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Cluster chemistry

LXXIII *. Preparation and X-ray structure of the hexanuclear cobalt-ruthenium cluster, $CoRu_5(\mu_4\text{-}PPh)(\mu_4\text{-}C_2Ph)(\mu\text{-}PPh_2)(CO)_{12}(\eta\text{-}C_5H_5)$

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Abstract

One of the products from the reaction between $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ and $Co(CO)_2(\eta\text{-}C_5H_5)$ is the heterometallic $CoRu_5$ cluster, $CoRu_5(\mu_4\text{-}PPh)(\mu_4\text{-}C_2Ph)(\mu\text{-}PPh_2)(CO)_{12}(\eta\text{-}C_5H_5)$. The Ru_5 core has an irregular envelope conformation, one edge of which is bridged by PPh_2; the Co is attached to three Ru atoms of the Ru_4 rhombus, the other side of which is capped by PPh. A C_2Ph ligand, formed by extrusion of PPh to the cluster, bridges the flap of the envelope and the Co atom, and also interacts with three Ru atoms.

Introduction

The pentanuclear ruthenium complex $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ (**1**) has given much interesting chemistry from its reactions with organic substrates [2]. We have now commenced a study of the formation of medium and high nuclearity homo- and hetero-nuclear clusters by addition of other transition metal complexes to the open skeleton present in **1**. This paper reports the synthesis of a hexanuclear $CoRu_5$ cluster from the reaction between **1** and $Co(CO)_2(\eta\text{-}C_5H_5)$.

Results and discussion

The reaction between **1** and $Co(CO)_2(\eta\text{-}C_5H_5)$ was carried out in toluene at 90 °C for 3 d. Several products were separated by preparative TLC, but only one

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[*] For Part LXXII, see ref. 1.

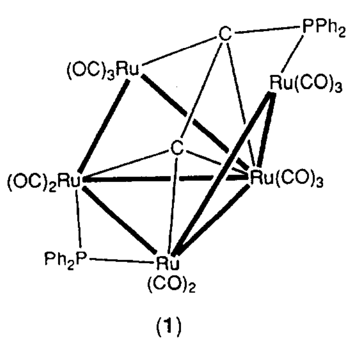
Table 1

Selected bond lengths (Å) for **2**

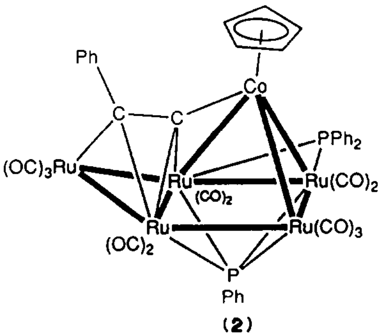
Ru(1)-Ru(2)	2.872(1)	Ru(3)-P(1)	2.371(2)
Ru(1)-Ru(4)	2.812(1)	Ru(4)-P(1)	2.379(2)
Ru(1)-Ru(5)	3.027(1)	Ru(1)-P(2)	2.365(2)
Ru(2)-Ru(3)	2.899(1)	Ru(4)-P(2)	2.254(2)
Ru(2)-Ru(5)	2.661(1)	Ru(1) · · · C(1)	3.190(6)
Ru(3)-Ru(4)	2.8718(9)	Ru(1)-C(2)	2.283(5)
Ru(1)-Co	2.697(1)	Ru(2)-C(1)	2.253(7)
Ru(3)-Co	2.691(1)	Ru(2)-C(2)	2.157(7)
Ru(4)-Co	2.657(1)	Ru(5)-C(1)	2.067(6)
Ru(1)-P(1)	2.527(2)	Co-C(2)	1.819(6)
Ru(2)-P(1)	2.278(2)	C(1)-C(2)	1.373(7)
Co-C(cp)		range 2.042(9)-2.12(1), av. 2.09_2 Å	
Ru-CO		range 1.880-1.969(8), av. 1.89_7 Å	
P-C(Ph)		range 1.805-1.831(5), av. 1.81_6 Å	
C-O		range 1.109-1.142(9), av. 1.13 Å.	

has given black crystals suitable for an X-ray study, two forms being obtained. The first, from dichloromethane/isopentane, was solvated and yielded inferior material with a resulting determination of poor precision. A second, unsolvated, form was then obtained from dichloromethane/methanol as nicely formed crystals, resulting in a superior study. Both are recorded, the second in more detail and forming the basis for the parameters of Table 1, Fig. 1 and the Discussion. The complex was thus characterised as $CoRu_5(\mu_4\text{-}PPh)(\mu_4\text{-}C_2Ph)(\mu\text{-}PPh_2)(CO)_{12}(\eta\text{-}C_5H_5)$ (**2**). Figure 1 shows two plots of a molecule of **2** and selected bond lengths are collected in Table 1.

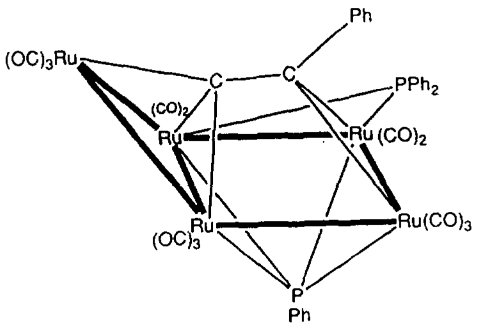
The structure of **2** is based on an irregular square pyramidal PRu_4 core, one edge of which is bridged by the PPh_2 group, and an adjacent edge by an $Ru(CO)_3$ group. The Co atom is attached to three Ru atoms of the Ru_4 face to give an irregular $CoRu_5$ polyhedron, best described as an edge-bridged $CoRu_4$ square-pyramid lacking one Co(ap)-Ru(bas) bond. An alternative description is of a metalla-alkyne, $PhC_2Co(\eta\text{-}C_5H_5)$, spanning the Ru_5 array. This description also emphasises the relationship between **2** and an isomer of **1**, $Ru_5(\mu_5\text{-}C_2Ph)(\mu_4\text{-}PPh)(\mu\text{-}PPh_2)(CO)_{13}$



(1)



(**2**)



(3)

(3) [3], which has been isolated from reactions of **1** with oxirane or $Fe_2(CO)_9$. Although the isolobal nature of the $Co(\eta\text{-}C_5H_5)$ and $Fe(CO)_3$ groups might suggest that **2** might have been formed from **3** and $Co(CO)_2(\eta\text{-}C_5H_5)$, a control experiment with these two reactants showed that no **2** was formed under similar reaction conditions.

The Ru_5 skeleton is related to those found in **3** [3] and in the μ_5-benzyne complex, $Ru_5(\mu_5\text{-}C_6H_4)(\mu_4\text{-PPh})(CO)_{13}$ [4], which have been compared to 'step-sites' on metal surfaces. The internal dihedrals Ru(1)–Ru(2)–Ru(5)/Ru(1)–Ru(2)–Ru(4) (the flap angle of the envelope), Ru(1)–Ru(2)–Ru(4)/Ru(2)–Ru(3)–Ru(4) (relating to the non-planarity of the Ru_4 rhombus) and Ru(1)–Ru(2)–Ru(3)/Co(1)–Ru(1)–Ru(3) are 162.23(4), 146.97(5) and 128.41(5)°, respectively.

Of the Ru–Ru distances, which range between 2.661(1) and 3.027(1) Å, the shortest is that bridged by C(1) of the alkyne and the longest is Ru(1)–Ru(5), which supports the C_2 unit of the alkyne. There is thus a considerable distortion of the Ru_3 triangle to which the $2\sigma,\eta^2$-CC unit of the alkyne is attached. For comparison, the Ru–Ru separations in $Ru_3(\mu\text{-H})(\mu_3\text{-}C_2{}^tBu)(CO)_9$ are all 2.795(3) Å [5] and those in $Ru_3\{\mu_3\text{-}C_2(CO_2Me)_2\}(\mu\text{-dppm})(\mu\text{-CO})(CO)_7$ lie between 2.717(1) and 2.817(1) Å [6]. The Co–Ru distances are between 2.657(1) and 2.697(1) Å. No structurally characterised Co–Ru clusters containing $Co(\eta\text{-}C_5H_5)$ groups are known to us, but Co–Ru distances in otherwise related complexes include 2.573(1) and 2.655(1) Å in $Co_2Ru(\mu_3\text{-CPh})(CO)_7(\eta\text{-}C_5H_5)$ [7], 2.618(1) and 2.628(1) Å in $Co_2Ru(\mu_3\text{-CCH}^tBu)(CO)_9$ [8], 2.699(1) Å (parallel to the CC bond) in $Co_2Ru(\mu_3\text{-}HC_2{}^tBu)(\mu\text{-CO})(CO)_8$ [8], 2.703(3) Å in $Co_2Ru_2(\mu\text{-CO})(CO)_9$ [9] and 2.716(5) and 2.723(2) Å in $Co_2Ru(\mu\text{-CO})(CO)10$ [9]. In a series of pseudo-octahedral $C_2Co_{4-n}Ru_n$ clusters ($n = 0\text{–}3$) containing μ_4-alkynes, non-hinge Co–Ru separations range between 2.481(2) and 2.614(1) Å; the only hinge Co–Ru distance was longer, at 2.725(2) Å [10].

The μ_4-PPh group is strongly bonded to Ru(2), Ru(3) and Ru(4) [2.278–2.371(2) Å] but only weakly to Ru(1) [2.527(2) Å]. The Ru(1)–Ru(4) vector is asymmetrically bridged by the $\mu\text{-PPh}_2$ group [2.365, 2.254(2) Å]. The alkyne caps the Ru(1)–Ru(2)–Ru(5) face in an asymmetric $\mu_3\text{-}\eta^2\text{-}\|$ mode, with shortest interactions Ru(2)–C(2) [2.157(7) Å] and Ru(5)–C(1) [2.067(7) Å], and weaker bonds to the other Ru atoms [Ru(1)–C(2) 2.283(5), Ru(2)–C(1) 2.253(7) Å]. The $Co(\eta\text{-}C_5H_5)$ group is also attached to C(2) [Co–C(2) 1.819(6) Å]. The C(1)–C(2) distance is 1.373(7) Å.

The twelve CO groups are distributed two each to Ru(1), Ru(2) and Ru(4), and three to each of Ru(3) and Ru(5). All Ru–C–O angles are > 175° with the exception of Ru(3)–C(33)–O(33) [168.5(6)′], which is incipiently semi-bridging the Ru(3)–Ru(4) vector.

Normal electron book-keeping suggests that Ru(1) is electron-rich and Ru(5) is electron-poor, although the cluster as a whole is electron-precise. The long Ru(1)–Ru(5) and short Ru(2)–Ru(5) distances suggest that some electron delocalisation occurs in this unit, with perhaps the best description of the former being an Ru → Ru donor bond. The structure can be interpreted as resulting from a flexible Ru_5 skeleton accommodating the steric and electronic requirements of the PPh and

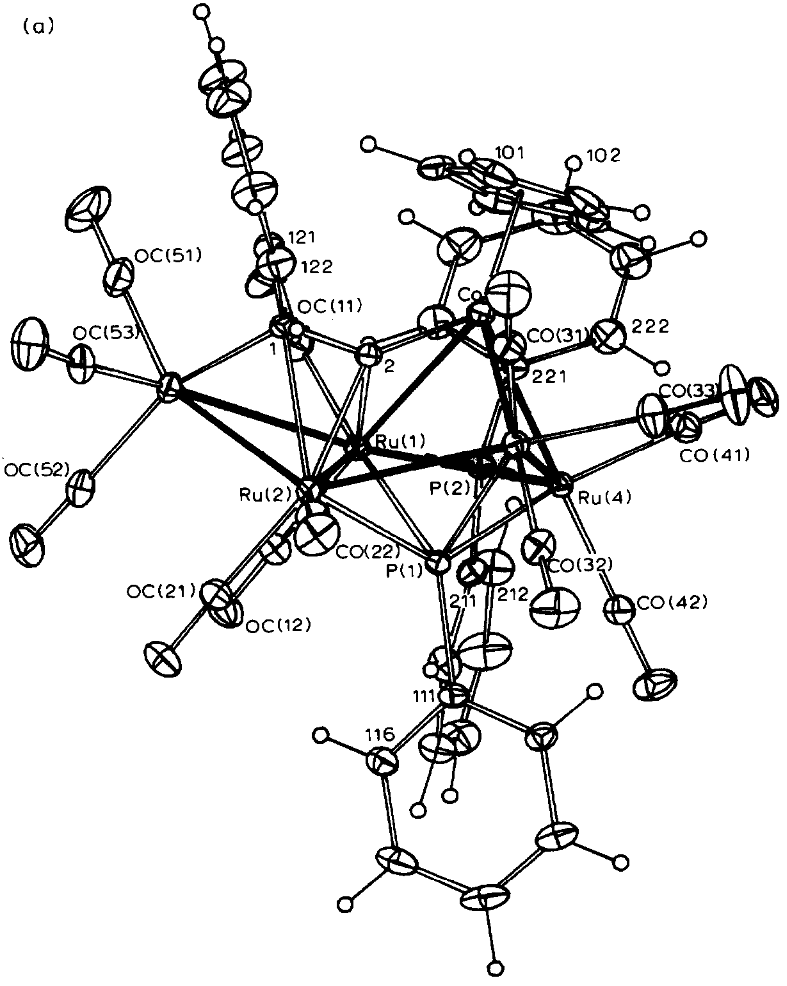


Fig. 1. Computer-generated plots of a molecule of $CoRu_5(\mu_4\text{-}PPh)(\mu_4\text{-}C_2Ph)(\mu\text{-}PPh_2)(CO)_{12}(\eta\text{-}C_5H_5)$ (2): (a) viewed from the side of the Ru_4 rhombus and (b) viewed approximately perpendicular to the Ru_4 rhombus, showing atom numbering scheme. Non-hydrogen atoms are shown as 20% thermal ellipsoids; hydrogen atoms have arbitrary radii of 0.1 Å.

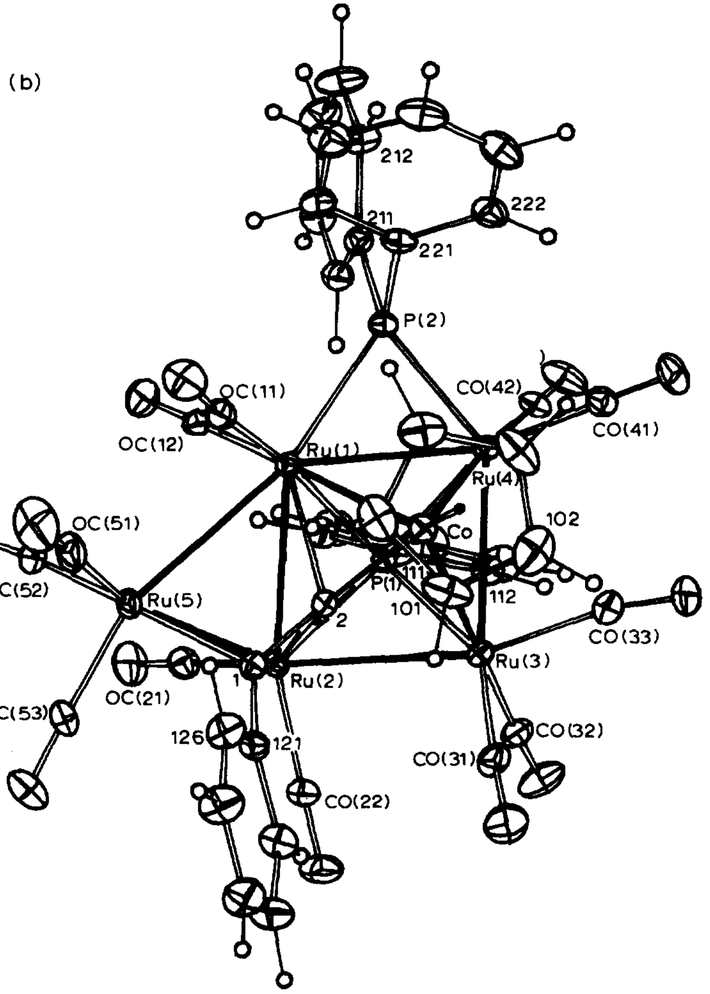


Fig. 1 (continued).

$PhC_2Co(\eta\text{-}C_5H_5)$ groups. This is consistent with the well-known relative weakness of M–M bonds in metal cluster complexes [11].

The spectroscopic properties were determined: the IR spectrum contains only terminal ν(CO) absorptions and the ^{1}H NMR spectrum contains a singlet at δ 4.49 for the C_5H_5 group as well as an extended series of multiplets between δ 6.0 and 8.3 for the phenyl protons. The ^{13}C resonances are found at δ 85.8 (C_5H_5), between δ 126–134 (Ph), between 137–147 (*ipso* C) and a series of signals between δ 188–212 can be assigned to the various CO groups. There are also two resonances, at δ 148.9 and 240.5, which we assign to C_β and C_α, respectively; the latter shows an unresolved coupling, probably to P. The FAB mass spectrum contained a molecular ion at m/z 1360, which fragmented by loss of the twelve CO ligands and a phenyl group from the carbonyl-free ion.

Complex **2** is the major product from the reaction between **1** and $Co(CO)_2(\eta$-

Table 2

Non-hydrogen atomic coordinates for solvated and unsolvated forms of **2**

Atom	Solvated form			Unsolvated form		
	x	*y*	*z*	*x*	*y*	*z*
Ru(1)	0.7183(2)	0.6022(3)	0.6884(3)	0.80518(3)	0.41146(3)	0.30177(5)
Ru(2)	0.8124(2)	0.6137(3)	0.8540(3)	0.81231(3)	0.17319(3)	0.18925(5)
Ru(3)	0.7592(2)	0.5074(3)	0.8749(3)	0.63777(3)	0.19064(4)	0.09940(5)
Ru(4)	0.6538(2)	0.5392(3)	0.7295(3)	0.62290(3)	0.40105(3)	0.28880(5)
Ru(5)	0.8339(2)	0.6286(3)	0.7424(3)	0.95899(3)	0.29253(4)	0.19022(5)
Co(1)	0.7289(4)	0.4776(4)	0.7235(5)	0.70726(5)	0.38827(6)	0.09960(8)
C(11)	0.732(3)	0.576(4)	0.623(5)	0.8812(4)	0.5152(5)	0.2697(7)
O(11)	0.726(1)	0.568(2)	0.553(2)	0.9227(3)	0.5828(4)	0.2506(6)
C(12)	0.708(2)	0.682(2)	0.668(2)	0.8687(4)	0.4211(4)	0.4460(6)
C(12)	0.703(1)	0.738(2)	0.651(2)	0.9072(3)	0.4267(4)	0.5315(5)
C(21)	0.821(2)	0.692(2)	0.865(3)	0.8778(4)	0.1365(5)	0.3065(7)
O(21)	0.829(2)	0.705(2)	0.880(2)	0.9150(3)	0.1120(4)	0.3764(5)
C(22)	0.872(2)	0.608(3)	0.976(3)	0.7861(4)	0.0182(5)	0.1061(7)
O(22)	0.898(2)	0.602(2)	1.039(3)	0.7681(3)	−0.0751(3)	0.0586(5)
C(31)	0.801(2)	0.440(2)	0.912(2)	0.6436(4)	0.1130(6)	−0.0686(7)
O(31)	0.836(2)	0.394(2)	0.938(2)	0.6428(4)	0.0637(5)	−0.1656(5)
C(32)	0.783(2)	0.535(3)	0.980(3)	0.5905(4)	0.0579(5)	0.1166(7)
O(32)	0.797(2)	0.554(2)	1.044(3)	0.5599(3)	−0.0212(4)	0.1266(6)
C(33)	0.718(2)	0.451(3)	0.873(3)	0.5296(4)	0.2457(6)	0.0735(8)
O(33)	0.681(2)	0.417(2)	0.863(2)	0.4633(3)	0.2624(5)	0.0416(6)
C(41)	0.613(2)	0.472(3)	0.703(3)	0.5297(4)	0.4694(5)	0.2418(7)
O(41)	0.579(2)	0.427(2)	0.689(2)	0.4708(3)	0.5080(4)	0.2163(5)
C(42)	0.601(2)	0.582(3)	0.741(3)	0.5587(4)	0.3933(5)	0.4149(6)
O(42)	0.570(2)	0.612(2)	0.746(2)	0.5199(3)	0.3892(4)	0.4902(5)
C(51)	0.840(3)	0.608(3)	0.656(4)	1.0277(4)	0.3997(6)	0.1521(8)
O(51)	0.855(2)	0.583(2)	0.617(3)	1.0690(4)	0.4607(5)	0.1250(8)
C(52)	0.830(2)	0.708(3)	0.719(3)	1.0280(4)	0.3075(5)	0.3390(7)
O(52)	0.822(2)	0.764(2)	0.704(3)	1.0689(3)	0.3097(5)	0.4195(6)
C(53)	0.893(5)	0.641(7)	0.795(8)	1.0228(4)	0.1799(6)	0.1017(8)
O(53)	0.949(2)	0.642(3)	0.853(3)	1.0600(3)	0.1111(5)	0.0405(7)
P(1)	0.7260(7)	0.6111(8)	0.8240(9)	0.70182(8)	0.2502(1)	0.2987(1)
C(111)	0.708(2)	0.670(2)	0.864(2)	0.6680(4)	0.2008(4)	0.4133(6)
C(112)	0.686(2)	0.655(3)	0.911(3)	0.5824(4)	0.1596(5)	0.4101(6)
C(113)	0.667(3)	0.698(3)	0.939(4)	0.5545(5)	0.1234(6)	0.4974(8)
C(114)	0.669(2)	0.757(3)	0.927(4)	0.6111(6)	0.1249(7)	0.5880(8)
C(115)	0.687(3)	0.774(3)	0.878(4)	0.6969(5)	0.1642(6)	0.5942(7)
C(116)	0.703(2)	0.728(2)	0.848(3)	0.7250(4)	0.2019(5)	−0.5082(7)
C(1)	0.833(2)	0.550(2)	0.783(3)	0.8596(3)	0.2426(4)	0.0543(6)
C(2)	0.784(2)	0.529(3)	0.775(3)	0.7893(3)	0.2941(4)	0.1061(5)
C(121)	0.882(3)	0.503(4)	0.827(4)	0.8725(4)	0.1858(5)	−0.0735(6)
C(122)	0.911(3)	0.479(4)	0.916(5)	0.8499(5)	0.0719(6)	−0.1390(8)
C(123)	0.955(3)	0.432(4)	0.944(5)	0.8689(5)	0.0219(6)	−0.2539(8)
C(124)	0.958(4)	0.420(4)	0.883(5)	0.9084(5)	0.0809(7)	−0.3125(8)
C(125)	0.938(5)	0.432(6)	0.806(7)	0.9309(5)	0.1941(7)	−0.2532(8)
C(126)	0.891(3)	0.479(4)	0.788(4)	0.9132(5)	0.2446(6)	−0.1354(7)
P(2)	0.6248(8)	0.5799(9)	0.608(1)	0.71388(9)	0.5528(1)	0.3959(2)
C(211)	0.577(2)	0.640(3)	0.576(3)	0.7172(3)	0.6019(5)	0.5575(6)
C(212)	0.519(3)	0.651(3)	0.487(4)	0.7146(5)	0.7158(5)	0.6296(7)
C(213)	0.494(3)	0.709(4)	0.475(4)	0.7171(6)	0.7456(6)	0.7509(8)
C(214)	0.503(5)	0.746(6)	0.547(8)	0.7222(5)	0.6722(7)	0.8046(7)
C(215)	0.550(4)	0.743(4)	0.605(5)	0.7243(5)	0.5594(6)	0.7391(7)

Table 2 (continued)

Atom	Solvated form			Unsolvated form		
	x	*y*	*z*	*x*	*y*	*z*
C(216)	0.585(3)	0.693(3)	0.622(4)	0.7216(4)	0.5259(5)	0.6157(7)
C(221)	0.597(2)	0.534(3)	0.506(3)	0.7150(4)	0.6856(4)	0.3705(6)
C(222)	0.563(2)	0.480(3)	0.501(3)	0.6392(4)	0.7240(5)	0.3401(7)
C(223)	0.545(3)	0.440(3)	0.423(4)	0.6408(5)	0.8233(6)	0.3197(8)
C(224)	0.550(2)	0.464(3)	0.369(3)	0.7163(6)	0.8858(5)	0.3320(8)
C(225)	0.575(2)	0.514(3)	0.379(3)	0.7934(5)	0.8522(6)	0.3651(9)
C(226)	0.600(3)	0.555(3)	0.445(4)	0.7931(4)	0.7515(5)	0.3846(7)
C(101)	0.769(2)	0.395(3)	0.738(3)	0.7096(6)	0.3759(6)	−0.0741(7)
C(102)	0.719(2)	0.381(3)	0.728(3)	0.6285(6)	0.4027(8)	−0.0424(9)
C(103)	0.678(3)	0.400(3)	0.659(4)	0.6380(5)	0.5060(8)	0.0519(8)
C(104)	0.694(2)	0.429(2)	0.609(3)	0.7248(6)	0.5436(6)	0.0772(8)
C(105)	0.757(3)	0.435(4)	0.669(4)	0.7703(5)	0.4634(7)	−0.0038(8)
O	0.525(6)	0.731(6)	0.283(9)			

C_5H_5) and speculations on the mode of its formation are of limited value. Possible reactions include:

(i) transfer of Ph to the C_2PPh_2 (or C_2—if (ii) precedes) ligand from the μ-PPh_2 group in **1**, thereby generating the μ_4-PPh group; this has precedent in the 'isomerisation' of **1** to **3**, and more closely in the formation of $Ru_4(\mu_4\text{-}PPh)(\mu_4\text{-}PhC_2PPh_2)(\mu\text{-}CO)(CO)_8$ [12];

(ii) cleavage of the Ph_2P–CC bond, with migration of the PPh_2 group to an Ru–Ru edge;

(iii) combination of the Co(η-C_5H_5) fragment with the C_2 or PhC_2 fragment and attachment of the Co to three Ru atoms of the cluster.

Reactions (i) and (ii) can be summarised:

$$Ph_2P\text{-}CC + Ph\text{-}PPh \rightarrow Ph_2P + CCPh + PPh$$

Conclusions

A novel heterometallic $CoRu_5$ cluster has been isolated from the reaction between **1** and $Co(CO)_2(\eta\text{-}C_5H_5)$, in the formation of which formal elimination of PPh from the C_2PPh_2 group to the cluster has occurred. The remaining C_2Ph fragment combines with a Co(η-C_5H_5) moiety which also bonds to the rhomboidal Ru_4 portion of the cluster.

Experimental

General. General reaction conditions were similar to those described previously [13]. Complex **1** was made as described previously [14]; $Co(CO)_2(\eta\text{-}C_5H_5)$ was obtained from Strem (Newburyport, MA) and used as received.

Reaction of $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ with $Co(CO)_2(\eta\text{-}C_5H_5)$.

A solution of $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ (120 mg, 0.095 mmol) and $Co(\eta\text{-}C_5H_5)(CO)_2$ (300 mg, 1.67 mmol) in toluene (10 cm^3) was heated in a Carius tube at

90 °C for 3 d. The solvent was removed and the residue purified by preparative TLC (light petroleum/acetone 10/3) to yield several coloured bands. Only one product (R_f 0.7) gave black crystals suitable for a single crystal X-ray study, identified as $CoRu_5(\mu_4\text{-}PPh)(\mu_4\text{-}C_2Ph)(\mu\text{-}PPh_2)(CO)_{12}(\eta\text{-}C_5H_5)$ (3) (41 mg, 32%), m.p. 197–202 °C (dec.). Found: C, 38.55; H, 2.12%; M^+, 1360. $C_{45}CoH_{25}O_{14}P_2Ru_5$ calc.: C, 38.17; H, 1.78%; M, 1360. IR: ν(CO) (cyclohexane) 2073s, 2050s, 2015vs, 2003vs, 1995(sh), 1980m, 1972m, 1952m, 1944m cm^{-1}. ^1H NMR: $\delta(CDCl_3)$ 4.49 (s, 5H, C_5H_5); 6.05–8.23 (extended m, 20H, Ph). ^{13}C NMR: $\delta(CDCl_3)$ 85.80 (s, C_5H_5); 126.3–134.0 (m, Ph); 137.26–146.77 (m, *ipso* C); 148.88 (s, C_β); 188.4, 189.05, 193.95, 194.4, 195.45, 200.3, 200.5, 206.65, 207.05, 211.75 (CO); 240.5 (m, C_α). FAB MS: 1360, M^+; 1332-1024, $[M-n\text{CO}]^+$ ($n = 1$–12); 947, $[M - 12\text{CO} - \text{Ph}]^+$.

Crystallography

Unique data sets were measured at ca 295 K within the specified $2\theta_{max}$ limits using an Enraf–Nonius CAD4 diffractometer ($2\theta/\theta$ scan mode; monochromatic Mo-K_α radiation, λ 0.7107_3 Å); N independent reflections were obtained, N_o with $I > 3\sigma(I)$ being considered 'observed' and used in the full matrix least squares refinement after gaussian absorption correction (unsolvated form). 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 $|F|$ are quoted, statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$ being used. Computation used the XTAL 2.6 program system [15] implemented by S.R. Hall; neutral atom complex scattering factors were employed. Pertinent results are given in Fig. 1 and Tables 1 and 2. Structure factor amplitudes, thermal and hydrogen atom parameters and full non-hydrogen geometries are available from the authors.

Crystal and refinement data

2, unsolvated form. $CoRu_5(\mu_4\text{-}PPh)(\mu_4\text{-}C_2Ph)(\mu\text{-}PPh_2)(CO)_{12}(\eta\text{-}C_5H_5) \equiv C_{43}CoH_{25}O_{12}P_2Ru_5$, $M = 1359.9$. Triclinic, space group $P\bar{1}$, (No. 2), $a = 15.495(7)$, $b = 12.803(4)$, $c = 12.039(5)$ Å, $\alpha = 110.99(3)$, $\beta = 93.64(4)$, $\gamma = 93.32(3)°$, $U = 2217$ Å^3. D_c $(Z = 2) = 2.04$ g cm^{-3}. $F(000) = 1312$. $\mu_{Mo} = 20.5$ cm^{-1}; specimen: 0.28 × 0.19 × 0.11 mm; $A^*_{min,max} = 1.29$, 1.51. $2\theta_{max} = 50°$, $N = 7790$, $N_o = 6697$; $R = 0.036$, $R' = 0.043$.

2, solvated form. $CoRu_5(\mu_4\text{-}PPh)(\mu_4\text{-}C_2Ph)(\mu\text{-}PPh_2)(CO)_{12}(\eta\text{-}C_5H_5) \equiv C_{43}CoH_{25}O_{12}P_2Ru_5$, $M = 1359.9$. Monoclinic, space group $C2/c$, (No. 15), $a = 29.697(13)$, $b = 21.202(7)$, $c = 19.874(14)$ Å, $\beta = 124.88(4)°$, $U = 10265$ Å^3. $D_c(Z = 8) = 1.76$ g cm^{-3}. $F(000) = 5248$. $\mu_{Mo} = 17.0$ cm^{-1}; specimen: flake, 0.05 × 0.15 × 0.15 mm; (no correction). $2\theta_{max} = 40°$, $N = 4515$, $N_o = 1644$; $R = 0.097$, $R' = 0.097$.

Abnormal features / variations in procedure. Two forms designated 'solvated' and 'unsolvated' have been recognised and their structures determined. Determination of the 'unsolvated' form was straight-forward. For the 'solvated' form, determined first, the data were of poor quality and limited extent, permitting anisotropic thermal parameter refinement for the metal atoms only; the isotropic form was used for the remaining non-hydrogen atoms. The complex molecule thus defined does not differ non-trivially from that of the 'unsolvated' form. A number of difference map residues were identified for the 'solvated' form; the only one of any substance was modelled as half-weighted oxygen. Clearly, however, it could be almost anything; the disordered solvent component appears to be considerable, although diffusely distributed—note the relative molecular volumes of the two forms—1283 cf. 1108 Å^3.

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