Synthesis and structural characterisation of tetranuclear palladium–cobalt clusters †

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The reactions between the palladium compounds $[Pd_4(\mu_3\text{-}CH)(\mu\text{-}Cl)_3(PBu^t{}_3)_4]$ or $[Pd_2(\mu\text{-}X)_2(PBu^t{}_3)_2]$ (X = Br or I) and $[Co_2(CO)_8]$ have led to the novel palladium–cobalt tetranuclear compounds $[CoPd_3(\mu_3\text{-}X)(\mu\text{-}CO)_3(\mu_3\text{-}CO)(CO)(PBu^t{}_3)_3]$ (X = Cl, Br or I). Structural characterisation of one of them (X = Cl) has shown that the metal cluster geometry is intermediate between a tetrahedron and a butterfly. A second product detected in this reaction {and additionally with $[Fe_2(CO)_9]$ and $[Pd_2(\mu\text{-}Br)_2(PBu^t{}_3)_2]$} is also reported and has been structurally characterised as $[Pd_6(\mu\text{-}Br)_4(\mu\text{-}CO)_4(PBu^t{}_3)_4]$ (when X = Br). This hexanuclear cluster has triangular cluster moieties linked by double bromide bridges.

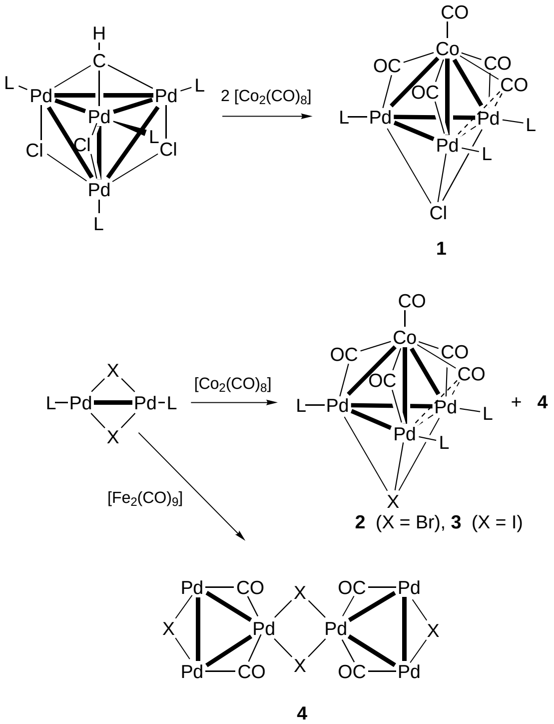
Heterometallic cluster compounds have received considerable attention, in part because they represent a synthetic challenge but more importantly because of their potential in novel catalytic and stoichiometric reactions.[1] The different possible reactivities of the constituent metals and the possible co-operation between the metal centres make multimetallic systems unique.[2]

The substitution of metal–halogen bonds by fragments such as $[Co(CO)_4]^-$ {generated by reacting $[Co_2(CO)_8]$ with Na–Hg} is a well established reaction for obtaining new heterometallic compounds.[3] This synthetic approach was used by Dehand and Pfeffer[4] in 1976 to prepare the first stable dimetallic species containing a Pd–Co bond. Subsequently other Pd–Co cluster compounds have been reported by Le Borgne *et al.*,[5] Pfeffer *et al.*[6] and Braunstein *et al.*[7] More recently, Hidai and coworkers[8] have reported the synthesis of a Pd–Co compound which models an intermediate in the catalytic carbonylation of aryl iodides.

These precedents encouraged us to study the reactions of the recently reported compounds $[Pd_4(\mu_3\text{-}CH)(\mu\text{-}Cl)_3(PBu^t{}_3)_4]$[9] and $[Pd_2(\mu\text{-}X)_2(PBu^t{}_3)_2]$[10] (X = Br or I) with $[Co_2(CO)_8]$ and with $[Fe_2(CO)_9]$. In this paper the synthesis and structural characterisation of the novel heterometallic clusters $[CoPd_3(\mu_3\text{-}X)(\mu\text{-}CO)_3(\mu_3\text{-}CO)(CO)(PBu^t{}_3)_3]$ (X = Cl, Br or I) are reported. A second product in this reaction has been identified as $[Pd_6(\mu\text{-}Br)_4(\mu\text{-}CO)_4(PBu^t{}_3)_4]$ and its crystal structure has also been determined using X-ray techniques.

Results and Discussion

The tetranuclear cluster $[Pd_4(\mu_3\text{-}CH)(\mu\text{-}Cl)_3(PBu^t{}_3)_4]$ and the dimeric species $[Pd_2(\mu\text{-}X)_2(PBu^t{}_3)_2]$ (X = Br or I) have been recently synthesised and their reactivity with H_2, CO, PR_3, CNXyl (CNXyl = 2,6-dimethylphenyl isocyanide) and C_2H_2 reported.[9,10] They exhibit interesting catalytic properties especially when treated with H_2 and C_2H_2. In some of these reactions, the compounds acted as halogen–palladium–phosphine fragment donors and this encouraged us to study their reactions with metal carbonyl fragments in the hope of preparing heterometallic clusters with interesting catalytic properties. The reactions which were studied are summarised in Scheme 1.



Scheme 1 Studied reactions

Synthesis of $[CoPd_3(\mu_3\text{-}X)(\mu\text{-}CO)_3(\mu_3\text{-}CO)(CO)(PBu^t{}_3)_3]$ (X = Cl, Br or I)

When $[Pd_4(\mu_3\text{-}CH)(\mu\text{-}Cl)_3(PBu^t{}_3)_4]$ in toluene was treated with $[Co_2(CO)_8]$ for 6 h, a dark red solution and a brown precipitate were obtained. After filtration the solvent was removed under reduced pressure and the dark red solid was recrystallised from benzene–ethanol at 4 °C. The $^{31}P\text{-}\{^1H\}$ NMR spectrum of the resulting dark red crystals showed a singlet at δ 77.2. The IR spectrum of solid samples as KBr discs showed a sharp and very strong band at 2022 cm^{-1} suggesting the presence of only a single terminal carbonyl ligand. Three more bands in the carbonyl region were observed: 1844, 1830 and 1807 cm^{-1} which can be assigned to bridging CO groups. Although the IR spectrum in benzene solution shows two bands at 2028 and 1959

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† Dedicated to the memory of Sir Geoffrey Wilkinson an extraordinarily imaginative chemist and a hard act to follow.

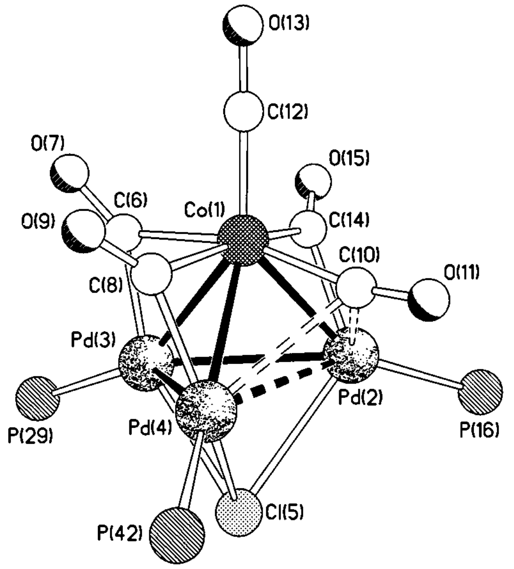
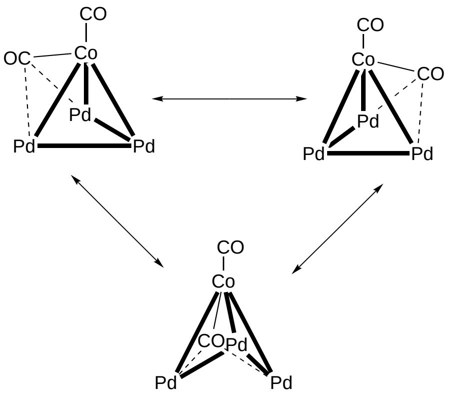


Fig. 1 Molecular structure of compound **1**. The carbon atoms of the Bu^t_3 groups of the phosphine ligands have been omitted for clarity

cm^{-1} which may be assigned to terminal and semibridging CO groups, and bands at 1847, 1822 and 1810 cm^{-1} which may be assigned to bridging COs, the strong band at 1959 cm^{-1} is not observed in CH_2Cl_2 solution. The apparent disappearance of the 1959 cm^{-1} band in the solid state and in CH_2Cl_2 is not readily explained.

The molecular structure of cluster **1** was determined by an X-ray structural analysis (Fig. 1) and showed that the compound obtained is the heterometallic palladium cluster $[CoPd_3(\mu_3\text{-}Cl)(\mu\text{-}CO)_3(\mu_3\text{-}CO)(CO)(PBu^t_3)_3]$. The metal core is formed by three palladium atoms and one cobalt atom in what may be described either as distorted tetrahedral or a butterfly type structure. The Pd–Co distances are 2.6093(8), 2.5845(7) and 2.6506(7) Å (Table 1) and lie in the range previously observed in palladium–cobalt cluster compounds.[4–8] The Pd–Pd distances are longer than those commonly observed in palladium cluster compounds [Pd(3)–Pd(4) 2.903(1), Pd(3)–Pd(2) 2.952(1) and Pd(2)–Pd(4) 3.324(8) Å]. The latter distance is appreciably longer than that usually associated with Pd–Pd bonds, but is still only 10% greater than the other Pd–Pd bonds indicating a probable weak bonding interaction. The Pd–Pd distances for palladium dimers generally lie in a range between 2.500(1) and 2.823(1) Å.[11] Therefore, the geometric description of the cluster is ambiguous and is intermediate between a regular tetrahedral and a butterfly structure. Capping the opposite side of the Pd_3 face is a Cl atom forming a secondary distorted tetrahedron with Pd–Cl distances 2.604(1), 2.538(1) and 2.740(1) Å. All three Pd–Co bonds are bridged by carbonyl ligands (explaining the IR bands at 1844, 1830 and 1807 cm^{-1}). A fourth carbonyl ligand is bonded to the Co in an axial position with a Co–C distance of 1.761(6) Å and a Co(1)–C(12)–O(13) angle of 177.8(6)°. The fifth CO group is non-linear [Co(1)–C(10)–O(11) angle is 165.9(6)°] and forms an asymmetric bridge on the Co(1)–Pd(2)–Pd(4) face. Both the Pd(4)– and Pd(2)–C(10) distances are long at 2.563(6) and 2.380(6) Å respectively and there is an accompanying lengthening of the associated Co–C(10) distance at 1.848(6) Å.

The presence of five carbonyl ligands around cobalt is unusual but not unprecedented in cases where there are several bridging CO groups.[12] The new palladium–cobalt cluster compound **1** has a polyhedral skeletal electron count of 60. According to the Polyhedral Skeletal Electron Pair Theory (PSEPT)[13] tetranuclear clusters with a tetrahedral structure should have an electron count of 60 whilst those with a butterfly structure should have a polyhedral skeletal electron count of 62. Transition-metal carbonyl clusters (*e.g.* tetracobalt clusters with butterfly structures) usually conform to the PSEPT. On the other hand, palladium and platinum do not have electron counting rules analogous to the transition-metal carbonyl clusters. For example, tetrapalladium clusters with a butterfly structure usually have 58 electrons instead of the expected 62. The electron counting rules give no indication as to why the present cluster should distort from a regular tetrahedral geometry. The capping of the putative Pd_3 triangular cluster (with three-fold symmetry) by a $Co(CO)_5$ fragment which has distorted C_{4v} symmetry may contribute to the observed distortion, especially since three of the carbonyls form conventional bridges with the palladium atoms whilst the fourth forms a semibridge over the bond which is lengthened (see above). This latter resembles an agostic type of interaction suggesting a weak CO *bridge*. This is consistent with the solution IR spectrum of **1** which shows two bands at 2028 and 1959 cm^{-1} but not with the solid-state spectrum.



Scheme 2 Hypothetical fluxional process undergone by the CO groups in compound **1**

The molecular structure shown in Fig. 1 indicates that there are two different phosphine environments in this cluster. However, at room temperature, the solution $^{31}P\text{-}\{^1H\}$ NMR spectrum showed only one singlet suggesting some fluxional process in solution. A rearrangement process involving CO mobility would make the phosphines equivalent in solution. This type of fluxionality has been extensively studied for carbonyl clusters of the Group 8 and 9 metals.[14] A plausible rearrangement process is shown in Scheme 2.

In order to study this possible fluxionality, a variable-temperature $^{31}P\text{-}\{^1H\}$ NMR study was carried out. However, even at −60 °C, only a sharp singlet was observed suggesting that this fluxional process has a very small energy barrier associated with it. In order to confirm the molecular structure for the bulk sample a solid-state ^{13}C and ^{31}P magic angle spinning NMR study was completed on solid samples of **1**. This study showed the presence of two unequivalent phosphine environments. Two signals in the ^{31}P NMR at δ 77.7 and 74.1 in a ratio 1:2 were observed. Unfortunately in the ^{13}C NMR spectrum the signals for the three different types of CO groups could not be differentiated. A small broad signal was observed at δ 215. These results therefore provide circumstantial evidence for a fluxional process in solution but do not provide sufficient information for a more detailed mechanistic analysis to be made.

Similar products to **1** were obtained on treating $[Pd_2(\mu\text{-}X)_2(PBu^t_3)_2]$ (X = Br or I) in toluene with 1 equivalent of $[Co_2(CO)_8]$. The compounds $[CoPd_3(\mu_3\text{-}X)(\mu\text{-}CO)_3(\mu_3\text{-}CO)(CO)(PBu^t_3)_3]$ (X = Br or I) were recrystallised from benzene–ethanol mixtures and characterised on the basis of IR, $^{31}P\text{-}\{^1H\}$ NMR spectroscopy, fast atom bombardment (FAB) mass spectrometry and elemental analyses. The spectroscopic data for the three palladium–cobalt clusters are summarised in Table 2.

Table 1 Selected interatomic distances (Å) and angles (°) in compound **1**

Co(1)–Pd(2)	2.585(1)	Co(1)–C(12)	1.761(6)	Pd(2)–Co(1)–Pd(4)	79.57(2)	Co(1)–C(10)–O(11)	165.9(6)
Co(1)–Pd(3)	2.651(1)	Co(1)–C(14)	1.961(5)	Pd(2)–Co(1)–Pd(3)	68.64(2)	Co(1)–C(6)–O(7)	132.5(4)
Co(1)–Pd(4)	2.609(1)	Co(1)–C(6)	1.998(5)	Pd(4)–Co(1)–Pd(3)	66.99(2)	Co(1)–C(8)–O(9)	136.6(5)
Pd(2)–Pd(3)	2.952(1)	Co(1)–C(10)	1.848(6)	Pd(2)–Pd(3)–Pd(4)	69.17(2)	Co(1)–C(12)–C(13)	177.8(6)
Pd(3)–Pd(4)	2.903(1)	Co(1)–C(8)	1.989(5)	Co(1)–C(10)–Pd(2)	74.2(2)	Co(1)–C(14)–O(15)	141.3(5)
Pd(2)–Pd(4)	3.324(8)	Pd(2)–Cl(5)	2.740(1)	Co(1)–C(10)–Pd(4)	70.4(2)	Pd(2)–Cl(5)–Pd(3)	67.88(3)
Pd(2)–P(16)	2.381(1)	Pd(3)–Cl(5)	2.538(1)	Co(1)–C(14)–Pd(2)	82.7(2)	Pd(2)–Cl(5)–Pd(4)	76.86(4)
Pd(3)–P(29)	2.390(1)	Pd(4)–Cl(5)	2.604(1)	Co(1)–C(6)–Pd(3)	84.9(2)	Pd(3)–Cl(5)–Pd(4)	68.72(3)
Pd(4)–P(42)	2.393(1)	Pd(2)–C(14)	1.952(6)	Co(1)–C(8)–Pd(4)	83.6(2)		
Pd(4)–C(6)	1.928(5)	Pd(2)–C(10)	2.380(6)				

Table 2 Infrared (KBr pellets), ^{31}P NMR (C_6D_6) and FAB mass spectral data for compounds **1**–**3**

X	ν(CO)/cm^{-1}	δ (ppm)	FAB mass spectrum fragments (*m*/*z*)
Cl	2021, 1845, 1830, 1809	77.3	1048 [M-4CO]$^+$, 1020 [M-5CO]$^+$, 817 [M-5CO-PBu$^t_3$]$^+$, 758 [M-5CO-PBu$^t_3$-Co]$^+$, 652 [M-5CO-PBu$^t_3$-Co-Pd]$^+$
Br	2018, 1846, 1832, 1811	78.7	1093 [M-4CO]$^+$, 1065 [M-5CO]$^+$
I	2011, 1849, 1832, 1811	82.3	1140 [M-4CO]$^+$, 1112 [M-5CO]$^+$, 802 [M-5CO-Pd-PBu$^t_3$]$^+$, 743 [M-5CO-Pd-Co-PBu$^t_3$]$^+$

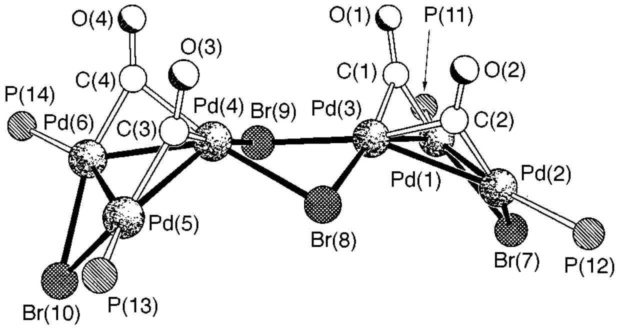


Fig. 2 Molecular structure of compound **4**. The carbon atoms of the Bu$^t_3$ groups of the phosphine ligands have been omitted for clarity

Synthesis and crystal structure of [Pd_6(μ-Br)$_4$(μ-CO)$_4$(PBu$^t_3$)$_4$]

In the reactions between the palladium–halogen compounds and the cobalt dimer, besides the heterometallic clusters, a second product was detected by ^{31}P-{^{1}H} NMR spectroscopy. In all the cases, a singlet between δ 83.0 and 88.0 was observed. For the reaction between [$Co_2(CO)_8$] and [Pd_2(μ-Br)$_2$(PBu$^t_3$)$_2$] in addition to **2** a second orange compound was isolated. Its ^{31}P-{^{1}H} NMR spectrum showed a singlet at δ 87.0 {this has also been observed for the product obtained in the reaction between [Pd_2(μ-Br)$_2$(PBu$^t_3$)$_2$] and CO}.[10] The IR, FAB mass spectrometry and elemental analyses of this compound suggested that it could be formulated as [$Pd_6(Br)_4(CO)_4$(PBu$^t_3$)$_4$]. A crystal suitable for X-ray analysis was obtained by slow evaporation of an acetone–toluene–ethanol mixture. The molecular structure (see Fig. 2) confirmed the formulation [Pd_6(μ-Br)$_4$(μ-CO)$_4$(PBu$^t_3$)$_4$] and showed it to be based on two palladium triangles bridged by two bromine atoms. A similar structure for the cluster [Pd_6(μ-Cl)$_4$(μ-CO)$_4$(PPh_3)$_4$] has been previously reported by Mednikov *et al.*[15]

The structure of cluster **4** has approximate C_{2v} symmetry and consists of two [Pd_3(μ-CO)$_2$(μ-Br)(PBu$^t_3$)$_2$] triangles linked by two bridging bromides. Formally, the oxidation state for the two palladium atoms linked by the two bridging bromides is +1 whereas the others have a fractional oxidation state of +$\frac{1}{2}$. Each of the triangles (considering that each is bonded to one of the bridging bromides) has an electron count of 44. Other examples of 44-electron palladium triangles are [Pd_3(μ-CO)$_3$(PPh_3)$_4$],[16] [Pd_3(μ-SO_2)$_2$(μ-Cl)(PPh_3)$_3$]$^-$,[17] [Pd_3(μ-SO_2)$_2$(CNBu^t)$_5$][18] and [Pd_3(μ-Cl)(μ-PPh_2)$_2$(PPh_3)$_3$]BF_4.[19] The Pd–Pd distance observed for these triangles (44-electron triangles usually have longer Pd–Pd distances than 42-electron triangles) covers the range 2.734(4)–3.000(5) Å. The Pd–Pd distances observed in the structure of compound **4** are within this range of bond lengths (see values in Table 3).

Table 3 Selected interatomic distances (Å) and angles (°) in compound **4**

Pd(1)–Pd(2)	2.893(2)	Pd(1)–C(1)	1.88(2)
Pd(1)–Pd(3)	2.686(2)	Pd(2)–P(12)	2.345(5)
Pd(4)–Pd(5)	2.750(2)	Pd(2)–Br(7)	2.534(2)
Pd(4)–Pd(6)	2.743(2)	Pd(2)–C(2)	1.88(2)
Pd(5)–Pd(6)	2.872(2)	Pd(3)–C(1)	2.10(2)
Pd(3)–Pd(4)	3.405(3)	Pd(3)–C(2)	2.04(2)
Pd(2)–Pd(3)	2.689(2)	Pd(3)–Br(8)	2.557(2)
Pd(1)–P(11)	2.349(4)	Pd(3)–Br(9)	2.562(3)
Pd(1)–Br(7)	2.535(2)		
Pd(1)–Pd(3)–Pd(2)	65.14(5)	Pd(1)–C(1)–Pd(3)	84.8(7)
Pd(3)–Pd(1)–Pd(2)	57.47(4)	Pd(1)–Br(7)–Pd(2)	69.60(6)
Pd(1)–Pd(2)–Pd(3)	57.38(4)	Br(8)–Pd(3)–Br(9)	89.66(8)
Pd(2)–C(2)–Pd(3)	86.5(9)		

The two Pd_3 triangles are not equilateral. The sides formed by Pd(2)–Pd(1) and Pd(5)–Pd(6) are, in each case, slightly longer [2.893(2) and 2.872(2) Å] than the other sides [the average Pd–Pd distance for these four bonds is 2.717(3) Å]. The longer sides are bridged by bromine atoms [the average Pd–Br distance being 2.547(3) Å] to form in each case a Pd_2Br ring which is folded by 35° [Br(7)] and 45° [Br(10)] out of the plane of its associated Pd_3 plane. The Pd–P bond distances are unexceptional and range between 2.349 and 2.387 Å. The transannular Pd(3) and Pd(4) separation, *i.e.* between the two distinct triangular clusters, is 3.405 Å and is too long for a Pd–Pd bond. The bridging Pd(3)–Br(8) and Pd(4)–Br(8) distances are 2.557(2) and 2.578(2) Å. The Pd_2Br_2 ring is non-planar and folded by 136° about the Br(8)–Br(9) vector.

The geometrical arrangement of the ligands (*i.e.* two CO groups and two bromine atoms) around Pd(3) and Pd(4) are each distorted square planar [Pd(3) is 0.25 Å out of plane and Pd(4) 0.13 Å]. The ligands around the other four palladium atoms are arranged in distorted trigonal geometry. The palladium atoms are, on average, 0.14 Å out of the plane formed by the three ligands (phosphine, bridging carbonyl and bridging bromide). It is interesting to note that in **4** the bridging carbonyls on each Pd_3 ring are in a *syn* geometry whereas in the related geometry previously reported by Mednikov *et al.*[15] are in an *anti* geometry.

Reactions between [Pd_2(μ-X)$_2$(PBu$^t_3$)$_2$] (X = Br or I) and [$Fe_2(CO)_9$]

When 1 mol equivalent of [$Fe_2(CO)_9$] was added to a solution of [Pd_2(μ-Br)$_2$(PBu$^t_3$)$_2$] in toluene, the original green colour of the solution changed to orange after 1 h. The reaction was stirred at room temperature for 6 h. The solvent was then removed and an orange compound was extracted after washing the remaining solid several times with acetone. A bright orange crystalline compound precipitated when this solution was kept at 4 °C overnight. The spectroscopic and analytic data showed that the compound is $[\mathrm{Pd_6(\mu\text{-}Br)_4(\mu\text{-}CO)_4(PBu^t{}_3)_4}]$. It is interesting that in this case $[\mathrm{Fe_2(CO)_9}]$ is only acting as a CO source. The palladium dimer reacts with $[\mathrm{Fe_2(CO)_9}]$ and an aggregation process leading to the hexanuclear palladium cluster follows. Similar results were obtained when $[\mathrm{Pd_2(\mu\text{-}I)_2(PBu^t{}_3)_2}]$ was reacted with $[\mathrm{Fe_2(CO)_9}]$.

Conclusion

The halogen-containing compounds $[\mathrm{Pd_4(\mu_3\text{-}CH)(\mu\text{-}Cl)_3(PBu^t{}_3)_4}]$ and $[\mathrm{Pd_2(\mu\text{-}X)_2(PBu^t{}_3)_2}]$ (X = Br or I) have proved to be good starting materials for the synthesis of heterometallic palladium clusters. They can act as sources of $\mathrm{X{-}Pd{-}PBu^t{}_3}$ (X = Cl, Br or I) fragments which readily react with $[\mathrm{Co_2(CO)_8}]$ to yield the heterometallic clusters **1**–**3**. However, the aggregation process leading to these clusters is not simple and more than one product is formed in each case. When X = Br this second product was isolated and structurally characterised as the hexanuclear palladium cluster **4**. The stoichiometry of the reactants (and the effective CO concentration in the medium) seems to be a determining factor for the product that is preferentially obtained. This, and the reactions between the palladium starting materials and other Group 8 and 9 metals are currently under investigation.

Experimental

General

All the reactions were routinely carried out using standard Schlenk-line techniques under an atmosphere of pure nitrogen. The solvents used were dry and free of oxygen. The compounds $[\mathrm{Pd_4(\mu_3\text{-}CH)(\mu\text{-}Cl)_3(PBu^t{}_3)_4}]$, $[\mathrm{Pd_2(\mu\text{-}Br)_2(PBu^t{}_3)_2}]$ and $[\mathrm{Pd_2(\mu\text{-}I)_2(PBu^t{}_3)_2}]$ were prepared according to literature procedures.[9,10] Other reagents were used as obtained from commercial sources. Infrared spectra were recorded on a Perkin-Elmer 1720 infrared Fourier-transform spectrometer between 4000 and 250 $\mathrm{cm^{-1}}$ as KBr pellets. Proton and ^{31}P-{^{1}H} NMR spectra were recorded on a JEOL JNM-EX270 Fourier-transform NMR spectrometer operating at a frequency of 290 MHz with chemical shifts reported relative to $\mathrm{SiMe_4}$ and $\mathrm{H_3PO_4}$ respectively. Mass spectra were recorded by Mr. J. Barton at Imperial College on a VG AutoSpec-Q as FAB using 3-nitrobenzyl alcohol as matrix. Microanalyses (C, H, N) were carried out by Miss H. O'Callaghan at Imperial College.

Syntheses

$[\mathrm{CoPd_3(\mu_3\text{-}Cl)(\mu\text{-}CO)_3(\mu_3\text{-}CO)(CO)(PBu^t{}_3)_3}]$ 1. The cluster $[\mathrm{Pd_4(\mu_3\text{-}CH)(\mu\text{-}Cl)_3(PBu^t{}_3)_4}]$ (0.053 g, 0.04 mmol) was dissolved in toluene (15 $\mathrm{cm^3}$). A suspension of $[\mathrm{Co_2(CO)_8}]$ (0.027 g, 0.08 mmol) in toluene was added under continuous stirring. After 6 h the solvent was removed under reduced pressure and the product extracted with benzene (10 $\mathrm{cm^3}$) and ethanol was added (10 $\mathrm{cm^3}$). The solution was allowed to stand for 3 d at 4 °C giving dark red crystals of $[\mathrm{CoPd_3(\mu_3\text{-}Cl)(\mu\text{-}CO)_3(\mu_3\text{-}CO)(CO)(PBu^t{}_3)_3}]$ (0.047 g, 43%) (Found: C, 42.5; H, 6.7. Required for $\mathrm{C_{41}H_{81}ClCoO_5P_3Pd_3}$: C, 42.5; H, 7.0%). ^{31}P-{^{1}H} NMR ($\mathrm{C_6D_6}$): δ 77.2 (s). IR (KBr pellets): ν(CO) 2021 (vs), 1845, 1830, 1809 (w) $\mathrm{cm^{-1}}$. IR (benzene): 2028 (s), 1959 (s), 1847, 1822 (w), 1810 (w) $\mathrm{cm^{-1}}$. Solid state: ^{31}P-{^{1}H} NMR: δ 77.7 (s) and 74.1 (s). Solid state ^{13}C NMR [two signals (in a 1 : 2 ratio) for the methyl groups of $\mathrm{PBu^t{}_3}$ were observed]: δ 33.2 and 39.2. A broad signal at δ 214.8 (CO groups).

$[\mathrm{CoPd_3(\mu_3\text{-}Br)(\mu\text{-}CO)_3(\mu_3\text{-}CO)(CO)(PBu^t{}_3)_3}]$ 2. The cluster $[\mathrm{Pd_2(\mu\text{-}Br)_2(PBu^t{}_3)_2}]$ (0.038 g, 0.05 mmol) was dissolved in toluene (15 $\mathrm{cm^3}$). A suspension of $[\mathrm{Co_2(CO)_8}]$ (0.017 g, 0.05 mmol) in toluene was added under continuous stirring. After 6 h the solvent was removed under reduced pressure and the product extracted with hexane (10 $\mathrm{cm^3}$). The hexane was then removed under reduced pressure and the product recrystallised from a benzene–ethanol mixture overnight at 4 °C giving dark cherry-red crystals of $[\mathrm{CoPd_3(\mu_3\text{-}Br)(\mu\text{-}CO)_3(\mu_3\text{-}CO)(CO)(PBu^t{}_3)_3}]$ (0.019g, 63%) (Found: C, 42.4; H, 6.4. Required for $\mathrm{C_{41}H_{81}BrCoO_5P_3Pd_3{\cdot}0.5C_6H_6}$: C, 42.5; H 6.6%). ^{31}P-{^{1}H} NMR ($\mathrm{C_6D_6}$): δ 78.7 (s). IR (KBr pellets): ν(CO) 2018 (vs), 1846, 1832, 1811 (w) $\mathrm{cm^{-1}}$.

$[\mathrm{CoPd_3(\mu_3\text{-}I)(\mu\text{-}CO)_3(\mu_3\text{-}CO)(CO)(PBu^t{}_3)_3}]$ 3. This cluster was prepared by the same method as for $[\mathrm{CoPd_3(\mu_3\text{-}Br)(\mu\text{-}CO)_3(\mu_3\text{-}CO)(CO)(PBu^t{}_3)_3}]$ using $[\mathrm{Pd_2(\mu\text{-}I)_2(PBu^t{}_3)_2}]$ (0.03 g, 0.03 mmol) and $[\mathrm{Co_2(CO)_8}]$ (0.01 g, 0.03 mmol). Recrystallisation from benzene–ethanol gave dark purple crystals of $[\mathrm{CoPd_3(\mu_3\text{-}I)(\mu\text{-}CO)_3(\mu_3\text{-}CO)(CO)(PBu^t{}_3)_3}]$. ^{31}P-{^{1}H} NMR ($\mathrm{C_6D_6}$): δ 82.3 (s). IR (KBr pellets): ν(CO) 2011 (vs), 1849, 1832, 1811 (w) $\mathrm{cm^{-1}}$.

$[\mathrm{Pd_6(\mu\text{-}Br)_4(\mu\text{-}CO)_4(PBu^t{}_3)_4}]$ 4. From the reaction between $[\mathrm{Pd_2(\mu\text{-}Br)_2(PBu^t{}_3)_2}]$ and $[\mathrm{Co_2(CO)_8}]$, a second product was isolated. The solid $[\mathrm{CoPd_3(\mu_3\text{-}Br)(\mu\text{-}CO)_3(CO)_2(PBu^t{}_3)_3}]$ was extracted with hexane. The remaining solid was redissolved in benzene and filtered. Ethanol was added to the mixture and an orange crystalline material was obtained after 24 h at 4 °C. Crystals suitable for X-ray analysis were obtained from slow evaporation of a toluene–acetone–ethanol mixture (Found: C, 35.4; H, 5.7. Required for $\mathrm{C_{52}H_{108}Br_4O_4P_4Pd_6{\cdot}C_6H_6}$: C, 35.6; H, 5.8%). ^{31}P-{^{1}H} NMR ($\mathrm{C_6D_6}$): δ 87.0 (s). IR (KBr pellets): ν(CO) 1879 (vs), 1844 (s) $\mathrm{cm^{-1}}$. FAB mass spectrum: *m/z* 1767 $[\mathrm{Pd_6Br_3(CO)_3(PBu^t{}_3)_4}]^+$, 1270 $[\mathrm{Pd_5Br(CO)_2(PBu^t{}_3)_3}]$, 697 $[\mathrm{Pd_2Br(PBu^t{}_3)_2}]^+$, 307 $[\mathrm{Pd(PBu^t{}_3)}]^+$.

Reaction between $[\mathrm{Pd_2(\mu\text{-}Br)_2(PBu^t{}_3)_2}]$ and $[\mathrm{Fe_2(CO)_9}]$

The cluster $[\mathrm{Pd_2(\mu\text{-}Br)_2(PBu^t{}_3)_2}]$ (0.024 g, 0.03 mmol) was dissolved in toluene (15 $\mathrm{cm^3}$). A suspension of $[\mathrm{Fe_2(CO)_9}]$ (0.011 g, 0.03 mmol) in toluene was added under continuous stirring. After 6 h the solvent was removed under reduced pressure and the product extracted with acetone (10 $\mathrm{cm^3}$). The reaction mixture was filtered and hexane added. Orange crystals were formed after 72 h at 4 °C (0.013 g, 68%) (Found: C, 34.8; H, 6.1. Required for $\mathrm{C_{52}H_{108}Br_4O_4P_4Pd_6{\cdot}0.5C_6H_6}$: C, 34.5; H, 5.8%). ^{31}P-{^{1}H} NMR ($\mathrm{C_6D_6}$): δ 87.1 (s). IR (KBr pellets): ν(CO) 1879 (vs), 1844 (w) $\mathrm{cm^{-1}}$.

X-Ray data collection and processing

Crystal data for cluster **1**: $\mathrm{C_{41}H_{81}ClCoO_5P_3Pd_3{\cdot}2C_6H_6}$, $M = 1316.76$, monoclinic, space group $P2_1/c$, $a = 15.452(3)$, $b = 16.655(1)$, $c = 23.818(4)$ Å, $\beta = 95.72(1)°$, $U = 7630(2)$ Å^3, $Z = 4$, $D_c = 1.434$ g cm^{-3}, $\mu = 1.300$ mm^{-1}, $F(000) = 2712$. Crystal dimensions 0.67 × 0.43 × 0.40 mm. 10 727 Independent reflections were collected at 293 K on a Siemens P4/PC diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.710\,73$ Å) using ω scans. Out of these 8082 reflections had $|F_o| > 4\sigma(|F_o|)$ and were considered observed. The data were corrected for Lorentz and polarisation effects, and absorption (maximum and minimum transmission factors 0.299 and 0.256). The structure was solved by direct methods. All full-weight non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned idealized position and isotropic $U(\mathrm{H}) = 1.2U_{\mathrm{eq}}$ (C) and $U(\mathrm{H}) = 1.5U_{\mathrm{eq}}$ (CMe) and allowed to ride on their parent atoms. Refinement was by full-matrix least squares based on F^2 and converged to give $R1 = 0.0437$, $wR2 = 0.1041$. The maximum and minimum residual electron densities in the final ΔF map were 0.71 and −0.37 e Å^{-3}. Computations were carried out using the SHELXTL package, version 5.03.[20]

Crystal data for cluster **4**: $\mathrm{C_{52}H_{108}Br_4O_4P_4Pd_6{\cdot}2EtOH}$,

$M = 1971.44$, monoclinic, space group $P2_1/n$, $a = 21.851(4)$, $b = 13.318(1)$, $c = 26.221(6)$ Å, $\beta = 79.54(1)°$, $U = 7630(2)$ Å^3, $Z = 4$, $D_c = 1.716$ g cm^{-3}, $\mu = 14.724$ mm^{-1}, $F(000) = 3920$. Crystal dimensions 0.30 × 0.20 × 0.17 mm. 10 637 Independent reflections were collected on a Siemens P4/PC RA diffractometer with graphite monochromated Cu-Kα radiation, using ω scans ($2\theta < 120°$) at 173 K. Out of these 6250 reflections had $|F_o| > 4\sigma(|F_o|)$ and were considered observed. The data were corrected for Lorentz and polarisation effects and for absorption (maximum and minimum transmission factors 0.3988, 0.1473). The structure was solved by direct methods. The EtOH solvent molecules were disordered over four half occupied positions. All full-weight non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned idealized positions and isotropic $U(\mathrm{H}) = 1.2U_{eq}$ (C) and $U(\mathrm{H}) = 1.5U_{eq}$ (CMe), respectively. Refinement was by full-matrix least squares based on F^2 and converged to give $R1 = 0.0778$, $wR2 = 0.1701$. The maximum and minimum residual electron densities in the final ΔF map were 1.17 and −1.09 e Å^{-3}. Computations were carried out using the SHELXTL package, version 5.03.[20]

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