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Acetylenephosphino gold(I) derivatives: structure, reactivity and luminescence properties

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Received 17th May 2002, Accepted 22nd July 2002

We have synthesised the acetylenephosphino gold(I) derivatives, $AuX(PPh_2CCH)$ (X = Cl, Br, I, C_6F_5). X-Ray diffraction studies show that the chloro derivative is a dimer connected by two short hydrogen bonds from the acetylenic hydrogen to chlorine, whilst the iodo derivative is also a dimer because of a gold–gold interaction of 3.0625(9) Å. The crystal structure of the pentafluorophenyl derivative shows the presence of intermolecular hydrogen bonds Au ··· H (3.07 Å, 143°), also from the acetylenic hydrogen, which link the molecules into chains. The possibility of preparing alkynyl derivatives has been investigated but only complex $[Au(C_6F_5)(PPh_2CC)Au(C_6F_5)][N(PPh_3)_2]$ **6** has been obtained in a pure state. Complex **6** luminesces at room temperature in the solid state, and all the complexes are luminescent at 77 K with excitation maxima in the range 292–335 nm and emission maxima between 445 and 533 nm.

Introduction

The supramolecular aggregates of gold(I) complexes of type L–Au–X (X = halide or pseudohalide) include dimers, trimers, higher oligomers and one-, two- and three-dimensional polymers. The association is usually based on sub-van der Waals gold–gold contacts with distances between 2.9 and 3.5 Å and bond energies in the range 21–46 kJ, comparable to hydrogen bonds. This aurophilic attraction has been explained by means of correlation effects strengthened by relativistic effects.[1,2] The degree of oligomerization is determined by several factors, the steric requirement of the ligands being the most clear.[3] It has been reported, by theoretical and experimental studies, that the gold–gold interaction increases with the softness of the ligand.[4,5] Aurophilic interactions seem to be responsible for the luminescent properties of some gold(I) complexes.[6–8]

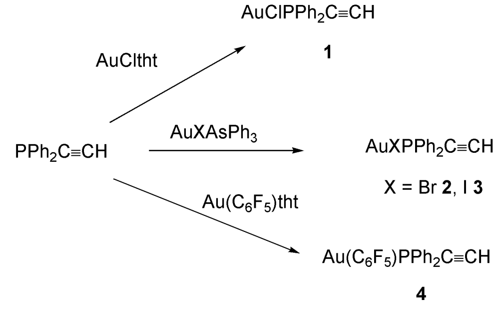
In some cases the aggregation of gold monomers is based on hydrogen bonds, as found if L is an amine[9] or an amidophosphine,[10] and there are also more complicated systems involving combination of aurophilic interactions and hydrogen bonds, as reported, for example, where X is an aminothiolate.[11] Both kinds of bonding are distinctly directional[12] and there are recent reports of rotator phases in chloro-(n-alkylisocyanide)gold(I) derivatives induced by aurophilic bonding, analogous to those found in (1-n)-alcohols by hydrogen bonding.[13]

In this paper we report a series of acetylenephosphino gold(I) derivatives, namely $AuX(PPh_2CCH)$ (X = Cl, Br, I, C_6F_5), in which a competition between aurophilic interactions and hydrogen bonds occurs. The chloro and the iodo derivatives can be considered as dimers *via* hydrogen or aurophilic bonding, respectively, whilst the pentafluorophenyl derivative also shows intermolecular hydrogen bonds. We have also prepared the alkynyl derivative $[Au(C_6F_5)(PPh_2CC)Au(C_6F_5)][N(PPh_3)_2]$, which luminesces at room temperature in the solid state. All the complexes are luminescent at 77 K in the solid state.

Results and discussion

Synthesis and spectroscopic characterization of complexes

We have prepared complex **1** which has been previously described,[14] but starting with AuCl(tht) (tht = tetrahydrothiophene). Similarly, the reaction of ethynyldiphenylphosphine with $AuX(AsPh_3)$ (X = Br, I) or $Au(C_6F_5)(tht)$ led by displacement of $AsPh_3$ or tht to complexes **2**–**4** with the acetylenephosphine ligand coordinated through the phosphorus donor atom (Scheme 1).



Scheme 1

These complexes are air- and moisture-stable white (**1**, **2** and **4**) or pale yellow (**3**) solids at room temperature. They were readily characterised by ^1H and $^{31}P\{^1H\}$ NMR. Their $^{31}P\{^1H\}$ NMR spectra show a singlet at 6.0 (**2**), 11.0 (**3**) and 17.2 (**4**) ppm, typically shifted downfield compared to the free phosphine (−33.6 ppm).[14] In the ^1H NMR spectra the resonance of the C≡C–H is observed *ca.* 3.50 ppm as a doublet, 0.2 ppm shifted downfield compared with the free ligand. The ^{19}F NMR spectrum of **4** shows the pattern of one pentafluorophenyl unit. Acetone solutions are non-conducting.

Their IR spectra show absorptions at 3275 and 3245 (complex **2**), 3275 and 3172 (complex **3**) and 3271 (complex **4**) cm^{-1}

DOI: 10.1039/b204791h

Table 1 Selected bond distances (Å) and angles (°) within molecules AuX(PPh_2CCH), X = Cl, I, (C_6F_5)

	AuCl(PPh_2CCH)	AuI(PPh_2CCH)[a]	Au(C_6F_5)(PPh_2CCH)
Au1–P	2.2238(12)	2.247(4)	2.283(2)
Au2–P		2.251(4)	
Au1–X	2.2892(12)	2.5649(12)	2.059(8)
Au2–X		2.5650(12)	
P1–C1	1.774(5)	1.743(16)	1.764(9)
P2–C3		1.733(16)	
C1–C2	1.169(7)	1.20(2)	1.141(14)
C3–C4		1.17(2)	
P–Au1–X	179.46(5)	172.57(10)	176.6(2)
P–Au2–X		172.90(11)	
C2–C1–P1	176.9(5)	175.0(16)	173.9(9)
C4–C3–P2		178.0(18)	

[a] Two independent molecules.

from ν(C≡C–H), and at 2056 (complex **2** and **4**) and 2049 (complex **3**) cm^{-1} from the asymmetric C≡C; in addition, the spectrum of complex **4** shows absorptions corresponding to the pentafluorophenyl ring at 951 and 792 cm^{-1}.[15] In the FAB^+ mass spectra the fragment $[Au(PPh_2C{\equiv}CH)]^+$ at m/z = 407 is always observed as the base peak, with further abundant peaks at 617 (29% for **2** and 63% for **3**) $[Au(PPh_2{\equiv}CH)_2]^+$ and 574 (23% abundance) for complex **4** corresponding to $[M]^+$. The FAB^- mass spectra show the base peak corresponding to $[M - H]^-$ at m/z = 485 for complex **2** and at 533 for complex **3**, whilst that of complex **4** is observed at 531 $[Au(C_6F_5)_2]^-$; other abundant peaks are seen at m/z = 357 (73%, $[AuBr_2]^-$, **2**), 451 (50%, $[AuI_2]^-$, **3**), 937 (52%, $[Au_2(C_6F_5)_2(PPh_2C{\equiv}CH)]^-$, **4**) and 573 (40%, $[M - H]^-$, **4**).

Crystal structures

The molecular structures of all three complexes AuX(PPh_2CCH), where X is Cl (**1**), I (**3**) or C_6F_5 (**4**), are similar. Complex **3** crystallizes with two independent molecules. Structural parameters for the group are set out in Table 1. Despite the similarities in molecular structures, there are considerable variations in the intermolecular organization in the solid state. All complexes show the typical two-coordinate, nearly linear geometry for the gold(I) centre, with the P–Au–X angle varying from 172.57(10)° and 172.90(11)° in complex **3** to 176.6(2)° and 179.46(5)° for derivatives **1** and **4**.

The Au–P bond lengths show the different *trans* influence of the X ligands. Accordingly, this distance varies from 2.2238(12) Å for X = Cl, to 2.247(4) and 2.251(4) Å for X = I, and finally to 2.283(2) Å for X = C_6F_5. These distances compare well with those reported for $[\{AuX(PPhMe_2)\}_2]$, 2.236(6) and 2.232(6) Å for X = Cl, and 2.245(5) and 2.259(5) Å for X = I.[5b] The Au–Cl bond length is 2.2892(12) Å, which is similar to those found in $[AuCl(PPh_2CH_2SiMe_3)]$ [2.292(2) Å],[16] in $AuCl(^iPr_2PC{\equiv}CH)$ [2.286(2) Å][14] and marginally shorter than in $[\{AuCl(PPhMe_2)\}_2]$ [2.316(6) and 2.311(6) Å].[5b] The Au–I bond lengths are 2.5649(12) and 2.5650(12) Å, shorter than in $[\{AuI(PPhMe_2)\}_2]$ [2.588(2) and 2.582(2) Å][5b] or in $[Au(TPAH)I][AuI_2]$ [2.579(2) Å, *trans* to P; TPAH = protonated P-(1,3,5-triaza-7-phosphaadamantane)].[17] The Au–C bond length is 2.059(8) Å, similar to those reported in $[\{Au(C_6F_5)\}_2(\mu\text{-dppm})]$ [dppm = bis(diphenylphosphino)methane].[18]

The acetylenephosphino ligand shows almost linear angles P–C–C ranging from 173.9(9)° in complex **4** to 178.0(18)° in complex **3**. The C1–C2 distances lie in the range 1.141(14)–1.20(2) Å, consistent with a triple bond, and compare well to the corresponding carbon–carbon triple bond in the related derivatives $(F_5C_6)_2Au(PPh_2C{\equiv}C)Au(PPh_3)$ [1.220(11) Å][19] and $AuCl(^iPr_2PC{\equiv}CH)$ [1.204(7) Å].[14]

The solid state structure of AuCl(PPh_2CCH) **1** is shown in Fig. 1. The main feature is that there are no short gold–gold contacts (the shortest is 4.127 Å), but the molecules nevertheless form dimers through two symmetry-equivalent hydrogen bonds. The acidic alkynyl proton acts as donor to the chloro ligand of a second molecule related by inversion, with a strikingly short C2–H2 ··· Cl1 distance of 2.45 Å (all contacts are quoted for normalised C–H distances of 1.08 Å) and a corresponding angle of 156°. There is also a short Au ··· H24 contact of 3.07 Å but the C–H ··· Au angle is narrow at 126°.

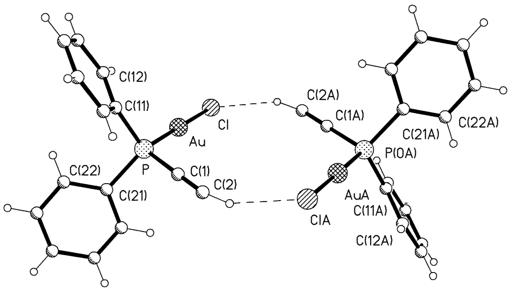


Fig. 1 View of the dimer of complex **1** AuCl(PPh_2CCH).

The solid state structure of AuI(PPh_2CCH) **3** is shown in Fig. 2. The main feature is the presence of gold(I)–gold(I) interactions of 3.0625(9) Å, which link the molecules as dimers. This fact rules out the idea that steric hindrance precludes aurophilic interactions in complex **1**. The shortest gold–gold distance between different dimers is 7.208 Å. The I1–I2 distance is 4.731 Å which precludes any significant interaction. There are several H ··· I contacts of 3.2–3.3 Å but, apart from C15–H15 ··· I2 with 3.23 Å and 144°, they are very far from linear. Similarly, there are two Au ··· H contacts; C25–H25 ··· Au2, with 2.98 Å and 143°, is the more linear.

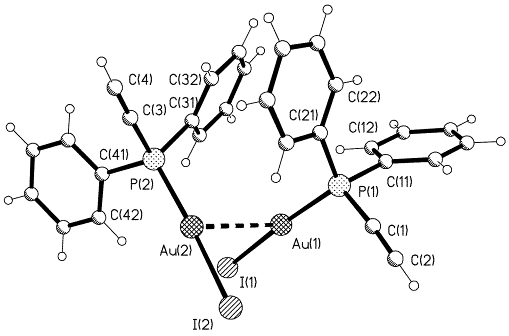


Fig. 2 View of the dimer of complex **3** AuI(PPh_2CCH).

In this case the expected trend is followed; aurophilic attractions increase with the softness of the ligand, as reported for the series $(AuX)_2(\mu\text{-dpph})$ [X = Cl, I; dpph = bis(diphenyl-

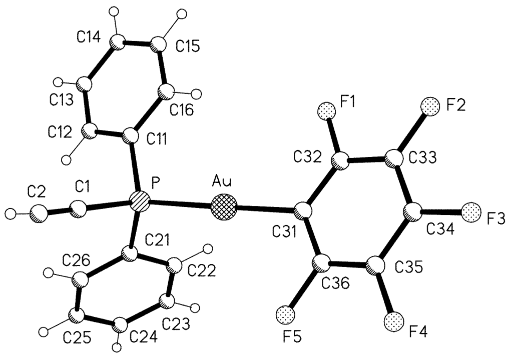


Fig. 3 Molecular structure of complex **4** $Au(C_6F_5)(PPh_2CCH)$.

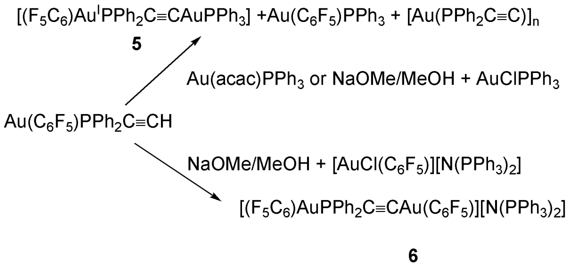
phosphino)hexane][20] and $[\{AuX(PPhMe_2)\}_2]$ (X = Cl, Br, I)[5b] and AuX(TPA) (X = Cl, Br).[21]

The molecular structure of complex $Au(C_6F_5)(PPh_2CCH)$ **4** is shown in Fig. 3. The molecular packing involves several Au ··· H contacts but only that from the acidic alkynyl proton, with an Au ··· H2 distance of 3.07 Å and an angle C2–H2–Au of 143°, might be considered as a genuine interaction; it links the molecules by translation parallel to the *a* axis. There are also several borderline C–H ··· F interactions with H ··· F 2.5–2.6 Å, *e.g.* C12–H12 ··· F3, with H ··· F 2.42 Å, C–H ··· F 161°. As found in complex **1** there are no aurophilic interactions, the shortest gold–gold distance being 5.523 Å. One could argue that the steric hindrance of the pentafluorophenyl ligand precludes the presence of any gold–gold interaction but, for instance, there is a gold–gold distance as short as 3.163(1) Å in $[\{Au(C_6F_5)\}_2(\mu\text{-dppm})]$.[18]

Reactivity

The synthesis of alkynyl gold derivatives starting from the alkynephosphino gold complexes can be achieved mainly in two ways: by deprotonation and further reaction with a chloro-gold derivative or by using acetylacetonato-gold derivatives.[22] We have recently reported that these two procedures applied on an acetylenephosphino gold(III) complex led to an unexpected anti-Markovnikov addition to the triple bond or to the expected alkynyl gold(I) complexes, respectively.[19]

The reaction of the gold(I) derivatives **1**–**3** with NaOMe/MeOH leads, as expected, to the deprotonation of the terminal alkyne and the formation of $[\{Au(PR_2CC)\}_n]$ as insoluble polymeric chains, as already reported for complex **1** with X = Cl.[14] We have carried out the reaction of complexes **1**–**3** with $Au(acac)(PPh_3)$ but the dinuclear alkynyl complex was not obtained; a phosphine substitution reaction takes place to give $AuX(PPh_3)$, accompanied by the formation of the acetylidephosphino gold(I) polymer. Therefore, neither of the two methods affords the alkynyl gold complexes $AuX(PPh_2CC)AuPPh_3$, which is presumably attributable to the high stability and insolubility of the polymer derivative (see Scheme 2).



Scheme 2

A similar reaction between complex **4** and $Au(acac)PPh_3$ gives a mixture of the polymer form, $Au(C_6F_5)(PPh_2CC)AuPPh_3$ (**5**) and $Au(C_6F_5)(PPh_3)$. Complex **5** was characterised by NMR: there are only phenyl resonances in the proton spectrum and two singlets at 41.6 (PPh_3) and 15.3 ppm (PPh_2CC; assignment by comparison with complex **6** and complexes reported in ref. 19) in the phosphorus spectrum. The same result is obtained by reaction of **4** and NaOMe/MeOH and $AuClPPh_3$; however, complex **4** is stable in the presence of the base and only after adding the chloro derivative does the reaction proceed. Therefore we carried out the reaction of complex **4** with NaOMe/MeOH in the presence of $[AuCl(C_6F_5)][N(PPh_3)_2]$, which afforded the alkynyl derivative **6** $[Au(C_6F_5)(PPh_2CC)Au(C_6F_5)][N(PPh_3)_2]$ (see Scheme 2).

Table 2 Electronic absorption data for complexes **1**–**4** and **6**[a]

Complex	λ/nm (ε/M^{-1} cm^{-1})
PPh_2CCH	230 (12000), 248 (8400)
1	232 (15000), 268 (1100), 278 (900)
2	232 (18000), 268 (sh, 2000), 276 (sh, 1200)
3	232 (23000)[b]
4	234 (30000), 256 (sh, 7500), 268 (sh, 2600), 276 (sh, 1300)
6	232 (58000), 262 (17000), 310 (850)

[a] In CH_2Cl_2 solution, 5×10^{-5} M. [b] There are no clear shoulders but there is absorption till *ca.* 300 nm.

Complex **6** is a white solid which is air- and moisture-stable. The IR spectrum shows absorptions at 2056 cm^{-1} from the asymmetric $\nu(C{\equiv}C)$ and at 950, 807 and 790 cm^{-1} corresponding to the pentafluorophenyl groups; the absorption from $\nu(C{\equiv}C\text{–}H)$ has disappeared. Their acetone solutions show the conductivity of a 1:1 electrolyte. The $^{31}P\{^1H\}$ NMR spectrum shows two singlets: one at 21.8 ppm from $N(PPh_3)_2^+$, and a second at 14.6 ppm from the alkynyl-phosphine ligand. In the ^1H NMR spectrum only the phenyl resonances are seen. The ^{19}F NMR spectrum shows two non-equivalent pentafluorophenyl units. In the FAB$^-$ mass spectrum the base peak is observed at *m*/*z* 937, corresponding to the fragment $[M\text{–}N(PPh_3)_2]^-$.

Photophysical studies

The absorption spectra in dichloromethane were measured in the range 200–600 nm and the results are summarised in Table 2. All the spectra are dominated by an absorption around 230 nm from the phenyl phosphine rings.[23] The extinction coefficients increase going from derivative **1** to **2** to **3** and the phenyl absorption becomes broader; therefore the bands at 268 and 278 nm observed for **1**, are only shoulders for **2** and are not seen for **3**, although they could be there (in fact in the spectrum of **3**, at 276 nm, ε is 2400 M^{-1} cm^{-1}). We suggest that these bands are related to the 248 nm absorption observed in the free ligand, which could be due to $\pi \longrightarrow \pi^*$ transitions in the acetylenic fragment, although we cannot exclude [5d (Au)]$\longrightarrow$[6p (Au), π^* (phosphine)] transitions.[24,25]

The spectrum of **4** is similar with an additional shoulder at 256 nm. There is absorption up to 300 nm for complexes **1**–**4**. The spectrum of **6** shows an intense absorption at 262 nm and a weak absorption at 310 nm. There is absorption up to 320 nm. Apart from the above mentioned assignations, in complex **6** Au–P to acetylide transitions are also possible and we do not rule out the possibility that the lower energy absorptions around 310 nm contain some metal to aceylide charge transfer.[26,27]

AuXL complexes are often luminescent, especially at low temperature and when aurophilic interactions are present. The emission has been explained by a variety of transitions: intraligand, metal-centered, metal to ligand or ligand to metal charge transfers.[5,7,17,21,28] On the other hand, alkynylphosphino gold(I) derivatives often luminesce at room temperature and the emission has been associated with intraligand electronic transitions, gold-centered transitions, Au–P to acetylide transitions or even gold–gold bond to acetylide transitions.[24,26]

Table 3 Excitation and emission data in the solid state at 77 K for complexes **1**–**4** and **6**

Complex	λ_{exc}/nm	λ_{emis}/nm
1	334	446, 458sh
2	300	527
	335	449, 527sh
3	292, 330sh	533
	335	483sh, 528
4	331	445
6	333	448

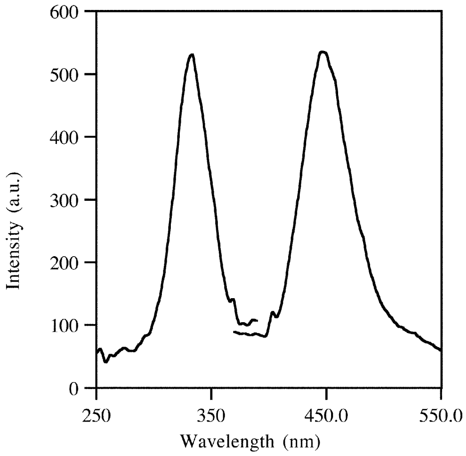


Fig. 4 Excitation and emission spectra of derivative **6** in the solid state at room temperature.

It is noteworthy that only the alkynyl derivative **6** is luminescent at room temperature in the solid state, the emission maximum being located at 446 nm whilst the excitation maximum is located at 333 nm (see Fig. 4). However all complexes luminesce at low temperature in the solid state, with excitation maxima in the range 292–335 nm and emission maxima between 445 and 533 nm. The results are summarised in Table 3. The acetylenephosphine ligand is not emissive in the same conditions. The excitation and emission maxima of derivatives **1**, **4** and **6** are similar, and are close to those found for complex **6** at room temperature. The emission cannot be attributed to aurophilic interactions (there are none in the crystal structures of **1** and **4**); the emission in complex **6** cannot be assigned to the alkynyl group,[24] because it is the same for the alkyne-phosphino complexes; therefore the emission should be related to the common fragment Au^{I}–PPh$_2$CC, probably involving the phosphine ligand perturbed by the gold(I) centre.

In contrast, for the bromo and iodo derivatives two spectra can be distinguished (see Fig. 5): the more intense shows the emission maximum around 530 nm with the corresponding excitation maximum around 300 nm, whilst the second spectrum shows an emission maximum about 450 nm with a shoulder at 527 nm for the bromo derivative and an emission maximum about 530 nm with a shoulder at 483 nm for the iodo derivative (both with excitation maxima at 335 nm). In complexes [{AuX(PPhMe$_2$)}$_2$] (X = Cl, Br, I)[5b] and AuX(TPA) [X = Cl, Br, I; TPA = P-(1,3,5-triaza-7-phosphaadamantane)][17] two emissions are also observed: the higher energy emission has been assigned to phosphine intraligand transitions or to halide to metal charge transfer, whilst the lower energy emission has been related to gold–gold interactions. In our case, we can also suggest for the higher energy emission a phosphine ligand transition perturbed by the gold(I) centre, and that the lower energy emission is related to metal–metal interactions, and thus only seen in the bromo and iodo derivatives, although we cannot assure the presence of these interactions in the bromo derivative. We can rule out halide to metal charge transfer because there is no gradual change in the chloro-bromo-iodo series.

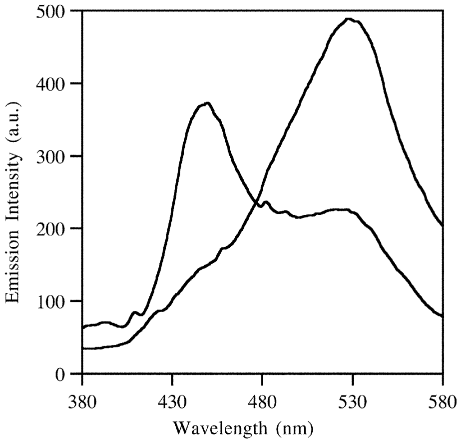


Fig. 5 Emission spectra of derivative **3** with λ_{exc} = 340 nm (lower intensity) and 300 nm (higher intensity) in the solid state at 77 K.

Conclusions

We have shown how in complexes AuX(PPh$_2$CCH) a different anionic ligand X can promote aurophilic bonding or hydrogen bonding (Cl–H or Au–H). It seems that aurophilic interactions are promoted by soft anion ligands as predicted by theoretical calculations. The synthesis of dinuclear alkynyl derivatives is only possible if X is pentafluorophenyl. The luminescence properties are also changed because of the anion ligand.

Experimental

General

All the reactions were carried out under an argon atmosphere at room temperature. IR spectra were recorded on a Perkin-Elmer 883 spectrophotometer, over the range 4000–200 cm^{-1}, by using Nujol mulls between polyethylene sheets. ^{1}H, ^{19}F and ^{31}P{^{1}H} NMR spectra were recorded on a Bruker ARX·300 or GEMINI 2000 apparatus in CDCl$_3$ solutions (if no other solvent is stated); chemical shifts are quoted relative to SiMe$_4$ (external, ^{1}H), CFCl$_3$ (external, ^{19}F) and 85% H$_3$PO$_4$ (external, ^{31}P). C, H, N and S analyses were performed with a Perkin-Elmer 2400 microanalyzer. Conductivities were measured in acetone solution with a Philips PW 9509 apparatus. Mass spectra were recorded on a VG Autospec using FAB technique (with Cs gun) and 3-nitrobenzyl alcohol as matrix. The luminescence spectra were recorded on a Perkin-Elmer LS-50B spectrofluorometer. UV–Vis absorption spectra in dichloromethane solution were recorded at 298 K on a Unicam UV/Vis 2.

Synthesis

Preparation of AuBr(PPh$_2$CCH) (2). To a 10 mL dichloromethane solution of AuBr(AsPh$_3$)[29] (0.117 g, 0.2 mmol) was added PPh$_2$CCH[14] (0.042 g, 0.2 mmol). After stirring for 1 h, the solution was evaporated to dryness. The white residue was washed with a 1:1 mixture of diethyl ether–pentane (2 × 5 mL) to remove AsPh$_3$. Yield of **2**: 73 mg, 75%. Found: C, 34.45; H, 2.1. C$_{14}$H$_{11}$AuBrP requires: C, 34.5; H, 2.3%; *M* = 487. IR: 3275, 3245 [m, ν(CC–H)], 2056 [m, ν(CC)] cm^{-1}. δ_H 3.48 [d, ^3J(HP) = 8.4 Hz, 1H, CH], 7.54 (m, 6H, Ph), 7.81 (m, 4H, Ph); δ_P 6.0. FAB$^-$ (*m*/*z*, %, assignment): 357 (73, [AuBr$_2$]$^-$), 485 (100, [M − H]$^-$), 763 (55, [Au$_2$Br2(PPh$_2$CC)]$^-$). FAB$^+$ (*m*/*z*, %, assignment): 407 (100, [Au(PPh$_2$CCH)]$^+$), 617 (29, [Au(PPh$_2$CCH)$_2$]$^+$). Λ = 11 ohm^{-1} cm^2 mol^{-1}.

Preparation of AuI(PPh$_2$CCH) (3). To a 10 mL dichloromethane solution of AuI(AsPh$_3$)[29] (0.063 g, 0.1 mmol) was added PPh$_2$CCH (0.021 g, 0.1 mmol). After stirring for 1 h, the

Table 4 Details of crystal data and structure refinement for complexes **1**, **3** and **4**

Compound	AuCl(PPh$_2$CCH)	AuI(PPh$_2$CCH)	Au(C$_6$F$_5$)(PPh$_2$CCH)
Empirical formula	C$_{14}$H$_{11}$AuClP	C$_{14}$H$_{11}$AuIP	C$_{20}$H$_{11}$AuF$_5$P
Formula weight	442.61	534.06	574.22
T/K	173(2)	173(2)	173(2)
λ/Å	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a/Å	8.7918(12)	16.395(2)	7.579(2)
b/Å	8.9684(12)	9.7397(14)	11.630(3)
c/Å	10.1562(12)	19.349(3)	11.671(3)
α/°	66.767(8)	90	117.21(2)
β/°	78.197(11)	105.996(12)	98.80(2)
γ/°	71.630(11)	90	96.50(2)
V/Å^3	695.40(16)	2970.0(7)	884.3(4)
Z	2	8	2
D_c/Mg m^{-3}	2.114	2.389	2.157
μ/mm^{-1}	10.859	12.070	8.460
$F(000)$	412	1936	540
Crystal habit	Irregular prism	Tablet	Irregular tablet
Crystal size/mm	0.35 × 0.2 × 0.2	0.40 × 0.35 × 0.15	0.35 × 0.3 × 0.2
θ Range for data collection/°	3.02 to 27.49	3.03 to 25.00	3.03 to 25.00
Index ranges	$-10 \leqslant h \leqslant 10$	$-18 \leqslant h \leqslant 19$	$-8 \leqslant h \leqslant 9$
	$-10 \leqslant k \leqslant 10$	$-11 \leqslant k \leqslant 0$	$-12 \leqslant k \leqslant 12$
	$-13 \leqslant l \leqslant 13$	$-22 \leqslant l \leqslant 0$	$-13 \leqslant l \leqslant 13$
Reflections collected	4312	5467	3523
Independent reflections	3099 (R_{int} = 0.0195)	5233 (R_{int} = 0.0562)	2938 (R_{int} = 0.0349)
Max. and min. transmission	0.985 and 0.645	0.980 and 0.359	0.923 and 0.608
Data/restraints/parameters	3099/41/158	5233/82/307	2938/73/247
Goodness-of-fit on F^2	0.945	0.818	1.123
R_1 [$I > 2\sigma(I)$][a]	0.0236	0.0472	0.0382
wR_2 (all data)[b]	0.0502	0.1020	0.1005
Largest diff. peak and hole/e Å^{-3}	1.054 and −0.774	1.524 and −1.334	1.938 and −1.996

[a] $R_1(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2(F^2) = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma\{w(F_o^2)^2\}]^{0.5}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = [F_o^2 + 2F_c^2]/3$ and a and b are constants adjusted by the program.

solution was evaporated to dryness. The pale yellow residue was washed with a 1:1 mixture of diethyl ether–pentane (2 × 5 mL) to remove AsPh$_3$. Yield of **3**: 43 mg, 80%. Found: C, 27.7; H, 2.0. C$_{14}$H$_{11}$AuIP requires: C, 27.4; H, 1.8%; M = 534.1. IR: 3275, 3172 [m, ν(CC–H)], 2049 [m, ν(CC)] cm^{-1}. δ_H 3.49 [d, ^3J(HP) = 8.2 Hz, 1H, CH], 7.52 (m, 6H, Ph), 7.83 (m, 4H, Ph); δ_P 10.2. FAB$^-$ (m/z, %, assignment): 451 (50, [AuI$_2$]$^-$), 533 (100, [M − H]$^-$), 857 (36, [Au$_2$I$_2$(PPh$_2$CC)]$^-$). FAB$^+$ (m/z, %, assignment): 407 (100, [Au(PPh$_2$CCH)]$^+$), 617 (63, [Au(PPh$_2$CCH)2]$^+$), 941 (32, [Au$_2$I(PPh$_2$CCH)$_2$]$^+$). Λ = 15 ohm^{-1} cm^2 mol^{-1}.

Preparation of Au(C$_6$F$_5$)(PPh$_2$CCH) (4). To a 20 mL dichloromethane solution of Au(C$_6$F$_5$)(tht)[30] (0.226 g, 0.5 mmol) was added PPh$_2$CCH (0.105 g, 0.5 mmol). After stirring for 2 h, the solution was concentrated to *ca.* 2 mL and the addition of petroleum ether afforded **4** as a white solid that was washed with petroleum ether. Yield of **4**: 235 mg, 82%. Found: C, 41.85; H, 1.7. C$_{20}$H$_{11}$AuF$_5$P requires: C, 41.85; H, 1.95%; M = 574.2. IR: 3271 [s, ν(CC–H)], 2056 [s, ν(CC)], 951 (s, C$_6$F$_5$), 792 (s, C$_6$F$_5$) cm^{-1}. δ_H 3.46 [d, ^3J(HP) = 7.7 Hz, 1H, CH], 7.53 (m, 6H, Ph), 7.88 (m, 4H, Ph); δ_F −117.0 (m, 2F$_o$), −159.0 (t, 1F$_p$), −163.4 (m, 2F$_m$); δ_P 17.2 (s). FAB$^-$ (m/z, %, assignment): 531 (100, [Au(C$_6$F$_5$)$_2$]$^-$), 573 (40, [M − H]$^-$), 937 (52, [Au$_2$(C$_6$F$_5$)$_2$(PPh$_2$CC)]$^-$), 1343 (17, [Au$_3$(C$_6$F$_5$)$_2$(PPh$_2$CC)$_2$)]$^-$). FAB$^+$ (m/z, %, assignment): 407 (100, [Au(PPh$_2$CCH)]$^+$), 574 (23, [M]$^+$), 981 (20, [Au$_2$(C$_6$F$_5$)(PPh$_2$CCH)$_2$]$^+$). Λ = 2 ohm^{-1} cm^2 mol^{-1}.

Preparation of [Au(C$_6$F$_5$)(PPh$_2$CC)Au(C$_6$F$_5$)][N(PPh$_3$)$_2$] (6). To a 15 mL methanol solution of Au(C$_6$F$_5$)(PPh$_2$CCH) (57 mg, 0.1 mmol) was added NaOMe (6 mg, 0.1 mmol). After stirring for 2 h, [Au(C$_6$F$_5$)Cl][N(PPh$_3$)$_2$][15] was added and the solution stirred for an additional hour. The solvent was removed, dichloromethane was added, then the mixture was filtered through celite. The clear solution was evaporated to dryness to give a white residue. Yield of **6**: 140 mg, 95%. Found: C, 50.85; H, 3.0; N, 0.95. C$_{62}$H$_{40}$Au$_2$F$_{10}$NP$_3$ requires: C, 50.45; H, 2.75; N, 0.95%; M = 1475.8. IR: 2056 [s, ν(CC)], 950 (s, C$_6$F$_5$), 807 (s, C$_6$F$_5$), 790 (s, C$_6$F$_5$) cm^{-1}. δ_H 7.3–8.0 (m, Ph); δ_F −115.9 (m, 2F$_o$), −116.2 (m, 2F$_o$), −160.7 (t, 1F$_p$), −163.2 (t, 1F$_p$), −164.0 (m, 2F$_m$), −165.2 (m, 2F$_m$); δ_P 14.6 (s, 1P, PPh$_2$), 21.8 (s, 2P, PPh$_3$). FAB$^-$ (m/z, %, assignment): 531 (76, [Au(C$_6$F$_5$)$_2$]$^-$), 573 (38, [Au(C$_6$F$_5$)(PPh$_2$CC)]$^-$), 937 (100, [M–N(PPh$_3$)$_2$]$^-$), 1343 (30, [Au$_3$(C$_6$F$_5$)$_2$(PPh$_2$CC)$_2$]$^-$). Λ = 105 ohm^{-1} cm^2 mol^{-1}.

Crystal structure determination of 1, 3 and 4

Crystal data and details of data collection and structure refinement of AuCl(PPh$_2$CCH) **1**, AuI(PPh$_2$CCH) **3** and Au(C$_6$F$_5$)(PPh$_2$CCH) **4** are given in Table 4. Single crystals of AuCl(PPh$_2$CCH), AuI(PPh$_2$CCH) and Au(C$_6$F$_5$)(PPh$_2$CCH) were obtained by slow diffusion, of diethyl ether into an acetone solution, of pentane into a dichloromethane solution, and of hexane into a diethyl ether solution, respectively. They were mounted in inert oil and transferred to the cold gas stream of the diffractometer. Data were measured on a Siemens P4 diffractometer. Absorption corrections were based on ψ-scans (program XEMP). The structures were refined anisotropically on F^2 (program SHELXL-97)[31] using a system of restraints (to light-atom U values and local ring symmetry). H atoms were included using a riding model (exceptions: acetylenic H atoms of **1** and **4**, freely refined).

CCDC reference numbers 186042–186044.

See http://www.rsc.org/suppdata/dt/b2/b204791h/ for crystallographic data in CIF or other electronic format.

Acknowledgements

We thank the Dirección General de Investigación Científica y Técnica (Project BQU2001-2409-C02-01) and the Fonds der Chemischen Industrie for financial support. We also thank

Dr J. Galbán (Universidad de Zaragoza, Spain) for kindly providing apparatus facilities.

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