The synthesis and characterisation of the cluster dianion [PtRu$_5$C(CO)$_{15}$]$^{2-}$ and its reactions with Au and Pt cationic fragments produced *in situ*

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The neutral mixed-metal cluster [PtRu$_5$C(CO)$_{16}$] was reduced by KOH in methanol to give [Ph$_4$P]$_2$[PtRu$_5$C(CO)$_{15}$] **1** in 84% yield. Reaction of **1** with Au(PPh$_3$)Cl afforded the gold derivative [PtRu$_5$C(CO)$_{15}$(AuPPh$_3$)$_2$] **2**. Other reactions of **1** with [Pt(COD)Cl$_2$] and [Pt(CO)(PPh$_3$)Cl$_2$] in the presence of silica yielded the new mixed-metal cluster compounds [Pt$_2$Ru$_4$C(CO)$_{13}$(COD)] **3**, [Ph$_4$P]$_2$[Pt$_3$Ru$_{10}$C$_2$(CO)$_{32}$] **4**, [Pt$_4$Ru$_5$C(CO)$_{16}$(PPh$_3$)$_3$] **5**, [PtRu$_4$C(CO)$_{13}$(PPh$_3$)] **6** and [Pt$_2$Ru$_4$C(CO)$_{14}$(PPh$_3$)] **7**. Compounds **1–7** were characterised spectroscopically and the molecular and crystal structures of compound **1–5** were determined by single crystal X-ray crystallography.

Introduction

Mixed-metal clusters have been studied for many years because of their fascinating metal core geometries, and more recently have attracted renewed interest as potential precursors to supported nano-catalysts. Our studies have shown cluster-derived Ru–Pt catalysts to be highly active in industrially important hydrogenation reactions.[1] The performance of such catalysts may be tuned by varying the nature and ratio of the two metals. This being the case there is a clear need for further research into the synthesis of mixed-metal clusters with different ratios of the bimetallic components. Recently, we reported the synthesis of Pt–Ru mixed-metal cluster compounds starting from the dianionic clusters [Ru$_5$C(CO)$_{14}$]$^{2-}$ or [Ru$_6$C(CO)$_{16}$]$^{2-}$ by reactions with dichloro mononuclear complexes of Pt(II) in the presence of silica.[2] The silica was employed as an active chloride scavenger, to produce *in situ* dicationic platinum fragments, most probably stabilised by direct interaction with the silica surface. Following this strategy, a number of compounds with different metal : metal ratios were synthesised. Herein, the same approach has been used in order to introduce additional Pt-units into the mixed-metal dianionic cluster [Ru$_5$PtC(CO)$_{15}$]$^{2-}$.

Results and discussion

The neutral cluster [PtRu$_5$C(CO)$_{16}$],[3] undergoes almost quantitative reduction to the dianionic [PtRu$_5$C(CO)$_{15}$]$^{2-}$ on reaction with KOH in methanol. This anion may be isolated either as its [PPN]$^+$ or [Ph$_4$P]$^+$ (**1**) salt. The C–O stretching frequencies (ν(CO)) in the infrared spectrum undergo a blue shift by 75 cm^{-1} with respect to the neutral [PtRu$_5$C(CO)$_{16}$],[3] indicating formation of a negatively charged product. The overall character of the IR spectrum is very similar to that of [Ru$_6$C-(CO)$_{16}$]$^{2-}$ suggesting similarities in the structural arrangements of the CO ligands in both anions. The ^{1}H NMR spectrum of **1**, recorded in CD$_2$Cl$_2$, displayed only a multiplet in the region 7.92–7.60 ppm corresponding to the phenyl protons of the [Ph$_4$P]$^+$ cation. The ^{13}C NMR spectrum (in CD$_2$Cl$_2$), displayed a multiplet at 201 ppm arising from the C atoms of the carbonyl ligands and a multiplet at 136.0–117.4 ppm attributed to the forty-eight C of the phenyl rings. In the mass spectrum acquired by negative ESI a strong peak is found at *m/z* 566, corre-

Table 1 Selected bond distances (Å) for [Ph$_4$P]$_2$[PtRu$_5$C(CO)$_{15}$] **1**

Ru(1)–Pt(1)	2.8016(5)	Pt(1)–C(0)	2.029(4)
Ru(2)–Pt(1)	2.9385(5)	Ru(1)–C(0)	2.032(4)
Ru(3)–Pt(1)	2.9512(4)	Ru(2)–C(0)	2.061(4)
Ru(4)–Pt(1)	2.9555(4)	Ru(3)–C(0)	2.061(4)
Ru(1)–Ru(2)	3.0083(5)	Ru(4)–C(0)	2.071(4)
Ru(1)–Ru(4)	2.9479(6)	Ru(5)–C(0)	2.051(4)
Ru(1)–Ru(5)	2.8794(5)	Pt(1)–C(1)	1.850(5)
Ru(2)–Ru(3)	2.8268(6)	Pt(1)–C(2)	2.160(5)
Ru(2)–Ru(5)	2.8758(5)	Ru(1)–C(2)	2.020(5)
Ru(3)–Ru(4)	2.8436(5)	Ru–C(terminal) (mean)	1.886(4)
Ru(3)–Ru(5)	2.9258(5)	Ru–C(bridging) (mean)	2.10(6)
Ru(4)–Ru(5)	2.8510(5)	C–O(mean)	1.144(3)

sponding to the half mass of the anion [PtRu$_5$C(CO)$_{15}$]$^{2-}$; this is followed by a weaker peak at *m/z* 552 attributed to the loss of one CO ligand.

Compound [Ph$_4$P]$_2$[PtRu$_5$C(CO)$_{15}$] **1** crystallises in the monoclinic space group $P2_1/n$. The anionic part of **1** is presented in Fig. 1 and selected bond parameters are listed in Table 1. The molecular structure of [PtRu$_5$C(CO)$_{15}$]$^{2-}$ consists of an octahedral PtRu$_5$C core. Twelve of the fifteen carbonyl ligands are terminal while the remaining three are found to be μ-bridging, unlike [PtRu$_5$C(CO)$_{16}$] where only one carbonyl is μ-bridging. The Pt atom bears one terminal CO group and shares one bridging CO with Ru1. As a result, the Pt1–Ru1 bond (2.8016(5) Å) is shorter than the other Pt–Ru bonds
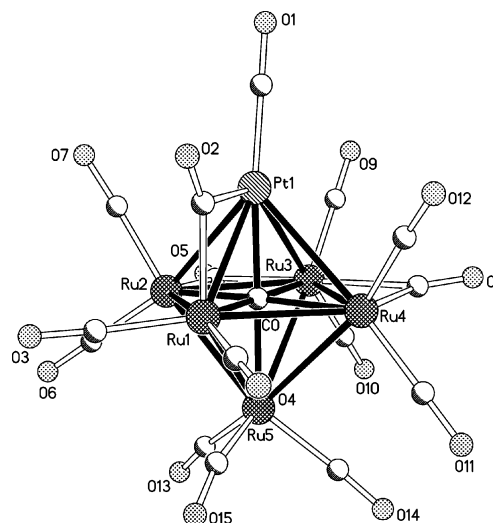
Fig. 1 Molecular structure of the anion [PtRu$_5$C(CO)$_{15}$]$^{2-}$ of **1**.

Table 2 Selected bond distances (Å) and angles (°) for [PtRu$_5$C(CO)$_{15}$-(AuPPh$_3$)$_2$] **2**

Ru(1)–Pt(1)	2.9657(11)	Pt(1)–C(0)	2.015(9)
Ru(2)–Pt(1)	2.9089(10)	Ru(1)–C(0)	2.070(12)
Ru(3)–Pt(1)	2.9957(10)	Ru(2)–C(0)	2.057(10)
Ru(4)–Pt(1)	2.8980(10)	Ru(3)–C(0)	2.047(12)
Ru(1)–Ru(2)	2.9131(15)	Ru(4)–C(0)	2.040(10)
Ru(1)–Ru(4)	2.8812(15)	Ru(5)–C(0)	2.090(9)
Ru(1)–Ru(5)	2.8233(14)		
Ru(2)–Ru(3)	2.8846(13)	Pt(1)–Au(1)	2.7461(7)
Ru(2)–Ru(5)	2.9045(14)	Ru(1)–Au(1)	2.7261(10)
Ru(3)–Ru(4)	2.9290(15)	Pt(1)–Au(2)	2.6995(7)
Ru(3)–Ru(5)	2.8326(15)	Ru(3)–Au(2)	2.7894(11)
Ru(4)–Ru(5)	2.8869(13)		
Ru–C(0)–Pt(1) (mean)	92.7(9)		

(2.9385(5)–2.9555(4) Å). The other two μ-CO ligands bridge the Ru2–Ru3 and Ru3–Ru4 bonds. All the metal–metal distances in compound **1** are similar to those found in other hexanuclear Ru carbido–carbonyl clusters,[4,5] and Pt–Ru mixed-metal clusters.[3,6] As observed with the neutral [PtRu$_5$C(CO)$_{16}$], there is no obvious deviation of the interstitial carbon from the centre of the octahedron.[3] Overall, the anion can be viewed as being bisected by a (non-crystallographic) mirror plane passing through the Pt1, Ru1, Ru5, Ru3 and C0 atoms. Compound **1** is isostructural with [PtFe$_5$C(CO)$_{15}$]$^{2-}$, which was obtained by reaction of [Pt(PPh$_3$)$_4$] with [Fe$_4$C(CO)$_{12}$]$^{2-}$,[7] or alternatively with [Fe$_5$C(CO)$_{14}$]$^{2-}$.[8]

Reaction with Au(PPh$_3$)Cl

When [Ph$_4$P]$_2$[PtRu$_5$C(CO)$_{15}$] **1** was reacted with 2.5 equivalent of [Au(PPh$_3$)Cl] in the presence of TlPF$_6$ the neutral cluster [PtRu$_5$C(CO)$_{15}$(AuPPh$_3$)$_2$] **2** was obtained in 67% yield. After purification by TLC, the IR spectrum displayed peaks corresponding to both terminal and edge-bridging carbonyls. The mass spectrum acquired by negative electrospray ionisation technique in the presence of sodium methoxide[9,10] comprised a high intensity peak at *m/z* = 2082 corresponding to [M + MeO]$^-$. The ^{1}H NMR spectrum (in CD$_2$Cl$_2$) showed only a multiplet at 7.6–7.4 ppm arising from the phenyl groups of the AuPPh$_3$ moiety. The ^{31}P NMR spectrum (in CD$_2$Cl$_2$) displayed only one signal at 69.6 ppm suggesting that the two AuPPh$_3$ units are equivalent. A small coupling ($^2J_{PtP}$ 411 Hz) to ^{195}Pt indicates that both AuPPh$_3$ groups are coordinated to Pt atom. This structural arrangement has been confirmed by an X-ray structural analysis.

The molecular structure of [PtRu$_5$C(CO)$_{15}$(AuPPh$_3$)$_2$] **2** is presented in Fig. 2 and selected bond parameters are listed in Table 2. The metal framework of **2** consists of a slightly distorted octahedron of PtRu$_5$C with two AuPPh$_3$ units bridging
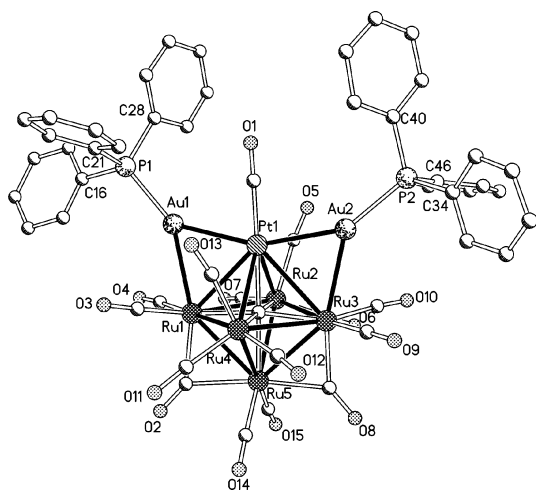
Fig. 2 Molecular structure of [PtRu$_5$C(CO)$_{15}$(AuPPh$_3$)$_2$] **5**.

non-adjacent Pt–Ru bonds. Thirteen CO ligands are terminal with the remaining two bridging the Ru5–Ru3 and Ru5–Ru1 bonds in the same plane as those bridged by AuPPh$_3$ fragments. This arrangement is similar to the one found in [Ru$_6$C(CO)$_{16}$-(AuPR$_3$)$_2$],[11,12] (PR$_3$ = PPh$_3$, PMePh$_2$), the only difference being that the two AuPR$_3$ groups bridge opposite sides of the Ru$_6$ octahedron. The Ru–Au distances in **2** lie within the expected range (Ru1–Au1 2.7261(10) Å, Ru3–Au2 2.7894(11) Å) and are close to those reported for other gold derivatives of Ru carbido–carbonyl clusters.[11,12] The Pt–Au distances are comparable with the Ru–Au distances (Pt1–Au1 2.7461(7) Å, Pt1–Au2 2.6995(7) Å) and with those reported for gold derivatives of triangulo-triplatinum compounds such as [Pt$_3$(CO)$_3$-(PPh$_3$)$_4$(AuPPh$_3$)][NO$_3$], [Pt$_3$(CO)$_3$(PCy$_3$)$_4$(AuPCy$_3$)][PF$_6$] and [Pt$_3$(dppm)$_3$(AuMe$_3$)$_2$][PF$_6$].[13–15] As observed for the neutral [PtRu$_5$C(CO)$_{16}$] and the anionic [PtRu$_5$C(CO)$_{15}$]$^{2-}$ **1** compounds, there is no deviation of the interstitial carbon atom towards the Pt atom.

To the best of our knowledge only two gold-containing Pt–Ru mixed-metal clusters have been reported up to date. These are derivatives of the Pt$_3$Ru$_6$ layer segregated cluster compound: namely [Pt$_3$Ru$_6$(CO)$_{21}$(μ-H)$_3$(AuPEt$_3$)] and [Pt$_3$Ru$_6$-(CO)$_{21}$(μ-H)$_2$(AuPEt$_3$)$_2$],[16] reported by Adams *et al*. In these compounds, the AuPEt$_3$ unit is found in a face-capping mode (to the basal Ru$_3$ triangle in the first cluster and to the two opposite PtRu$_2$ faces in the second), while in our case both of the AuPPh$_3$ units are in an edge-bridging mode.

These results obtained with Au(PPh$_3$)Cl show that the anion [PtRu$_5$C(CO)$_{15}$]$^{2-}$ readily adds cationic monometallic fragments in order to form stable, neutral, mixed-metal clusters of higher nuclearity. In order to test this further reactions of **1** with Pt(II) dichloro complexes were investigated.
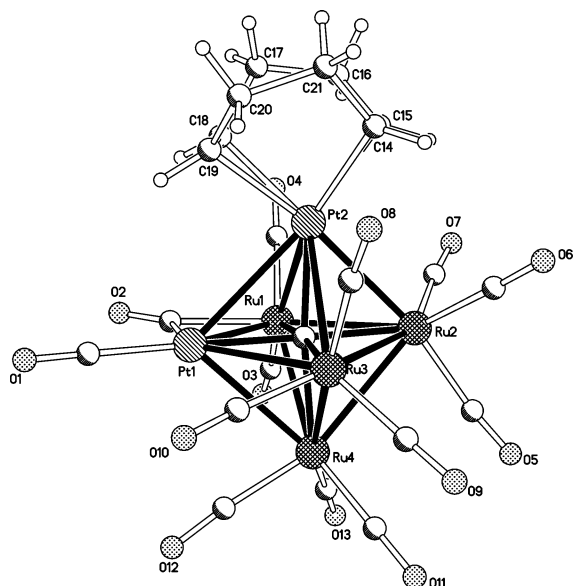
Reactions with mononuclear Pt compounds

The initial aim of the reduction of [PtRu$_5$C(CO)$_{16}$] was to obtain the negatively charged species which could then readily be deposited inside the channels of mesoporous silica for use as precursors for catalysts.[1] An additional aim was to introduce another Pt-containing unit, following a similar strategy to that described previously,[2] in order to obtain compounds with higher Pt to Ru ratio. Reactions were carried out between [PtRu$_5$C(CO)$_{15}$]$^{2-}$ and [Pt(L$_2$)Cl$_2$] complexes where L$_2$ = (COD) and (PPh$_3$)(CO). Both reactions were conducted in the presence of silica and were completed within half an hour after addition of the silica to a dichloromethane solution of the starting material. Several products were isolated in each case, in contrast to the reactions involving [Ru$_5$C(CO)$_{14}$]$^{2-}$ or [Ru$_6$C(CO)$_{16}$]$^{2-}$ under similar conditions.[2] This significant change in reactivity of the dianion [PtRu$_5$C(CO)$_{15}$]$^{2-}$ compared to the ruthenium homometallic clusters must be attributed to substitution of one of the ruthenium atoms for platinum.

In a typical experiment [Ph$_4$P]$_2$[PtRu$_5$C(CO)$_{15}$] **1** was reacted with a small excess of [Pt(COD)Cl$_2$] in dichloromethane in the presence of silica. After work-up by TLC three products were isolated. The red compound (top band) was identified as [Pt$_2$Ru$_4$C(CO)$_{13}$(COD)] **3**, on the basis of its mass spectrum, acquired by electrospray ionisation technique run in negative mode in the presence of sodium methoxide.[9,10] This displayed a high intensity peak at *m/z* = 1311 calculated for [M + MeO]$^-$, followed by a peak at *m/z* = 1280 attributed to the loss of MeO group. Unfortunately, the low yield in which compound **3** was obtained precluded its full characterisation.

The compound [Pt$_2$Ru$_4$C(CO)$_{13}$(COD)] **3** crystallises in the monoclinic space group *P*2$_1$/*c*. The molecular structure of **3** is shown in Fig. 3 and selected bond parameters are listed in Table 3. The compound **3** consists of an octahedron of Pt$_2$Ru$_4$C, twelve terminal carbonyl ligands and one CO μ-bridging the Pt1–Ru1 edge. As a consequence, this bond is significantly shorter (2.7942(6) Å) than the others (2.9173(6) Å for Pt1–Ru3

Table 3 Selected bond distances (Å) and angles (°) for $[Pt_2Ru_4C(CO)_{13}(COD)]$ **3**

Pt(1)–Pt(2)	2.9950(3)	Pt(2)–C(14)	2.186(5)
Pt(1)–Ru(1)	2.7942(6)	Pt(2)–C(15)	2.191(6)
Pt(1)–Ru(3)	2.9173(6)	Pt(2)–C(18)	2.245(7)
Pt(1)–Ru(4)	2.9882(6)	Pt(2)–C(19)	2.271(7)
Pt(2)–Ru(1)	2.9244(6)	C(14)–C(15)	1.389(9)
Pt(2)–Ru(2)	2.7511(6)	C(18)–C(19)	1.354(9)
Pt(2)–Ru(3)	3.0363(6)	Pt(1)–C(0)	2.037(6)
Ru(1)–Ru(2)	2.9504(7)	Pt(2)–C(0)	2.045(6)
Ru(1)–Ru(4)	2.8903(8)	Ru(1)–C(0)	2.045(6)
Ru(2)–Ru(3)	2.8929(7)	Ru(2)–C(0)	2.028(6)
Ru(2)–Ru(4)	2.8780(6)	Ru(3)–C(0)	2.060(6)
Ru(3)–Ru(4)	2.8224(8)	Ru(4)–C(0)	2.104(6)
Pt(2)–C(0)–Ru(4)	173.2(3)	Ru(1)–C(0)–Ru(3)	172.9(3)

Table 4 Selected bond distances (Å) and angles (°) for $[Ph_4P]_2[Pt_3Ru_{10}-C_2(CO)_{32}]$ **4**.

Pt(1)–Pt(2)	2.7807(2)	Pt(1)–C(1)	1.902(7)
Pt(1)–Ru(1)	3.0073(5)	Pt(2)–C(2)	1.864(7)
Pt(2)–Ru(1)	3.0741(5)	Pt(2)–C(0)	2.012(5)
Pt(2)–Ru(2)	2.9557(5)	Ru(1)–C(0)	2.069(6)
Pt(2)–Ru(3)	2.8159(5)	Ru(2)–C(0)	2.045(5)
Pt(2)–Ru(4)	2.9208(5)	Ru(3)–C(0)	2.086(6)
Ru(1)–Ru(2)	2.9733(7)	Ru(4)–C(0)	2.046(5)
Ru(1)–Ru(4)	2.9533(6)	Ru(5)–C(0)	2.086(5)
Ru(1)–Ru(5)	2.8554(6)		
Ru(2)–Ru(3)	2.8482(6)	Ru(1)–Pt(1)–Pt(2)	64.021(10)
Ru(2)–Ru(5)	2.8424(7)	Ru(1A)–Pt(1)–Pt(2)	115.979(10)
Ru(3)–Ru(4)	2.8727(7)	Ru(2)–C(0)–Ru(4)	172.4(3)
Ru(3)–Ru(5)	2.9145(7)		
Ru(4)–Ru(5)	2.8467(6)		

Symmetry operator A: $-x, -y, -z$.

Fig. 3 Molecular structure of $[Pt_2Ru_4C(CO)_{13}(COD)]$ **3**.

and 2.9882(6) Å for Pt1–Ru4). The Pt2–Ru bonds also vary over a wide range, *i.e.* between 2.7511(6) Å (for Pt2–Ru2) and 3.0363(6) Å (for Pt2–Ru3). The Ru–Ru distances are found to be within the usual limits (2.8224(8)–2.9504(7) Å) and are similar to those found in other Pt–Ru mixed-metal cluster compounds.[2] The conformation of the cyclooctadiene ligand is very similar to that found in other cluster compounds containing the [Pt(COD)] unit, and in particular in $[PtRu_5C(CO)_{14}(COD)]$.[2]

The formation of **3** occurred as a result of the substitution of one $[Ru(CO)_2]$ unit for a [Pt(COD)] unit. Such a substitution seems to be preferable over the addition of one or more platinum containing units. The other Pt_2Ru_4 mixed-metal cluster compounds known so far include $[Pt_2Ru_4(CO)_{18}]$ with an open metal framework,[17,18] $[Pt_2Ru_4(CO)_{11}(COD)_2(\mu_3\text{-}H)_2]$ which consists of a bicapped tetrahedron of Ru atoms,[19] and $[Pt_2Ru_4(CO)_{14}-(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)(\mu_4\text{-}\eta^2\text{-}PhC_2Ph)]$.[20] To the best of our knowledge compound **3** is the first example of a Pt_2Ru_4 carbido carbonyl cluster. It has a total of 86 electrons, consistent with the number predicted by PSEPT rules for a *closo* octahedral geometry.

The second brown product isolated from the reaction mixture in very low yield was identified as $[PtRu_5C(CO)_{14}(COD)]$ on the basis of its IR spectrum.[2] In this case a simple ligand substitution of one CO for COD occurred. The main product of the reaction was isolated from the bottom of the TLC plate and had a characteristic violet colour. Its IR spectrum consisted of peaks at 2038, 2024, 1997, 1953 and 1800 cm^{-1} and the mass spectrum, obtained using electrospray ionisation technique run in negative mode, displayed a high intensity peak at $m/z = 1257.5$ corresponding to the formulation $[Pt_3Ru_{10}C_2(CO)_{32}]^{2-}$, which alternatively can be presented as $[\{PtRu_5C(CO)_{15}\}_2\text{-}Pt(CO)_2]^{2-}$. On the basis of this formula, the structure of this

compound may be envisaged as two $PtRu_5C$ octahedra joined by a Pt atom (Fig. 4). The total electron count for this dianion is 184e, which suggests two $PtRu_5$ octahedra joined by a Pt atom in an 'edge-bridging' coordination with one broken metal–metal bond accounting for the excess of two electrons. Although a complete rearrangement of the metal core, similar to that observed for $[Pt_2Ru_{10}C_2(CO)_{28}]^{2-}$,[21] can also not be ruled out, the number of carbonyl ligands present indicates a more open structure, as the condensed metal core would require a smaller number of CO ligands to be stabilised. Compound **4** was also characterised by energy-dependent electrospray ionisation mass-spectrometry (EDESI-MS), and was shown to fragment under experimental conditions, which was followed by sequential loss of carbonyl ligands.[22]
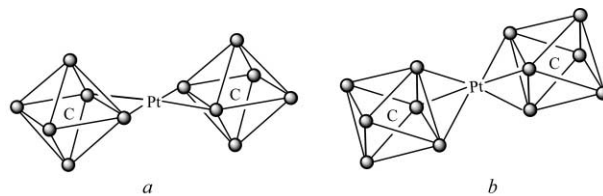
Fig. 4 Two possible metal core arrangements for $[Pt_3Ru_{10}C_2(CO)_{32}]^{2-}$.

The compound $[Ph_4P]_2[Pt_3Ru_{10}C_2(CO)_{32}]$ **4** crystallises in the triclinic space group $P\bar{1}$. The asymmetric unit contains half of a molecule with the Pt1 atom positioned on the centre of inversion. The molecular structure of the anion of **4** is shown in Fig. 5 and selected bond parameters are listed in Table 4. As expected, the anion $[Pt_3Ru_{10}C_2(CO)_{32}]^{2-}$ consists of two $PtRu_5$ octahedra joined by a Pt atom, which is bridging the Pt–Ru edge of each octahedron. The central Pt1 atom is also coordinated by two carbonyl ligands and overall is six-coordinated, indicating an 18-electron Pt-centre. All of the metal–metal bond distances are within the usual limits and vary between 2.8159(5) and 3.0741(5) Å for Pt–Ru bonds and between 2.9733(7) and 2.8424(7) Å for Ru–Ru bonds. No
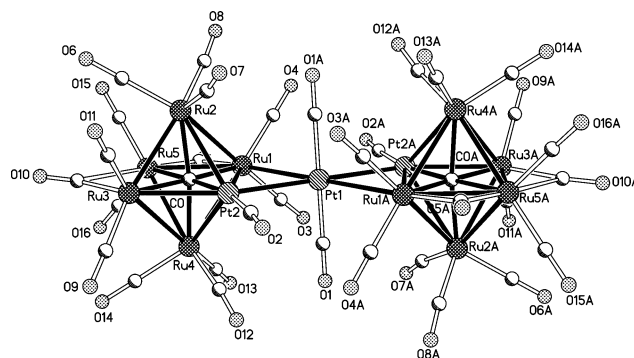

Fig. 5 Molecular structure of the anion $[Pt_3Ru_{10}C_2(CO)_{32}]^{2-}$ of **4**.

Table 5 Selected bond distances (Å) and angles (°) for $[Pt_4Ru_5C(CO)_{16}(PPh_3)_3]$ **5**

|	Molecule 1	Molecule 2		Molecule 1	Molecule 2
Pt(1)–Pt(2)	2.7333(5)	2.7386(5)	Ru(1)–Ru(2)	2.8353(10)	2.8470(11)
Pt(2)–Pt(3)	2.7375(5)	2.7578(5)	Ru(1)–Ru(4)	3.0044(11)	3.0071(11)
Pt(3)–Pt(4)	2.7949(5)	2.7992(5)	Ru(1)–Ru(5)	2.7798(9)	2.7961(10)
Pt(4)–Pt(1)	2.7448(5)	2.7394(5)	Ru(2)–Ru(3)	2.8317(10)	2.8333(10)
Pt(1)–Ru(1)	2.7480(7)	2.7830(9)	Ru(2)–Ru(5)	2.8916(9)	2.8797(11)
Pt(1)–Ru(2)	2.8381(7)	2.8428(7)	Ru(3)–Ru(4)	2.9509(10)	2.9308(11)
Pt(2)–Ru(2)	2.9159(7)	2.8719(9)	Ru(3)–Ru(5)	2.8145(11)	2.8117(10)
Pt(3)–Ru(2)	2.7703(8)	2.7862(8)	Ru(4)–Ru(5)	2.8639(12)	2.8905(10)
Pt(3)–Ru(3)	2.8925(7)	2.8329(9)	Pt(1)–P(1)	2.268(2)	2.270(2)
Pt(4)–Ru(2)	3.0492(9)	3.0329(7)	Pt(2)–P(2)	2.292(2)	2.293(3)
Pt(4)–Ru(3)	2.9443(8)	2.9441(7)	Pt(3)–P(3)	2.271(2)	2.283(2)
Pt(4)–Ru(4)	2.7919(7)	2.7908(9)			
Pt(4)–Pt(1)–Pt(2)	91.639(14)	90.839(15)	Pt(4)–Pt(1)–Ru(1)	73.80(2)	72.62(2)
Pt(1)–Pt(2)–Pt(3)	89.046(14)	89.937(16)	Pt(1)–Pt(4)–Ru(4)	111.14(2)	112.85(2)
Pt(2)–Pt(3)–Pt(4)	90.479(14)	89.195(15)	Pt(4)–Ru(4)–Ru(1)	69.25(2)	68.54(3)
Pt(3)–Pt(4)–Pt(1)	87.647(14)	89.062(15)	Pt(1)–Ru(1)–Ru(4)	105.01(3)	105.38(3)
Pt(4)–C(0)–Ru(1)	104.8(3)	104.8(4)	Ru(1)–C(0)–Ru(3)	165.1(5)	165.4(4)
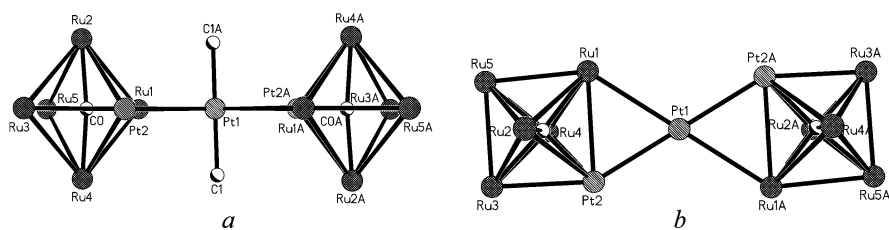
Fig. 6 Metal core of the anion $[Pt_3Ru_{10}C_2(CO)_{32}]^{2-}$: side (a) and top view (b).

metal–metal bond is particularly elongated, which suggests that cluster **4** is in fact electron rich (two electrons in excess of the PSEPT rules). This is unusual for Pt-containing clusters which usually tend to be electron deficient.[23] The Pt2–Ru1 bond is the longest, since it accommodates a Pt1 bridge. The interstitial carbon atoms are positioned in the centres of the two PtRu$_5$ octahedra and are slightly shifted towards the Pt2–Ru1 edge, *i.e.* the linking Pt atom. Four carbonyls bridge 'equatorial' Ru–Ru edges (two in each octahedron) and the remaining 32 are terminal. Fig. 6 shows side and top views of the metal core of compound **4**. All 'equatorial' metal atoms are essentially planar. The atoms Ru3, Ru5 and C0 deviate from the plane defined by the Pt1, Pt2 and Ru1 atoms only by −0.035, −0.011 and −0.016 Å, respectively.

In the absence of silica in the reaction mixture, the rate of reaction was reduced significantly. Even with double excess of [Pt(COD)Cl$_2$], a week was required for completion, yielding a mixture of products, all in very low yield. The same reaction of [PtRu$_5$C(CO)$_{15}$]$^{2-}$ with [Pt(COD)Cl$_2$] using AgBF$_4$ as a chloride scavenger gave one main product, which was readily identified as [Ph$_4$P]$_2$[Pt$_2$Ru$_{10}$C$_2$(CO)$_{28}$],[21] and also required more than two equivalents of Pt(II) complex to finish the reaction. Clearly, the presence of silica is crucial for the synthesis of both [Pt$_2$Ru$_4$-C(CO)$_{13}$(COD)] **3** and [Ph$_4$P]$_2$[Pt$_3$Ru$_{10}$C$_2$(CO)$_{32}$] **4**.

The anion [PtRu$_5$C(CO)$_{15}$]$^{2-}$ was then reacted with an excess of *cis*-[Pt(CO)(PPh$_3$)Cl$_2$] in the presence of silica. After separation by TLC five products in very poor yields were isolated. One of the products identified as [Pt$_4$Ru$_5$C(CO)$_{16}$(PPh$_3$)$_3$] **5** was formed as a result of the addition of not one but three Pt containing units. The first was added as a result of the addition of [PtRu$_5$C(CO)$_{15}$]$^{2-}$ and [Pt(CO)(PPh$_3$)]$^{2+}$ species. The second and third Pt-units were added by carbonyl substitution to give a total of 16 CO ligands.

Compound [Pt$_4$Ru$_5$C(CO)$_{16}$(PPh$_3$)$_3$] **5** crystallises in the triclinic space group $P\bar{1}$ with two independent molecules in an asymmetric unit. The molecular structure of **5** is presented in Fig. 7 and selected bond parameters are listed in Table 5. The metal core of **5** consists of an almost intact PtRu$_5$ octahedron,
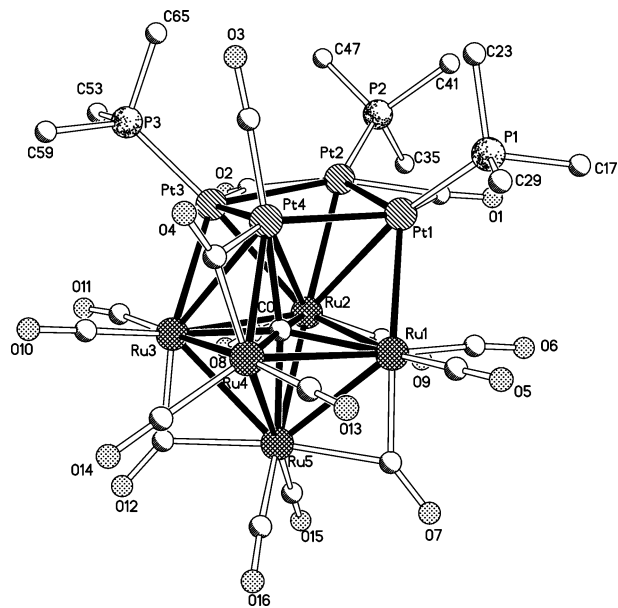
Fig. 7 Molecular structure of $[Pt_4Ru_5C(CO)_{16}(PPh_3)_3]$ **5**.

with the three remaining Pt atoms and the unique Pt atom forming a square, which serves as a base for a Pt$_4$Ru square-based pyramid. Such an arrangement has not been found in any other mixed-metal cluster and is most likely the result of the high affinity between Pt atoms, since the formation of both polynuclear clusters of group 10 metals and mixed-metal clusters containing 'segregated' units are very common.[23] Although there are numerous examples of square planar Pt$_4$ homonuclear complexes, it is more common for this metal to adopt a triangular motif,[24] and especially in mixed-metal clusters.[23] The interaction between the Pt4 and Ru1 atoms may be considered to be non-bonding since the Pt4–Ru1 distances in both molecules are much longer (3.2983(8) Å in molecule 1 and 3.2703(8) Å in molecule 2) than the longest known Pt–Ru bond, reported

for $[PtRu_5C(CO)_{11}(\eta^2\text{-dppe})(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_{60})]$,[25] (3.1478(6) Å). The other Pt4–Ru bonds remained unchanged in comparison with those in the starting compound $[Ph_4P]_2[PtRu_5C(CO)_{15}]$ **1**. The Pt4–Ru4 edge (2.7919(7) Å in molecule 1, 2.7908(9) Å in molecule 2 and 2.8016(5) Å in $[Ru_5PtC(CO)_{15}]^{2-}$ **1**) is bridged by a CO ligand and as a result is shorter than the others, which vary between 2.9441(7) and 3.0492(9) Å in **5** compared to 2.9385(5)–2.9555(4) Å in **1**. All other Pt–Ru distances in compound **5** span the range of 2.7480(7)–2.9159(7) Å (in molecule 1) and 2.7830(9)–2.8719(9) Å (in molecule 2). The Pt–Pt bond lengths are very closely distributed with the two edges bridged by CO being only slightly shorter. Two of the Ru–Ru bonds are also spanned by bridging CO ligands, which induced their shortening. Overall the Ru–Ru bond lengths remained largely unchanged compared with **1**. All three phosphine ligands are coordinated to the platinum atoms, eleven carbonyl ligands are terminal and the remaining five are bridging two Pt–Pt, one Pt–Ru and two Ru–Ru edges, as already mentioned. The interstitial carbon atom is somewhat shifted towards the Pt_4 square.

The total electron count for $[Pt_4Ru_5C(CO)_{16}(PPh_3)_3]$ **5** is equal to 122 electrons, which would lead to the prediction of a tricapped octahedral metal core. The metal core of **5** is different, but it is difficult to assign an electron count for such structural arrangement unambiguously. It is probable, however, that formation of this cluster occurs as suggested in Scheme 1. The first $Pt(CO)(PPh_3)$ unit caps a $PtRu_2$ face of the $PtRu_5$ octahedron. The second Pt-containing unit then caps an adjacent $PtRu_2$ face, forming one of the three possible isomers of the bicapped octahedron, and the third Pt-unit caps the newly available face formed by the Pt1, Pt3 and Ru2 atoms, facilitated by breakage of one Pt–Ru bond. A similar explanation was given for the formation of $[(CH_3CN)_2Cu_2Ru_6C(CO)_{16}]$,[26] in which the first Cu atom caps a Ru_3 face and the second Cu caps a newly formed $CuRu_2$ face.
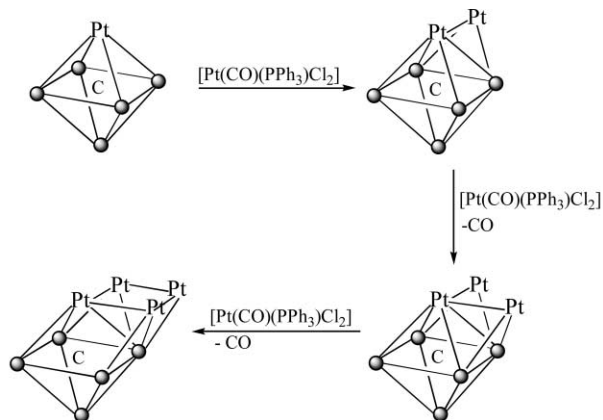
Scheme 1 Possible route of formation of $[Pt_4Ru_5C(CO)_{16}(PPh_3)_3]$ **4** (ligands are omitted for clarity).

Two new compounds were identified as $[PtRu_4C(CO)_{13}(PPh_3)]$ **6** and $[Pt_2Ru_4C(CO)_{14}(PPh_3)]$ **7** on the basis of their mass spectra acquired in the negative mode in the presence of sodium methoxide. Thus, a high intensity peak at $m/z = 1269$ has been observed in the mass spectrum of **6**, corresponding to $[M + MeO]^-$ and followed by the peaks attributed to the sequential loss of the phosphine and carbonyl ligands. Preliminary single-crystal X-ray data confirmed the identity of this product and showed the metal core of the cluster to consist of a $PtRu_4C$ square-based pyramid with a phosphine ligand linked to the Pt atom. The mass spectrum of **7** displayed a high intensity peak at $m/z = 1492$ (attributed to $[M + MeO]^-$), also followed by the peaks attributed to the stepwise loss of the phosphine and carbonyl ligands. The formation of this compound is not surprising as a similar compound has been isolated from the related reaction of **1** with $[Pt(COD)Cl_2]$. Therefore, one might expect the structure of compound **7** to

resemble that of **3**. Unfortunately, the very low yields in which these compounds have been isolated precluded their full characterisation. Two other products were identified as $[Ph_4P]_2$-$[Pt_3Ru_{10}C_2(CO)_{32}]$ **4** and $[Ph_4P]_2[Pt_2Ru_{10}C_2(CO)_{28}]$.

Finally, $[PtRu_5C(CO)_{15}]^{2-}$ was reacted with $[Pt(PPh_3)_2Cl_2]$ and $[Pt(CO)_2Cl_2]$ in dichloromethane. In the first case, the reaction was completed within 0.5 h. However it was impossible to isolate any products due to decomposition of the reaction mixture on silica. Any attempts to separate the products by precipitation were also unsuccessful. In the second reaction, no silica was added, and no peaks attributable to the starting materials were detected by IR spectroscopy just after the mixing of components. After usual work-up by thin layer chromatography, the main product isolated was identified as $[Ph_4P]_2$-$[Pt_3Ru_{10}C_2(CO)_{32}]$ **4** on the basis of the IR and mass spectra.

Conclusions

We have shown that the mixed-metal cluster $[PtRu_5C(CO)_{16}]$ may be readily reduced to the dianion $[PtRu_5C(CO)_{15}]^{2-}$ in a procedure similar to that of penta- or hexa-ruthenium carbido carbonyls. Reactions involving the addition of various cationic mononuclear fragments to the anion $[PtRu_5C(CO)_{15}]^{2-}$ were investigated, and $Au(PPh_3)Cl$ was shown to react selectively to produce $[PtRu_5C(CO)_{15}(AuPPh_3)_2]$ **2**. On the other hand, in reactions involving Pt(II) complexes, using a method which with Ru-only anionic clusters allowed great selectivity, the products were less predictable. Nevertheless, they are of interest because of their unusual metal core geometries and Ru to Pt ratios. We have established that there is considerable scope for the use of the obtained Pt–Ru clusters as precursors for nanocatalysts, and studies in that direction are under way.

Experimental

All the reactions were carried out using standard Schlenk techniques, under water- and oxygen-free nitrogen. All solvents were dried and distilled immediately before use. Reactants and chemicals were purchased from Aldrich Chemicals and used without further purification. The silica used in reaction media (Silica gel 60 (0.040–0.063 mm) for column chromatography) was purchased from Merck. The compounds $[PtRu_5C(CO)_{16}]$[3] and cis-$[Pt(CO)(PPh_3)Cl_2]$,[27] were synthesised following literature procedures.

All chromatographic separations were performed on the open bench without any precaution to exclude air. Thin-layer chromatography (TLC) was carried out using glass plates (20 × 20 cm) coated with a layer of silica gel 60 F_{254}, supplied by Merck. The eluents used were standard grade laboratory solvents.

Infrared spectra were collected in dichloromethane solution, using a NaCl liquid cell (0.5 mm path length) supplied by Specac Ltd., on a Perkin Elmer Paragon 1000 FT-IR spectrometer. The mass spectra were obtained on a Micromass Quattro-LC spectrometer using electrospray ionisation technique (ESI) in negative mode. The ^{13}C-, ^{31}P- and ^1H-NMR spectra were recorded on a Bruker DPX-400 instrument. The elemental analyses were performed in the microanalysis service of the department.

Crystallography

Single-crystal X-ray diffraction analyses were performed on a Nonius Kappa CCD system with a sealed-tube Mo-Kα source, and an open-flow N_2 cryostream. The structures were solved by direct methods using the SIR-92[28] or SHELXS-97[29] programs, and refined by full-matrix least-squares on F^2 using SHELXL-97[30] program. All non-hydrogen atoms in compounds **1**–**5**, apart from those of the solvent molecules and disordered groups, were refined with anisotropic atomic displacement parameters.

Table 6 Crystallographic data for compounds **1**–**5**

	1	**2**	**3**	**4**	**5**
Chemical formula	$C_{64}H_{40}O_{15}P_2PtRu_5$	$C_{52}H_{30}Au_2O_{15}P_2PtRu_5$	$C_{22}H_{12}O_{13}Pt_2Ru_4$	$C_{82}H_{40}O_{32}P_2Pt_3Ru_{10}\cdot$ $(C_2H_5)_2O$	$C_{71}H_{45}O_{16}P_3Pt_4Ru_5\cdot$ $0.75CH_2Cl_2$
M	1811.34	2051.07	1278.78	3269.17	2596.38
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/n$	$C2/c$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a/Å	19.9966(5)	32.9658(7)	9.5081(2)	9.6330(3)	13.2537(1)
b/Å	15.2038(3)	12.5706(2)	18.9662(8)	14.7529(4)	13.9213(2)
c/Å	22.1662(6)	30.1546(6)	15.9045(6)	16.9993(5)	44.3366(6)
α/°	90	90	90	76.962(2)	83.243(1)
β/°	112.918(1)	115.229(1)	98.153(2)	77.017(2)	85.780(1)
γ/°	90	90	90	89.506(2)	64.436(1)
V/Å³	6207.1(3)	11304.1(4)	2839.1(2)	2291.15(12)	7326.02(15)
Z	4	8	4	1	4
μ(Mo-Kα)/mm^{-1}	3.549	9.053	11.953	6.273	8.792
D_c/g cm^{-3}	1.938	2.410	2.992	2.369	2.354
Total data	38581	32417	21474	26963	48263
Unique data	14069	12771	6461	10326	21911
R_{int}	0.0635	0.1088	0.0674	0.0529	0.0534
$R1\ [I > 2\sigma(I)]$	0.0412	0.0779	0.0334	0.0357	0.0392
$wR2$ (all data)	0.0899	0.2088	0.0661	0.0823	0.0821
S	1.01	1.01	0.98	1.04	1.04

Data in common: $\lambda = 0.7107$ Å, $T = 180(1)$ K.

All hydrogen atoms were placed in geometric positions and allowed to ride on the parent carbons. The crystal data for **1**–**5** is summarised in Table 6.

CCDC reference numbers 206579–206583.

See http://www.rsc.org/suppdata/dt/b3/b303178k/ for crystallographic data in CIF or other electronic format.

Syntheses

Preparation of [Ph₄P]₂[PtRu₅C(CO)₁₅] 1. To a solution of [PtRu₅C(CO)₁₆] (200 mg, 0.17 mmol) in methanol an excess of KOH (500 mg) was added. The solution was stirred for 2 h at room temperature, followed by an addition of an excess of Ph₄PCl (160 mg, 0.43 mmol) to yield **1** as a dark red microcrystalline powder. The solid was filtered off and washed with hexane. Yield: 268 mg (0.15 mmol, 87%). Found: C, 40.62; H, 2.27; P, 3.42. $C_{64}H_{40}O_{15}P_2PtRu_5$ requires C, 42.44; H, 2.23; P, 3.42%; ν_{max}/cm^{-1} (CO) 2049w, 2033w, 1975s (br), 1939w (br), 1821w (br), 1769w (br); δ_H (300 K, CD₂Cl₂) 7.92–7.60 (m, 40H, P(C₆H₅)₄); δ_C (300 K, CD₂Cl₂) 201.0 (m, CO), 136.0–117.37 (m, 48C, C₆H₅); ESI-MS (−ve): m/z 566 [M²⁻/2]. Crystals suitable for X-ray structure determination were grown by slow diffusion of ethanol into a dichloromethane solution of **1**.

Preparation of [PtRu₅C(CO)₁₅(AuPPh₃)₂] 2. To a solution of [Ph₄P]₂[PtRu₅C(CO)₁₄] **1** (50 mg, 0.028 mmol) in CH₂Cl₂ (15 ml) a solution of [Au(PPh₃)Cl] (35 mg, 0.069 mmol) and TlPF₆ (25 mg, 0.069 mmol) in a mixture of CH₂Cl₂ and acetone, 5 : 1 v/v) was added. After stirring for 30 min at room temperature, the mixture was filtered and the solvent evaporated to dryness *in vacuo*. The crude product was dissolved in a minimum amount of acetone and purified by TLC (acetone–hexane, 1 : 1). The top bright-red band was identified as **5** (38 mg, 0.019 mmol, 67%). Found: C, 30.18; H, 1.41; P, 2.83. $C_{52}H_{30}Au_2P_2$-$PtRu_5$ requires C, 30.45; H, 1.47; P, 3.02%; ν_{max}/cm^{-1} (CO) 2069m, 2038s, 2015vs, 1968m, 1859m and 1833m; δ_H (300 K, CD₂Cl₂) 7.6–7.4 (m, 30H, P(C₆H₅)₃); δ_P (300 K, CD₂Cl₂) 69.6 (t, P(C₆H₅)₃, ²J(Pt–Au–P) 411 Hz); δ_C (300 K, CD₂Cl₂) 134.2–128.5 (m, 36C, C₆H₅); ESI-MS (−ve): m/z 2082 [M + MeO]⁻, EI-MS: m/z 2053 [M]. Crystals suitable for X-ray structure determination were grown by slow diffusion of hexane into a dichloromethane solution of **2**.

Preparation of [Pt₂Ru₄C(CO)₁₃(COD)] 3 and [Ph₄P]₂-[Pt₃Ru₁₀C₂(CO)₃₂] 4. To a solution of [Ph₄P]₂[PtRu₅C(CO)₁₅] **1** (60 mg, 0.03 mmol) in CH₂Cl₂ (15 ml) one equivalent of [Pt(COD)Cl₂] (11 mg, 0.03 mmol) and silica (approx. 0.5 g) were added. The mixture was stirred for 0.5 h at room temperature. Subsequently, the mixture was separated by thin layer chromatography using CH₂Cl₂–hexane (4 : 6, v/v) as eluent. The top brick-red compound was identified as **3** (3 mg, 0.002 mmol, 7.8% yield) and the bottom violet compound as **4** (7 mg, 0.002 mmol, 6.7%).

Analysis for **3**: ν_{max}/cm^{-1} (CO) 2076m, 2030s, 1995m and 1859m (br); ESI-MS: m/z 1311 [M + MeO]⁻, 1280 [M + H]⁻. Unfortunately, the low yield in which compound **3** was isolated precluded its full characterisation. Crystals suitable for X-ray structure determination were grown by slow evaporation of CH₂Cl₂–hexane solution of **3** at room temperature.

Analysis for **4**: Found: C, 30.44; H, 1.26; P, 1.86. $C_{82}H_{40}$-$O_{32}P_2Pt_3Ru_{10}$ requires C, 30.83; H, 1.26; P, 1.94%; ν_{max}/cm^{-1} (CO) 2038vs, 2024s, 1997m, 1953w (sh) and 1800m (br); ESI-MS: m/z 1257.5 [M²⁻/2]. Crystals suitable for X-ray structure determination were grown by slow diffusion of diethyl ether into a dichloromethane solution of **4**.

Preparation of [Pt₄Ru₅C(CO)₁₆(PPh₃)₃] 5, [PtRu₄C(CO)₁₃-(PPh₃)] 6 and [Pt₂Ru₄C(CO)₁₄(PPh₃)] 7. To a solution of [PPh₄]₂[PtRu₅C(CO)₁₅] **1** (75 mg, 0.042 mmol) in CH₂Cl₂ (20 ml) an excess of [Pt(CO)(PPh₃)Cl₂] (50 mg, 0.09 mmol) and silica (approx. 750 mg) were added. The mixture was stirred for 0.5 h at room temperature. In the next step, the silica was filtered off and the mixture purified by TLC using a mixture of CH₂Cl₂–hexane (4 : 6, v/v) as eluent. This yielded brown **5** (2 mg, 0.7 × 10⁻³ mmol, 1.9% yield), red [PtRu₄C(CO)₁₃(PPh₃)] **6** (1 mg, 0.8 × 10⁻³ mmol, 1.9% yield) and brown [Pt₂Ru₄C(CO)₁₄-(PPh₃)] **7** (4 mg, 0.003 mmol, 6.5% yield).

Analysis for **5**: Found: C, 33.97; H, 1.98; P, 3.41. $C_{71}H_{46}$-$O_{16}P_3Pt_4Ru_5$ requires C, 33.67; H, 1.79; P, 3.67%; ν_{max}/cm^{-1} (CO) 2055m, 2016s, 1990m (sh), 1835m and 1799m (br); ESI-MS: m/z 2563 [M + MeO]⁻, 2532 [M + H]⁻. Crystals suitable for X-ray determination were grown by slow diffusion of ethanol into a dichloromethane solution of **5**.

Analysis for **6**: ν_{max}/cm^{-1} (CO) 2083w, 2048s, 2027m, 2016m and 1975w; ESI-MS: m/z 1269 [M + MeO]⁻, 1241 [M + MeO − CO]⁻.

Analysis for **7**: ν_{max}/cm^{-1} (CO) 2082w, 2038s, 1993w, 1977w and 1868 (br); ESI-MS: m/z 1492 [M + MeO]⁻.

Reaction of [Ph₄P]₂[PtRu₅C(CO)₁₅] with [Pt(CO)₂Cl₂]. To a solution of [Ph₄P]₂[PtRu₅C(CO)₁₅] **1** (60 mg, 0.03 mmol) in

CH$_2$Cl$_2$ (15 ml) one equivalent of [Pt(CO)$_2$Cl$_2$] (10 mg, 0.03 mmol) was added. The mixture was stirred for 0.5 h at room temperature. Subsequently, the mixture was separated by thin layer chromatography using CH$_2$Cl$_2$–acetone–hexane (4 :1 : 5, v/v) as eluent. The violet compound was identified as **4** (10 mg, 0.003 mmol, 10%).

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