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Some molecular rods: gold(I) complexes of 1,3-diynes. Crystal structures of $Au(C{\equiv}CC{\equiv}CH)(PPh_3)$ and $\{Cu_3(\mu\text{-dppm})_3\}(\mu_3\text{-I})$-$(\mu_3\text{-}C{\equiv}CC{\equiv}CAuC{\equiv}CC{\equiv}CH)$

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Reaction of buta-1,3-diyne with $AuCl(PPh_3)$ and $(AuCl)_2(\mu\text{-dppm})$ in the presence of base gave the diynyl complexes $Au(C{\equiv}CC{\equiv}CH)(PPh_3)$ **1** and $\{Au(C{\equiv}CC{\equiv}CH)\}_2(\mu\text{-dppm})$ **2**, respectively. Similar reaction of $W(C{\equiv}CC{\equiv}CH)(CO)_3Cp$ with the two gold(I) complexes gave the heteronuclear diyndiyls $W\{C{\equiv}CC{\equiv}C[Au(PPh_3]\}(CO)_3Cp$ (known) and $\{Au(C{\equiv}CC{\equiv}C[W(CO)_3Cp])\}_2(\mu\text{-dppm})$ **3**. Reaction of $[ppn][Au(acac)_2]$ with the appropriate diynes afforded $[ppn][Au(C{\equiv}CC{\equiv}CH)_2]$ **4**, $[ppn][Au\{C{\equiv}CC{\equiv}C[W(CO)_3Cp]\}_2]$ **5**, $[ppn][Au\{C{\equiv}CC{\equiv}C[Au(PPh_3)]\}_2]$ **6** and $[ppn][Au(C{\equiv}CC_6H_4C{\equiv}CPh)_2]$ **7**; the latter anion was also obtained as the very unstable NMe_4 salt. The reaction between **2** and $\{Au(OTf)\}_2(\mu\text{-dppm})$ likely afforded *cyclo*-$\{Au_2(\mu\text{-}C{\equiv}CC{\equiv}C)(\mu\text{-dppm})\}_2$ **8**, although this compound was not structurally characterised. On one occasion, the molecular rod $\{Cu_3(\mu\text{-dppm})_3\}(\mu_3\text{-I})(\mu_3\text{-}\eta^1\text{-}C{\equiv}CC{\equiv}CAuC{\equiv}CC{\equiv}CH)$ **9** was isolated and crystallographically characterised; a rational approach to **8** from $[ppn][Au(C{\equiv}CC{\equiv}CH)_2]$ and $[\{Cu_3(\mu\text{-dppm})_3\}(\mu_3\text{-I})_2]I$ gave instead the molecular dumbbell $[\{Cu_3(\mu_3\text{-I})(\mu\text{-dppm})_3\}_2(\mu_3{:}\mu_3\text{-}C{\equiv}CC{\equiv}CAuC{\equiv}CC{\equiv}C)]I$ **10**.

Introduction

Gold(I) chemistry continues to excite researchers. This stems, in part, from its linear two-coordination[1] and from the property of aurophilicity,[2] or the weak intra-molecular attractions between gold atoms, displayed in many of its compounds. The former results in formation of rigid-rod polymeric materials,[3] currently of interest for their unusual photo-emission[4] and non-linear optical properties,[5] while aurophilic effects have resulted in the construction of systems having a variety of unusual geometries.[6]

There is much current interest in preparing molecules containing linear conjugated systems end-capped by two metal–ligand fragments (molecular wires or rods). One reason for this is that suitable substructures may allow electronic communication between the two units which cap each end of the rod.[7] Recent examples include the poly-yndiyl complexes of transition metals, among which complexes containing $MnI(dppe)_2$,[8] $Re(NO)(PPh_3)Cp^*$,[9] $Fe(dppe)Cp^*$,[10] $Ru(PPh_3)_2Cp$[11] or $PtR\{P(tol)_3\}_2$ (R = tol, C_6F_5)[12] fragments as end-caps to C_n chains (n = 2, 4, 6, 8, 12, 16, 20) have been studied recently. Others have used the linear two-coordinate geometry of gold(I), in particular, to link alkynyl ligands, thereby generating molecular rods, squares, rectangles and sundry other geometries,[13] together with catenanes, all of which form readily by self-assembly.[14] Extension to cyclic and polymeric materials containing dialkynylaryl,[15] isocyanide[16] and alkynylisocyanide ligands[3] as the carbon linkers has also been achieved.

Several gold(I) complexes have been used as precursors for alkynylgold(I) derivatives. These include $AuCl(L)$ ($L = PPh_3$, SC_4H_8),[17] $(AuCl)_2(\mu\text{-dppm})$[18] and $[ppn][Au(acac)_2]$.[19] The dppm complex is notable for the presence of an aurophilic interaction between the two gold atoms, resulting in the two Cl atoms being on the same side of the molecule.[18] A similar structure has been found for $\{Au(C{\equiv}CBu^t)\}_2(\mu\text{-dppm})$.[20] We hoped to use this feature to generate novel systems in which the two diynyl units also occupied sites on the same side of the molecule. Formation of molecular rectangles based on the $Au_2(\mu\text{-dppm})$ subunit is also possible, complexes such as $\{Au(C{\equiv}CC_6H_4C{\equiv}C)\}_2(\mu\text{-}PPh_2\text{-}C_6H_4PPh_2)$ having been described previously.[5] The lability of the acac ligands in $[Au(acac)_2]^-$ in reactions of compounds containing acidic CH, NH, PH or SH groups enables an extensive range of neutral and anionic gold(I) complexes to be prepared.[19] This paper describes some of our results obtained when examining the synthesis and behaviour of gold(I) derivatives of buta-1,3-diyne.

Results and discussion

Copper-catalysed coupling of $AuCl(PPh_3)$ and buta-1,3-diyne under Cadiot–Chodkiewicz conditions resulted in the formation of $Au(C{\equiv}CC{\equiv}CH)(PPh_3)$ **1** (Scheme 1) in 75% yield. This compound was identified from IR, ^1H and ^{13}C NMR, and electrospray (ES) mass spectrometry, elemental analysis and, ultimately, X-ray crystallography albeit with some co-crystallised material modelled as the iodide. The IR spectrum contained $\nu({\equiv}CH)$ (3283) and $\nu(C{\equiv}C)$ bands (2148 and 2081 cm^{-1}). The ^1H NMR spectrum had a singlet for the diynyl hydrogen at δ 1.76, while the ^{13}C NMR spectrum showed resonances at δ 60.39, 69.43, 128.79 and 129.55 for C_δ, C_γ, C_β and C_α, respectively, assigned by comparison with other buta-1,3-diynyl compounds described previously.[21,22] The ES mass spectrum contained a molecular ion at m/z 508, with an ion at m/z 459 corresponding to $[Au(PPh_3)]^+$.

Although seemingly pure by other criteria, the only usefully crystalline sample of **1** obtained for structural work has a co-crystallised contaminant most sensibly modelled as $AuI(PPh_3)$. Two independent molecules comprise the asymmetric unit of the structure, each site having some 'iodide' residue in association with the C_4H ligand. Occupancies of the 'iodide' component were 0.043 and 0.097(2) (for molecules 1 and 2, respectively); C_4H occupancies were modelled as the complements. Despite this perturbation and these differences, associ-

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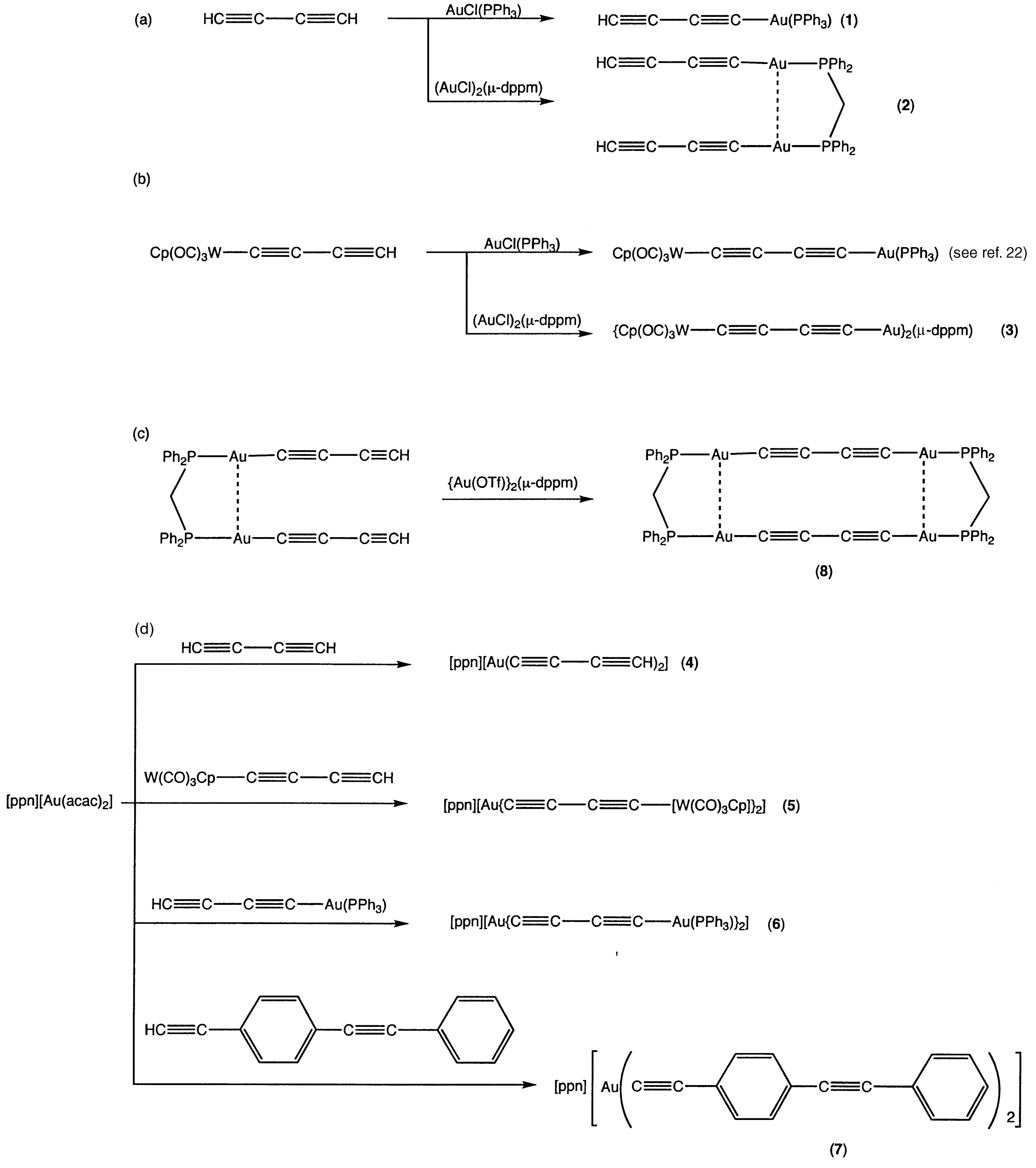
ated geometries as presented in Table 1 are plausible. A plot of molecule 1 is given in Fig. 1. The PAuC$_4$H fragment is essentially linear, with angles at the Au and C atoms of between 170.6(4) and 178.0(6)° (molecule 1), and 172.6(6) and 172.7(2)° (molecule 2). The Au–P and Au–C(1) distances are 2.276(1) and 2.001(5) Å (molecule 1), and 2.273(1) and 1.970(5) Å (molecule 2), respectively, while the carbon chains show alternating short/long/short arrangements of the C–C separations [1.204(7), 1.379(7), 1.190(8) Å (molecule 1); 1.226(7), 1.374(8), 1.188(9) Å (molecule 2)] corresponding to the conjugated 1,3-diyne (–C≡C–C≡C–) formulation. These values may be compared with those found in the electron diffraction study of buta-1,3-diyne itself [1.217(1), 1.383(1) Å; strictly linear],[23] replacement of one H atom by the isolobal Au(PPh$_3$) group having no significant effect on the geometry.

Similarly, addition of (AuCl)$_2$(μ-dppm) to buta-1,3-diyne resulted in the formation of cream {Au(C≡CC≡CH)}$_2$(μ-dppm) **2** in 74% yield. The IR spectrum showed a ν(≡CH) band at 3131 cm^{-1} and two ν(C≡C) bands at 2140 and 2080 cm^{-1}. The ^{1}H NMR spectrum contained a singlet resonance at δ 2.52 for the ≡CH protons, together with multiplets at δ 3.57 and 7.06–7.76 arising from the dppm ligand. The ^{13}C NMR had resonances at δ 65.36, 71.37, 84.07 and 89.72 assigned to C$_\delta$, C$_\gamma$, C$_\beta$ and C$_\alpha$, respectively, as well as those for the dppm ligand. The ES mass spectrum contained M$^+$ at *m*/*z* 874, which loses C$_4$H to give [Au$_2$(dppm)(C$_4$H)]$^+$ at *m*/*z* 826. Crystals suitable for an X-ray study have not yet been obtained, but it is likely that the structure is closely related to that of {Au(C≡CBu^t)}$_2$(μ-dppm),[20] which has a U-shaped geometry, with an intramolecular Au ··· Au contact of 3.331(1) Å, each Au(I) centre being



Scheme 1

Table 1 Selected structural data for Au(C≡CC≡CH)(PPh$_3$) (**1**)

Bond distances/Å (molecules 1, 2)		Bond angles/° (molecules 1, 2)	
Au–P	2.276, 2.273(1)	P–Au–C(1)	173.2(1), 172.7(2)
Au–C(1)	2.001, 1.970(5)	Au–C(1)–C(2)	170.6(4), 172.2(6)
C(1)–C(2)	1.204, 1.226(7)	C(1)–C(2)–C(3)	177.7(5), 176.9(7)
C(2)–C(3)	1.379(7), 1.374(8)	C(2)–C(3)–C(4)	178.0(6), 176.5(7)
C(3)–C(4)	1.190(8), 1.188(9)		
P–C(11)	1.813, 1.819(4)	Au–P–C(11)	115.1, 115.6(1)
P–C(12)	1.820(5), 1.805(4)	Au–P–C(12)	111.8(1), 112.7(2)
P–C(13)	1.815, 1.808(5)	Au–P–C(13)	110.9, 110.0(2)
Au–'I'	2.59(1), 2.659(4)	'I'–Au–P	175.5(3), 176.24(9)

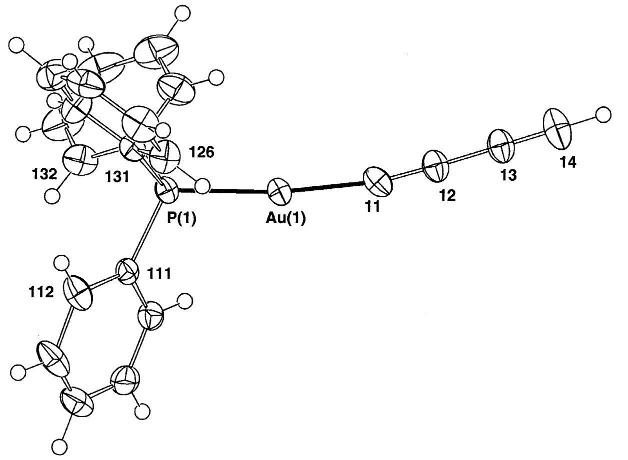


Fig. 1 Plot of a molecule of Au(C≡CC≡CH)(PPh$_3$) (**1**), showing the atom numbering scheme.

approximately linearly coordinated by the phosphorus atom and the alkynyl group.

Yellow {Au(C≡CC≡C[W(CO)$_3$Cp])}$_2$(μ-dppm) **3** was obtained in 77% yield from the CuI-catalysed reaction between two equivalents of W(C≡CC≡CH)(CO)$_3$Cp and (AuCl)$_2$(μ-dppm) in diethylamine. The IR spectrum had a *ν*(C≡C) band at 2144 cm^{-1} and the *ν*(CO) bands of the W(CO)$_3$Cp group occurred at 2039 and 1954 cm^{-1}. The ^{1}H NMR spectrum contained a singlet Cp resonance at *δ* 5.60, together with the expected signals from the phosphine ligand at *δ* 3.94 (CH$_2$) and between *δ* 7.29 and 7.64 (Ph). The carbons of the butadiynyl chain were not detected in the ^{13}C NMR spectrum, probably due to their long relaxation times. However, the Cp and dppm methylene carbons were seen at *δ* 91.91 and 44.05, respectively. The ES mass spectrum, from solutions containing NaOMe, showed ions at *m*/*z* 1563 for [M + Na]$^+$, with additional ions at *m*/*z* 1159 and 778 formed by successive loss of C≡CC≡C-[W(CO)$_3$Cp] fragments. The increased steric bulk of the W(CO)$_3$Cp moieties is likely to result in breaking of the intramolecular Au ··· Au contact, with twisting of the Au–phosphine backbone; presently we have been unable to obtain crystals suitable for X-ray analysis to confirm the exact conformation of **3**.

Addition of buta-1,3-diyne to [ppn][Au(acac)$_2$] under basic conditions (NHEt$_2$) gave white [ppn][Au(C≡CC≡CH)$_2$] **4** in 96% yield. The IR spectrum showed two bands at 3302 and 2141 cm^{-1} assigned to *ν*(≡CH) and *ν*(C≡C), respectively. The ^{1}H NMR spectrum contained a singlet at *δ* 2.50 for the ≡CH protons and a Ph multiplet between *δ* 7.39 and 7.66. The ^{13}C NMR spectrum displayed butadiynyl carbon resonances at *δ* 83.56 (C$_\alpha$), 71.84 (C$_\beta$) and 56.73 (C$_\delta$), C$_\gamma$ not being detected. The negative ion ES mass spectrum showed a single intense ion at *m*/*z* 295 corresponding to [Au(C$_4$H)$_2$]$^-$.

The related complex [ppn][Au{C≡CC≡C[W(CO)$_3$Cp]}$_2$] **5** was prepared as a yellow solid in 85% yield from W(C≡CC≡CH)(CO)$_3$Cp using the same method. The IR spectrum had *ν*(CO) bands at 1959 and 1924 cm^{-1} and a single *ν*(C≡C) band at 2029 cm^{-1}. The ^{1}H and ^{13}C NMR spectra contained singlet resonances for the Cp groups at *δ*$_\mathrm{H}$ 5.20 and *δ*$_\mathrm{C}$ 91.60, while the ppn cation gave multiplets between *δ*$_\mathrm{H}$ 7.40 and 7.67 and between *δ*$_\mathrm{C}$ 126.22 and 133.91. Only one carbon of the C$_4$ chain was detected, at *δ* 63.57 (probably C–Au). The negative ion ES mass spectrum showed [Au{C$_4$[W(CO)$_3$Cp]}$_2$]$^-$ as the base peak at *m*/*z* 959, with two other ions at *m*/*z* 931 and 903 formed by loss of CO groups.

Addition of **1** to [ppn][Au(acac)$_2$] resulted in the formation of white [ppn][Au{C≡CC≡C[Au(PPh$_3$)]}$_2$] **6** in 73% yield. The IR spectrum had *ν*(C≡C) bands at 2140 and 2080 cm^{-1}. The ^{1}H NMR spectrum contained only a Ph multiplet between *δ* 7.46–7.73 ppm. The ^{13}C NMR spectrum showed two peaks of low intensity at *δ* 88.34 and 118.78, which are assigned to two carbons of the butadiynyl chain, with a multiplet between *δ* 126.18–134.38 due to the phenyl carbons. The negative ion ES mass spectrum displayed a single ion at *m*/*z* 1211 assigned to [Au{C$_4$[Au(PPh$_3$)]}$_2$]$^-$.

A further example of a long molecular rod was obtained in the course of studies of the reactions of 4-HC≡CC$_6$H$_4$C≡CPh. White [ppn][Au(C≡CC$_6$H$_4$C≡CPh)$_2$] **7** was obtained in 68% yield from the diyne and [ppn][Au(acac)$_2$]. The resonances of the four alkynyl carbons were observed in the ^{13}C NMR spectrum as sharp singlets between *δ* 89.56 and 119.10, while an ES mass spectrum contained a strong negative ion at *m*/*z* 598, assigned to the molecular anion. While the ppn salt is stable to air and light over prolonged periods, the analogous [NMe$_4$]$^+$ salt decomposes rapidly so that, despite being more soluble than the ppn salt, no ^{13}C NMR spectrum could be obtained.

A molecular rectangle

We sought to prepare rectangular complexes that contained butadiyndiyl ligands (C$_4$) as two of the edges. Addition of a solution of {Au(OTf)}$_2$(μ-dppm), from (AuCl)$_2$(μ-dppm) and AgOTf, to a solution of **2** containing diethylamine *via* syringe pump under high dilution conditions afforded, after concentration and precipitation with hexane, a cream compound formulated as *cyclo*-{Au$_2$(μ-C≡CC≡C)(μ-dppm)}$_2$ **8** (87%). The IR spectrum contained a single *ν*(C≡C) band at 2141 cm^{-1}. The NMR spectra showed signals at *δ*$_\mathrm{H}$ 2.49 and *δ*$_\mathrm{C}$ 24.26 (CH$_2$), and *δ*$_\mathrm{H}$ 7.28–8.05 and *δ*$_\mathrm{C}$ 128.74–133.36 for the phenyl groups. An unresolved multiplet at *δ* 89.39 is assigned to the carbons of the buta-1,3-diynyl chain. The ^{31}P NMR spectrum had a single peak at *δ* 34.50 (dppm). The ES mass spectrum of a solution containing NaOMe displayed three ions at *m*/*z* 1725, 1675 and 1653 corresponding to [M + NH$_2$Et$_2$]$^+$, [M + Na]$^+$ and [M + H]$^+$, respectively. The former peak originates from the interaction with [NH$_2$Et$_2$][OTf], formed as a by-product; similar adducts were found in the spectra of the square molecules *cyclo*-{Pt(μ-C≡CC≡C)(PR$_3$)$_2$}$_4$ (PR$_3$ = PEt$_3$, ½dppe)[24] and between organic macrocycles and secondary amines.[25] Alternative formulations, for example as a salt of [Au(C≡CC≡CH)$_2$]$^-$ with an Au–dppm cation, can be ruled out on the basis of the mass spectra (which contain neither this anion nor any sensible cationic peaks) and the IR spectrum, which does not contain a *ν*(≡CH) absorption (*cf.* **4**). Unfortunately, crystals suitable for an X-ray study have not yet been obtained. The

Table 2 Selected structural data for {Cu_3(μ-dppm)$_3$}(μ_3-I)(μ_3-C≡CC≡CAuC≡CC≡CH) (**9**)

Bond distances/Å (molecules 1, 2)		Bond angles/° (molecules 1, 2)	
Cu(1)–Cu(2)	2.7236, 2.7761(9)	Cu(1)–I–Cu(2)	57.19, 59.03(2)
Cu(1)–Cu(3)	2.7722, 2.7354(8)	Cu(1)–I–Cu(3)	58.10, 57.61(2)
Cu(2)–Cu(3)	2.6846(8), 2.6894(9)	Cu(2)–I–Cu(3)	57.51, 56.73(2)
Cu(1)–I	2.9055(8), 2.8259(9)		
Cu(2)–I	2.7804, 2.8092(7)	Cu(1)–C(11)–Cu(2)	81.4, 82.6(2)
Cu(3)–I	2.8001(7), 2.8514(8)	Cu(1)–C(11)–Cu(3)	81.4, 81.2(2)
Cu(1)–P(1)	2.285, 2.276(1)	Cu(2)–C(11)–Cu(3)	78.6, 79.1(2)
Cu(1)–P(6)	2.290, 2.282(1)		
Cu(2)–P(2)	2.264, 2.266(1)	P(1)–C(1)–P(2)	109.8, 111.6(3)
Cu(2)–P(3)	2.275, 2.277(1)	P(3)–C(3)–P(4)	110.9, 109.6(3)
Cu(3)–P(4)	2.267, 2.271(1)	P(5)–C(5)–P(6)	109.9(2), 112.0(3)
Cu(3)–P(5)	2.250, 2.256(1)		
Cu(1)–C(11)	2.096(4), 2.094(5)	C(11)–C(12)–C(13)	176.1, 174.8(5)
Cu(2)–C(11)	2.082, 2.112(6)	C(12)–C(13)–C(14)	176.2, 173.0(6)
Cu(3)–C(11)	2.156(5), 2.110(5)	C(13)–C(14)–Au	177.8, 172.6(5)
Au–C(14)	1.964, 1.975(6)	C(14)–Au–C(21)	178.3, 176.7(2)
Au–C(21)	1.972, 1.970(6)	Au–C(21)–C(22)	176.8, 175.0(5)
C(11)–C(12)	1.196, 1.184(8)	C(21)–C(22)–C(23)	177.7(6), 178.8(7)
C(12)–C(13)	1.380, 1.404(8)	C(22)–C(23)–C(24)	178.1(6), 178.8(7)
C(13)–C(14)	1.238, 1.226(9)		
C(21)–C(22)	1.224(8), 1.225(9)		
C(22)–C(23)	1.345(8), 1.379(9)		
C(23)–C(24)	1.210(9), 1.18(1)		

high selectivity for ring formation relies on the U-shaped conformations of **2** and {Au(OTf)}$_2$(μ-dppm) being maintained in solution, a process favoured by the short intramolecular Au ··· Au contacts, together with the reactions being carried out under high dilution conditions to minimise polymer formation.

On one occasion, attempted crystallisation of the product from a copper(I)-catalysed reaction between **2** and (AuCl)$_2$(μ-dppm) gave material suitable for a single crystal X-ray structure determination. Unexpectedly, however, this product was found to be the *triangulo*-tricopper complex {Cu_3(μ-dppm)$_3$}(μ_3-I)(μ_3-η^1-C≡CC≡CAuC≡CC≡CH) **9**; again two molecules comprise the asymmetric unit of the structure, as for **1**. Fig. 2 shows a plot of molecule 1 of **9**, while selected bond distances and angles are listed in Table 2. Many complexes containing this *triangulo*-tricopper cluster attached to an η^1-alkynyl group have been described previously[26] and the structure of **9** is closely related to them.

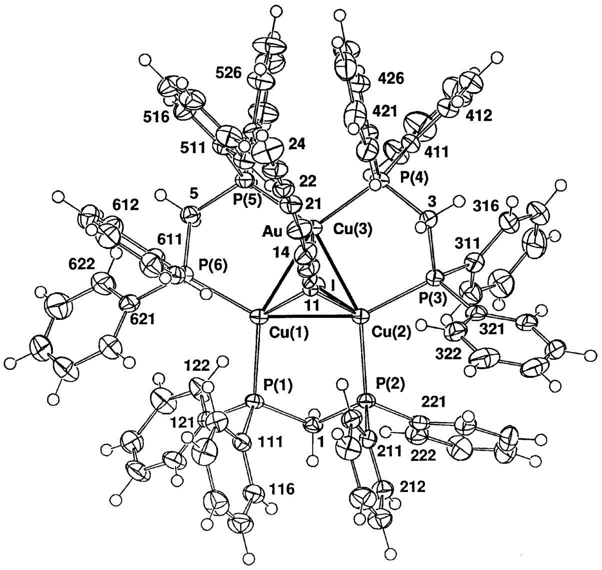


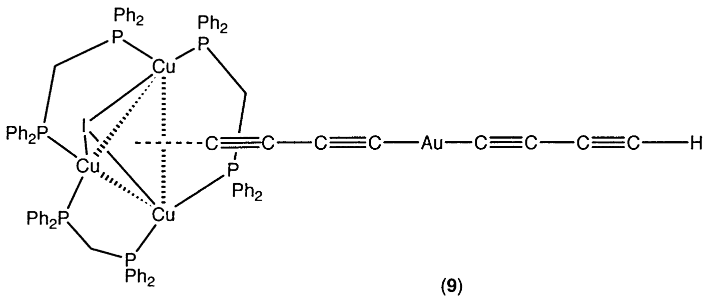
Fig. 2 Plot of a molecule of {Cu_3(μ-dppm)$_3$}(μ_3-I)(μ_3-η^1-C≡CC≡CAuC≡CC≡CH) (**9**).

In **9**, the Cu_3 cores are equilateral triangles, with internal angles at the three Cu atoms ranging between 58.41(2) and 61.67(2)°. The C_4AuC_4H chains are slightly bent, with angles at the carbon atoms of between 172.6 and 178.8(7)°, those at the central Au atoms being 178.3(2), 176.7(2)°. The Cu–I distances range between 2.7804(7) and 2.9055(8) Å [average 2.83(4) Å], with Cu–C separations of 2.082–2.156(5) Å [average 2.11(3) Å]. The Au–C(14, 21) separations average 1.970(5) Å. The C–C distances show the expected short and long alternation, the formal C≡C triple bonds being between 1.18(1) and 1.238(9) Å and the C–C single bond lengths being between 1.345 and 1.404(8) Å. There are significant differences among the C≡C triple bond lengths, those attached to the Cu_3 cluster or to H [1.18(1)–1.210(9) Å] being shorter than those appended to Au [1.224(8)–1.238(9) Å]. Previously described examples of this type of complex have widely varying Cu–Cu separations (between 2.557 and 2.758 Å when spanned by two alkynyl groups, or between 2.754 and 2.927 Å when a μ-halide ligand is present).

The *triangulo*-Cu_3 core is presumably formed by transfer of dppm from gold to CuI and subsequent aggregation and rearrangement of the butadiyndiyl groups around the gold centre. The $[Au(C≡CC≡CH)_2]^-$ fragment so-formed *in situ* reacts further with the copper cluster.

The reaction between equimolar amounts of [{Cu_3(μ-dppm)$_3$}(μ_3-I)$_2$]$^+$ and **4** was examined as a potential direct route to **9**. This reaction gave instead the salt [{Cu_3(μ_3-I)(μ-dppm)$_3$}$_2$(μ_3-C≡CC≡CAuC≡CC≡C)]I **10** in 50% yield, increasing to 100% if a 2 : 1 ratio of reagents was used. Under these reaction conditions, the addition of the second Cu_3(μ_3-I)(μ-dppm)$_3$ fragment appears to be the favoured process. The compound was identified by microanalysis, IR, NMR and mass spectrometry. The IR spectra contained two ν(C≡C) bands at 2137 and 2084 cm^{-1}. The NMR spectra displayed multiplets between δ_H 3.12–3.81 and at δ_C 28.42 (CH_2), and between δ_H 6.82–7.62 and at δ_C 127.93–133.93 (Ph). The resonances of the carbon atoms of the C_4 chains were not observed. The ES mass spectrum showed a peak corresponding to [M + H]$^+$ (*m*/*z* 3232), which loses three dppm ligands to give fragment ions at *m*/*z* 2847, 2463 and 2079.

Compounds **4**–**7** further demonstrate the ability of gold(I) compounds to form linear complexes. The complex [ppn][Au(acac)$_2$] was considered as a possible source of linked systems, either to extend the length of molecular wires or to prepare larger molecular species. Thus, addition of [ppn][Au(acac)$_2$] to Pt(C≡CC≡CH)$_2$(dppe) *via* syringe pump over 1 h resulted in the formation of [ppn]$_4$[*cyclo*-{Pt(μ-C≡CC≡CAu-



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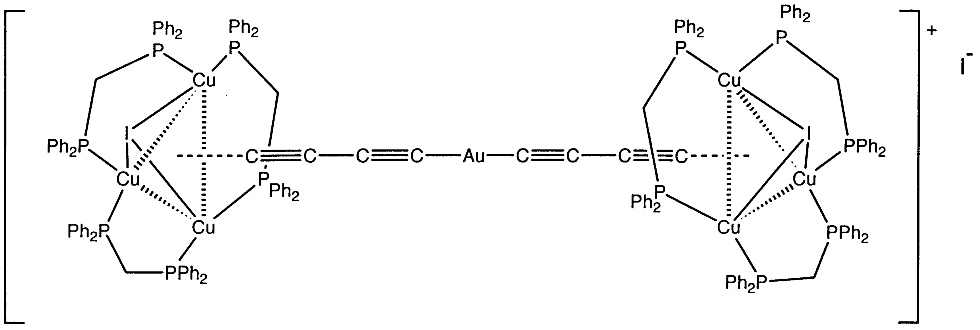

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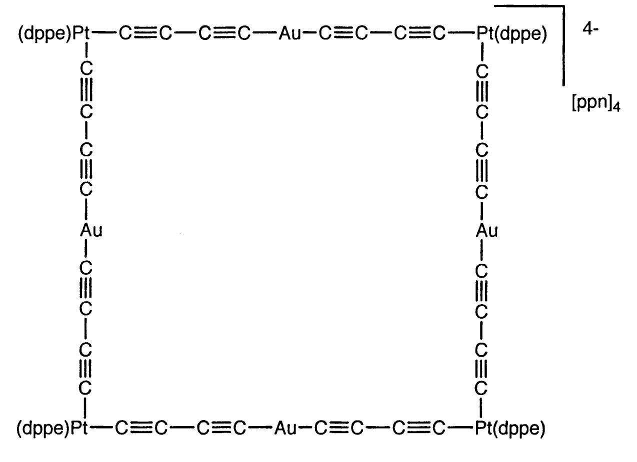
$C{\equiv}CC{\equiv}C)(dppe)\}_4]$ **11** in a yield of 91%. Correct microanalyses and spectroscopic data are consistent with the proposed formulation. The IR spectrum contained two $\nu(C{\equiv}C)$ bands at 2142 and 2073 cm^{-1}. The NMR spectra showed only peaks arising from the dppe ligands, with multiplets at δ_H 2.46 and δ_C 26.99 (CH_2) and between δ_H 7.15–7.94 and δ_C 126.10–133.74 (Ph). Resonances due to the butadiynyl carbons were found at δ 60.31 (C_δ), 76.08 (C_γ), 97.26 (C_β) and 99.56 (C_α). The ES mass spectrum contained an ion centred at *m*/*z* 2310.5 assigned to $[M - 2ppn]^{2-}$.



(11)

Conclusions

The work described above shows that alkynylgold(I) chemistry is readily extended to derivatives of 1,3-diynes, including the parent buta-1,3-diyne. It is possible to attach several common gold(I) fragments, including $Au(PPh_3)$ and $Au_2(\mu\text{-dppm})$, to the diyne, replacing the ≡CH proton. In addition, reaction of the $[Au(acac)_2]^-$ anion readily proceeds with loss of the labile β-diketonate ligands. Extension to systems in which an aurophilic interaction holds two gold atoms in a defined manner, such as $Au_2(\mu\text{-dppm})$, allowed synthesis of the bis-diynylgold complex **2**. By analogy with a previously described *t*-butylalkynyl complex, the structure of **2** is probably as depicted in Scheme 1. Further replacement of the remaining ≡CH protons, using triflate as the leaving group, allowed construction of the molecular rectangle **8**.

In one case, X-ray crystallographic characterisation of an HC_4AuC_4 rod capped by a $Cu_3(\mu\text{-dppm})_3$ triangle in **9** was achieved; directed syntheses gave instead the bicapped C_4AuC_4 dumb-bell **10**.

Combination of two linear diynyl ligands on the otherwise ligand-free Au(I) centre gives the anionic molecular rod $[Au(C{\equiv}CC{\equiv}CH)_2]^-$, in which a linear eleven-atom sequence is probably (no X-ray structure being available) present. Extension of the above reactions to a metalladiyne, $W(C{\equiv}CC{\equiv}CH)(CO)_3Cp$, gives heterometallic systems containing C_4 ligands; the anion $[Au\{C{\equiv}CC{\equiv}C[W(CO)_3Cp]\}_2]^-$ also contains a linear eleven-atom fragment. Finally, evidence has been obtained for the formation of a tetra-anionic 40-atom square **11**, in which the corners are Pt(dppe) groups and the edges are C_4AuC_4 fragments.

Experimental

General reaction conditions

Reactions were carried out under an atmosphere of nitrogen, but no special precautions were taken to exclude oxygen during work-up. Common solvents were dried and distilled under nitrogen before use. Elemental analyses were performed by the Canadian Microanalytical Service, Delta, B.C., Canada.

Instrumentation

IR: Perkin Elmer 1720X FT IR. NMR: Bruker CXP300 or ACP300 (^1H at 300.13 MHz, ^{13}C at 75.47 MHz, ^{13}P at 121.50 MHz) or Varian Gemini 200 (^1H at 199.8 MHz, ^{13}C at 50.29 MHz). Unless otherwise stated, spectra were recorded using solutions in $CDCl_3$ in 5 mm sample tubes. ES mass spectra: Finnegan LCQ. Solutions were directly infused into the instrument, chemical aids to ionisation being used as required.[27]

Starting materials

$AuCl(PPh_3)$,[28] $(AuCl)_2(\mu\text{-dppm})$,[20] $\{Au(OTf)\}_2(\mu\text{-dppm})$,[20] $[ppn][Au(acac)_2]$,[29] $W(C{\equiv}CC{\equiv}CH)(CO)_3Cp$[22] and $[Cu_3(\mu_3\text{-}I)_2(\mu\text{-dppm})_3]I$[30] were prepared by literature methods.

Syntheses

$Au(C{\equiv}CC{\equiv}CH)(PPh_3)$ 1. To a suspension of $AuCl(PPh_3)$ (1.17 g, 2.37 mmol) in $NHEt_2$–thf (30 ml/15 ml) containing CuI (46 mg, 0.24 mmol) was added $HC{\equiv}CC{\equiv}CH$ (23 ml of a 1.34 M solution in thf, 3.1 mmol) and the mixture was stirred at r.t. for 15 min. The solvent was removed and the residue extracted with CH_2Cl_2 and loaded onto a squat column. The product was eluted with CH_2Cl_2, addition of hexane and reduction of solvent volume resulting in precipitation of pale yellow $Au(C{\equiv}CC{\equiv}CH)(PPh_3)$ **1** (908 mg, 75%). Anal. found: C, 49.75; H, 3.26; $C_{22}H_{16}AuP{\cdot}0.5CH_2Cl_2$ (M = 508) requires: C, 49.09; H, 3.12. IR (Nujol): $\nu(\equiv CH)$ 3283; $\nu(C{\equiv}C)$ 2081 cm^{-1}. ^1H NMR: δ 1.76 (s, 1H, $C{\equiv}CH$), 7.30–7.63 (m, 15H, Ph). ^{13}C NMR: δ 60.45 (s, C_δ), 69.45 (s, C_β), 85.79 (s, C_α), 128.79–133.80 (m, Ph). ES mass spectrum (CH_2Cl_2–MeOH, m/z): 508, M^+; 459, $[M - C_4H]^+$.

$\{Au(C{\equiv}CC{\equiv}CH)\}_2(\mu\text{-dppm})$ 2. $HC{\equiv}CC{\equiv}CH$ (1.5 ml of 2.4 M solution in thf, 3.4 mmol) was rapidly added to $(AuCl)_2(\mu\text{-dppm})$ (300 mg, 0.34 mmol) dissolved in $NHEt_2$–thf (10 ml/5 ml) containing CuI (5 mg) and stirred at r.t. for 30 min. The resulting white precipitate was filtered, washed with EtOH, MeOH and Et_2O and then air dried, to give $\{Au(C{\equiv}CC{\equiv}CH)\}_2(\mu\text{-dppm})$ **2** (220 mg, 74%). Anal. found: C, 45.57; H, 2.77; $C_{33}H_{24}Au_2P_2$ (M = 876) requires: C, 45.23; H, 2.76%. IR (Nujol): $\nu(\equiv CH)$ 3131; $\nu(C{\equiv}C)$ 2140, 2080 cm^{-1}. ^1H NMR: δ 2.52 (s, 2H, $\equiv CH$), 3.57 (m, 2H, CH_2), 7.06–7.76 (m, 20H, Ph). ^{13}C NMR (d_6-dmso): δ 25.57 (s, CH_2), 65.36 (s, C_δ), 71.37 (s, C_γ), 84.07 (s, C_β), 89.72 (s, C_α), 129.03–133.60 (m, Ph). ES mass spectrum (dmso–MeOH with added NaOMe, m/z): 874, M^+; 826, $[M - C_4H]^+$.

$\{Au(C{\equiv}CC{\equiv}C[W(CO)_3Cp])\}_2(\mu\text{-dppm})$ 3. CuI (5 mg) and $W(C{\equiv}CC{\equiv}CH)(CO)_3Cp$ (90 mg, 0.22 mmol) were added to a solution of $(AuCl)_2(\mu\text{-dppm})$ (100 mg, 0.11 mmol) in $NHEt_2$ (10 ml) and stirred at r.t. for 10 min. The resulting bright yellow precipitate was filtered, washed with EtOH, MeOH and Et_2O and air dried, to give $\{Au(C{\equiv}CC{\equiv}C[W(CO)_3Cp])\}_2(\mu\text{-dppm})$ **3** (130 mg, 77%). IR (Nujol): $\nu(C{\equiv}C)$ 2144; $\nu(CO)$ 2039, 1954 cm^{-1}. ^1H NMR: δ 3.94 (s, 2H, CH_2), 5.60 (s, 10H, Cp), 7.29–7.64 (m, 20H, Ph). ^{13}C NMR (d_6-dmso): δ 44.05 (s, CH_2), 91.91 (s, Cp), 129.28–133.80 (m, Ph). ES mass spectrum (MeOH with added NaOMe, m/z): 1563, $[M + Na]^+$; 1159, $[M - C_4W(CO)_3Cp]^+$; 778, $[M - 2C_4W(CO)_3Cp]^+$.

$[ppn][Au(C{\equiv}CC{\equiv}CH)_2]$ 4. $HC{\equiv}CC{\equiv}CH$ (0.5 ml of 2.4 M solution in thf, 1.1 mmol) was added to a solution of $[ppn][Au(acac)_2]$ (100 mg, 0.11 mmol) in $NHEt_2$–CH_2Cl_2 (10 ml/2 ml) and stirred at r.t. for 1 h. The colour changed to yellow. The solvent was removed and a filtered CH_2Cl_2 extract of the residue was added dropwise to cold Et_2O to give cream $[ppn][Au(C{\equiv}CC{\equiv}CH)_2]$ **4** (85 mg, 96%). Anal. found: C, 63.16; H, 3.86, N, 1.77; $C_{44}H_{32}AuNP_2$ (M = 833) requires: C, 63.37; H, 3.87; N, 1.68%. IR (Nujol): $\nu(\equiv CH)$ 3302; $\nu(C{\equiv}C)$ 2141 cm^{-1}. ^1H NMR: δ 2.50 (s, 2H, $\equiv CH$), 7.39–7.66 (m, 30H, Ph). ^{13}C NMR: δ 56.73 (s, $\equiv CH$), 71.84, 83.56 (2 × s, $C{\equiv}C$), 125.83–133.89 (m, Ph). ES mass spectrum (CH_2Cl_2–MeOH, m/z): 295, $[Au(C_4H)_2]^-$.

$[ppn][Au\{C{\equiv}CC{\equiv}C[W(CO)_3Cp]\}_2]$ 5. Similarly, $[ppn][Au(acac)_2]$ (100 mg, 0.12 mmol) and $W(C{\equiv}CC{\equiv}CH)(CO)_3Cp$ (91.4 mg, 0.24 mmol) in $NHEt_2$–CH_2Cl_2 (10 ml/2 ml) gave yellow $[ppn][Au\{C{\equiv}CC{\equiv}C[W(CO)_3Cp]\}_2]$ **5** (157 mg, 85%). Anal. found: C, 48.05; H, 2.74, N, 0.98; $C_{60}H_{40}AuNO_6P_2W_2$ (M = 1497) requires: C, 48.12; H, 2.69; N, 0.94%. IR (Nujol): $\nu(C{\equiv}C)$ 2029; $\nu(CO)$ 1959, 1924 cm^{-1}. ^1H NMR: δ 5.20 (s, 10H, Cp), 7.40–7.67 (m, 30H, Ph). ^{13}C NMR (d_6-dmso): δ 63.57 (s, $C{\equiv}C$), 91.60 (s, Cp), 126.22–133.91 (m, Ph). ES mass spectrum (CH_2Cl_2–MeOH, with added NaOMe, m/z): 959, $[Au\{C_4[W(CO)_3Cp]\}_2]^-$ (≡ M); 931, $[M - CO]^-$; 903, $[M - 2CO]^-$.

$[ppn][Au\{C{\equiv}CC{\equiv}C[Au(PPh_3)]\}_2]$ 6. Similarly, $[ppn][Au(acac)_2]$ (92 mg, 0.1 mmol) and **1** (100 mg, 0.2 mmol) in $NHEt_2$–CH_2Cl_2 (1 ml/10 ml) gave white $[ppn][Au\{C{\equiv}CC{\equiv}C[Au(PPh_3)]\}_2]$ **6** (125 mg, 73%). Anal. found: C, 54.91; H, 3.61, N, 1.21; $C_{80}H_{60}Au_3NP_4$ (M = 1750) requires: C, 54.89; H, 3.43; N, 0.80%. IR (Nujol): $\nu(C{\equiv}C)$ 2140, 2080 cm^{-1}. ^1H NMR: δ 7.46–7.73 (m, 60H, Ph). ^{13}C NMR: δ 88.34, 118.78 (2 × s, $\equiv C$), 126.18–134.38 (m, Ph). ES mass spectrum (CH_2Cl_2–MeOH with added NaOMe, m/z): 1211, $[Au\{C_4Au(PPh_3)\}_2]^-$.

$[X][Au(C{\equiv}CC_6H_4C{\equiv}CPh)_2]$ (X = ppn, NMe_4) 7. *(a) X = ppn.* A solution containing $[ppn][Au(acac)_2]$ (120 mg, 0.13 mmol) and $HC{\equiv}CC_6H_4C{\equiv}CPh$ (51 mg, 0.42 mmol) in $NHEt_2$–CH_2Cl_2 (10 ml/4 ml) was stirred at r.t. for 1 h. The solvent was removed and the residue was extracted with CH_2Cl_2. The filtered solution was added dropwise to cold Et_2O (50 ml) to precipitate white $[ppn][Au(C{\equiv}CC_6H_4C{\equiv}CPh)_2]$ **7** (100 mg, 68%). Anal. found: C, 69.89; H, 3.95; N, 1.53; $C_{68}H_{48}AuNP_2{\cdot}0.5CH_2Cl_2$ (M = 1136) requires: C, 69.70; H, 4.18; N, 1.19%. IR (Nujol): $\nu(C{\equiv}C)$ 2101 cm^{-1}. ^1H NMR: δ 7.38–7.67 (m, Ph + C_6H_4). ^{13}C NMR: δ 89.56, 90.05, 102.65, 119.10 (4 × s, 4 × $\equiv C$), 126.09–133.81 (m, Ph + C_6H_4). ES mass spectrum (MeCN, m/z): 598, $[M - 2ppn]^-$.

(b) X = NMe_4. Similarly, addition of $[NMe_4][Au(acac)_2]$ (235 mg, 0.5 mmol) to a solution of $HC{\equiv}CC_6H_4C{\equiv}CPh$ (202 mg, 1.0 mmol) in $NHEt_2$–CH_2Cl_2 (10 ml/4 ml) afforded cream $[NMe_4][Au(C{\equiv}CC_6H_4C{\equiv}CPh)_2]$ (220 mg, 60%). IR (Nujol): $\nu(C{\equiv}C)$ 2101 cm^{-1}. ^1H NMR: δ 3.50 (s, 12H, NMe_4), 7.34–7.54 (m, 18H, Ph + C_6H_4). ES mass spectrum ($C_2H_4Cl_2$, m/z): 615, $[M + O]^-$; 599, M^-. This compound is extremely sensitive to light and air, decomposing to a brown solid; reproducible analyses were not obtained.

***cyclo*-$\{Au_2(\mu\text{-}C{\equiv}CC{\equiv}C)(\mu\text{-dppm})\}_2$ 8.** $\{Au(OTf)\}_2(\mu\text{-dppm})$ (209 mg, 0.20 mmol) in CH_2Cl_2 (10 ml) was added over 1 h *via* syringe pump to a solution of **2** (170.4 mg, 0.20 mmol) in $NHEt_2$–CH_2Cl_2 (1 ml/20 ml). After stirring for an additional 30 min, the solvent was removed and a CH_2Cl_2 extract of the residue was added to cold hexane, precipitating cream *cyclo*-$\{Au_2(\mu\text{-}C{\equiv}CC{\equiv}C)(\mu\text{-dppm})\}_2$ **8** (280 mg, 87%). IR (Nujol): $\nu(C{\equiv}C)$ 2141 cm^{-1}. ^1H NMR (d_6-dmso): δ 2.49 (m, 4H, CH_2), 7.28–8.05 (m, 40H, Ph). ^{13}C NMR (d_6-dmso): δ 24.26 (m, CH_2), 89.39 (m, $C{\equiv}C$), 128.74–133.36 (m, Ph) . ^{31}P NMR (d_6-dmso): δ 34.50 (s, dppm). ES mass spectrum (MeOH containing NaOMe, m/z): 1725, $[M + NH_2Et_2]^+$; 1675, $[M + Na]^+$; 1653, $[M + H]^+$.

$[\{Cu_3(\mu_3\text{-}I)(\mu\text{-dppm})_3\}_2(\mu_3{:}\mu_3\text{-}C{\equiv}CC{\equiv}CAuC{\equiv}CC{\equiv}C)]I$ 10. $[Cu_3(\mu_3\text{-}I)_2(\mu\text{-dppm})_3]I$ (41.4 mg, 0.02 mmol) and $[ppn][Au(C{\equiv}CC{\equiv}CH)_2]$ (20 mg, 0.02 mmol) were dissolved in thf (5 ml) and stirred for 4 h. Evaporation, extraction of the residue (CH_2Cl_2) and addition to hexane precipitated white $[\{Cu_3(\mu_3\text{-}I)(\mu\text{-dppm})_3\}_2(\mu_3{:}\mu_3\text{-}C{\equiv}CC{\equiv}CAuC{\equiv}CC{\equiv}C)]I$ **10** (41 mg, 50%). Anal. found: C, 56.46; H, 4.08; $C_{158}H_{132}AuCu_6I_3P_{12}$ (M = 3361) requires: C, 56.49; H, 3.96%. IR (Nujol): $\nu(C{\equiv}C)$ 2137, 2084 cm^{-1}. ^1H NMR: δ 3.12–3.81 (m, CH_2), 6.82–7.62 (m, Ph). ^{13}C NMR (d_6-dmso): δ 28.42 (m, CH_2), 127.93–133.93 (m, Ph). ES mass spectrum (CH_2Cl_2, m/z): 3232, $[M + H]^+$; 2847, $[M - dppm]^+$; 2463, $[M - 2dppm]^+$; 2079, $[M - 3dppm]^+$; 1346, $[Cu_3(dppm)_3]^+$.

$[\mathrm{ppn}]_4[$*cyclo*-$\{\mathrm{Pt}(\mu\text{-}\mathrm{C{\equiv}CC{\equiv}CAuC{\equiv}CC{\equiv}C})(\mathrm{dppe})\}_4]$ 11. $[\mathrm{ppn}][\mathrm{Au(acac)_2}]$ (135 mg, 0.15 mmol) in CH_2Cl_2 (10 ml) was added *via* syringe pump over a period of 1 h to $\mathrm{Pt(C{\equiv}CC{\equiv}CH)_2(dppe)}$ (100 mg, 0.15 mmol) in the same solvent (20 ml). After evaporation to dryness, a CH_2Cl_2 extract of the residue was added dropwise to cold hexane, to give white $[\mathrm{ppn}]_4[$*cyclo*-$\{\mathrm{Pt}(\mu\text{-}\mathrm{C{\equiv}CC{\equiv}CAuC{\equiv}CC{\equiv}C})(\mathrm{dppe})\}_4]$ **11** (191 mg, 91%). Anal. found: C, 58.38; H, 4.08, N, 0.99; $C_{280}H_{216}Au_4N_4P_{16}Pt_4$ (M = 5697) requires: C, 58.98; H, 3.82; N, 0.98%. IR (Nujol): $\nu(\mathrm{C{\equiv}C})$ 2142, 2073 $\mathrm{cm^{-1}}$. ^{1}H NMR (d_6-dmso): δ 2.46 (m, CH_2), 7.15–7.94 (m, Ph). ^{13}C NMR (d_6-dmso): δ 26.99 (m, PCH_2), 60.31, 76.08, 97.26 (3 × m, 3 × $\equiv$C), 99.56 (s, $\equiv$CAu), 126.10–133.74 (m, Ph). ^{31}P NMR (d_6-dmso): δ 21.39 [s, J(PPt) 107 Hz, ppn], 43.03 [s, J(PPt) 2289 Hz, dppe] . ES mass spectrum (CH_2Cl_2, m/z): 2310.5 $[\mathbf{11} - 2\mathrm{ppn}]^{2-}$.

Structure determinations

Full spheres of data were measured at *ca*. 153 K using a Bruker AXS CCD area-detector instrument and merged to unique sets after "empirical"/multiscan absorption corrections (proprietary software). N_{tot} data gave N unique (R_{int} quoted), N_o with $F > 4\sigma(F)$ being used in the refinements. All data were measured using monochromatic Mo-Kα radiation, λ 0.7107$_3$ Å. In the refinements, anisotropic thermal parameter forms were used for the non-hydrogen atoms, $(x, y, z, U_{\mathrm{iso}})_{\mathrm{H}}$ being constrained at estimated values.

In all cases, conventional residuals R, R_w on $|F|$ (statistical weights) are quoted. Neutral atom complex scattering factors were used: computation was carried out using the XTAL 3.7 program system.[31] Pertinent results are given in the figures (which show 50% thermal ellipsoids for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å) and tables.

Crystal data for 1. $0.93\mathrm{Au(C{\equiv}CC{\equiv}CH)(PPh_3)}\cdot0.07\mathrm{AuI(PPh_3)}\cdot0.5\mathrm{PhMe} \equiv (C_{22}H_{16}AuP)_{0.93}\cdot(C_{18}H_{15}AuIP)_{0.07}\cdot C_7H_8$, M = 559.8. Monoclinic, space group $P2_1/n$, a = 9.9695(5), b = 27.819(1), c = 15.4860(7) Å, β = 90.242(1)°, V = 4295 Å^3 for Z = 8, ρ = 1.73$_1$ g cm^{-3}. Crystal: 0.35 × 0.13 × 0.13 mm, μ = 70 cm^{-1}, 'T'$_{\mathrm{min,max}}$ = 0.34, 0.70. 2θ = 68°, N_{tot} = 58585, N = 16831 (R_{int} = 0.033), N_o = 12380, R = 0.040, R_w = 0.048.

Variata. As described above, significant residues in the vicinities of the gold atoms were modelled in terms of cocrystallised iodide.

Crystal data for 9. $\{\mathrm{Cu_3}(\mu\text{-dppm})_3\}(\mu_3\text{-I})(\mu_3\text{-}\mathrm{C{\equiv}CC{\equiv}CAuC{\equiv}CC{\equiv}CH}) \equiv C_{83}H_{67}AuCu_3IP_6$, M = 1764.8. Monoclinic, space group $P2_1/c$, a = 30.858(2), b = 26.304(1), c = 19.0257(9) Å, β = 105.150(1)°, V = 14906 Å^3 for Z = 8, ρ = 1.57$_3$ g cm^{-3}. Crystal: 0.25 × 0. 13 × 0.06 mm, μ = 33.9 cm^{-1}, 'T'$_{\mathrm{min,max}}$ = 0.55, 0.72. 2θ = 58°, N_{tot} = 166649, N = 38015 (R_{int} = 0.037), N_o = 22941, R = 0.045, R_w = 0.043.

CCDC reference numbers 168997 and 168998.

See http://www.rsc.org/suppdata/dt/b1/b107446f/ for crystallographic data in CIF or other electronic format.

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