191.64, 192.21 (3 × s, Ru—CO), 200.84, 204.92 (2 × s, Co-CO). FAB MS (m/z): 1017, $[M]^+$; 961-625, $[M-n\text{CO}]^+$ ($n = 2$-14; $n = 5$ had maximum intensity).

Reaction between $Co_2(\mu\text{-}\eta^2\text{-}PhC_2C_2Ph)(CO)_6$ *and* $Ru_3(CO)_{10}(NCMe)_2$

A solution of $Co_2(\mu\text{-}\eta^2\text{-}PhC_2C_2Ph)(CO)_6$ (156 mg, 0.319 mmol) in CH_2Cl_2 (10 cm^3) was added to one of $Ru_3(CO)_{10}(NCMe)_2$ [from 200 mg (0.312 mmol) $Ru_3(CO)_{12}$] in 14/3 CH_2Cl_2/MeCN (85 cm^3) and the mixture was stirred overnight. TLC of the reaction products gave $Ru_3(CO)_{12}$ (53 mg, 26%), $Ru_3(\mu_3\text{-}\eta^2\text{-}PhC_2C_2Ph)(CO)_{10}$ (5 mg) and $\{Co_2(CO)_6\}_2(\mu,\mu\text{-}\eta^2{:}\eta^2\text{-}PhC_2C_2Ph)$ (11 mg), all identified from their IR ν(CO) spectra.

Crystallography

A unique data set was measured at *ca* 22°C to $2\theta_{max} = 55°$ using an Enraf–Nonius CAD4 diffractometer ($2\theta/\theta$ scan mode; monochromatic Mo-Kα radiation. $\lambda = 0.7107_3$ Å); 7613 independent reflections were obtained, 4373 with $I > 3\sigma(I)$ being considered "observed" and used in the full-matrix least-squares refinement after Gaussian absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were included constrained at estimated values. Conventional residuals R, R' on $|F|$ were 0.035 and 0.030, respectively, statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$ being used. Computation used the XTAL3.2 program system[14] implemented by S. R. Hall; neutral atom complex scattering factors were employed. Pertinent results are given in Fig. 1 and Table 1.

Crystal data. $Co_2Ru_3(\mu_5\text{-}\eta^2,\eta^2\text{-}PhC_2C_2Ph)(CO)_{14} \equiv C_{30}H_{10}Co_2O_{14}Ru_3$, $M = 1015.5$. Crystals are monoclinic, space group $P2_1/c$, $a = 8.905(2)$, $b = 20.483(5)$, $c = 18.271(6)$ Å, $\beta = 94.78(2)°$, $V = 3321(1)$ Å^3, $d_c = 2.03$ g cm^{-3}, $F(000) = 1952$; μ(Mo-$K\alpha$) = 23.8 cm^{-1}, specimen 0.34 × 0.08 × 0.09 mm; A^* (min, max) = 1.19, 1.25.

Supplementary data. Tables of non-hydrogen atom and hydrogen atom positional and isotropic displacement parameters, atomic anisotropic displacement parameters, bond distances and angles and structure-factor amplitudes.

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