Available online at www.sciencedirect.com

SCIENCE DIRECT®

Inorganica Chimica Acta 358 (2005) 1365–1372

Inorganica Chimica Acta

www.elsevier.com/locate/ica

Luminescent dinuclear gold complexes of bis(diphenylphosphano)acetylene

Manuel Bardají [a,b], M. Teresa de la Cruz [a], Peter G. Jones [c], Antonio Laguna [a,*], Julia Martínez [a], M. Dolores Villacampa [a]

[a] *Departamento de Química Inorgánica, Facultad de Ciencias, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC, E50009 Zaragoza, Spain*

[b] *Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, 47005 Valladolid, Spain*

[c] *Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Postfach 3329, D-38023 Braunschweig, Germany*

Received 2 April 2004; accepted 1 May 2004

Available online 26 June 2004

Dedicated to F. Gordon, A. Stone

Abstract

We have synthesized a series of dinuclear gold(I) derivatives with the diphosphane bis(diphenylphosphano)acetylene, namely $[(AuX)_2(\mu\text{-dppa})]$ (X = Cl, C_6F_5, SC_6F_5, $S_2CN(CH_2Ph)_2$). X-ray structure determinations for the first three derivatives reveal a linear geometry for the gold centres. There are no intramolecular gold–gold interactions, although for X = Cl intermolecular gold(I)–gold(I) interactions of 3.0694(4) Å lead to an infinite twisted chain; the further presence of C–H···Cl contacts leads to a more complex three-dimensional structure. All the derivatives are luminescent in the solid state at low temperature in the range 455–593 nm; most of them are emissive at room temperature in the range 470–598 nm. We have also prepared the dinuclear gold(III) derivative $[(Au(C_6F_5)_3)_2(\mu\text{-dppa})]$. Finally, we have prepared the derivative $[(AuCl)_2(\mu\text{-dppa})_3]$, which forms a cage with two tetrahedrally coordinated gold(I) centres at the apical positions bridged by three rigid diphosphane ligands, with a helical twist of 26.2°, and a gold–gold distance of 5.769 Å. The gold(III) and the four-coordinate gold(I) derivatives are not luminescent.

Keywords: Gold; Aurophilicity; Diphosphane ligands; Luminescence

1. Introduction

The vast majority of gold(I) complexes are two-coordinate, linear, 14-electron species, whereas three- and especially four-coordinate species are less common [1]. Linear gold(I) complexes can group by means of aurophilic interactions to give supramolecular structures, such as pairs, rings, chains or layers, which are not present for the higher coordination numbers [2]. The aggregation of gold(I) monomers can also be based on hydrogen bonds [3] or a combination of aurophilic and hydrogen bonds [4].

Diphosphane ligands in gold(I) derivatives can act in chelating mode, typically $[Au(PR_2ZPR_2)_2]^+$ (Z = CH_2, $(CH_2)_n$, NH···) or in bridging mode; the latter usually affords dinuclear derivatives, namely $[(AuX)_2(\mu\text{-}PR_2ZPR_2)]$ and $[Au_2(\mu\text{-}R_2ZPR_2)_2]^{2+}$ [5]. Much less common is the formation of polymers $[\{Au(\mu\text{-}PR_2ZPR_2)\}_n]^{n+}$ or even catenanes or metallocryptands [6].

The replacement of a proton by an $AuPR_3^+$ fragment is a well-established synthetic procedure, which has been thoroughly used in cluster chemistry [7]. In the same way, $AuPR_2ZPR_2Au^{2+}$ fragments have been used, e.g., the $Au(dppa)Au^{2+}$ unit (dppa = bis(diphenylphosphano)acetylene) [8] obtained from the chloro derivative [9].

In this paper, we report the synthesis and structural characterization of a series of dinuclear gold(I) derivatives $[(AuX)_2(\mu\text{-dppa})_n]$ (n = 1, 3), which present line-

---

[*] Corresponding author. Tel.: +34-976-761185; fax: +34-976-761187.
E-mail address: alaguna@unizar.es (A. Laguna).

0020-1693/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.ica.2004.05.017

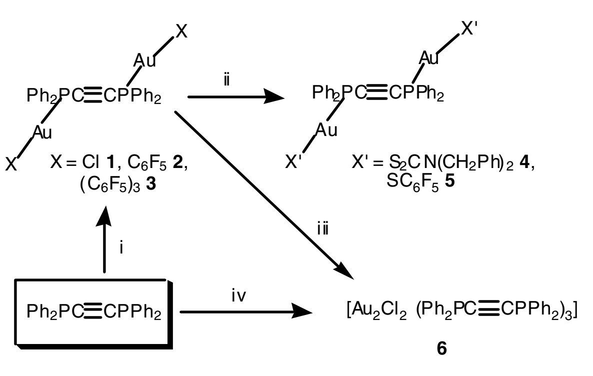
arly coordinated gold(I) centres for $n = 1$. In the case of $X = Cl$, a different supramolecular structure is observed because of aurophilic and hydrogen interactions. For $n = 3$, the one structure displays a helical cage with tetrahedrically coordinated gold(I) centres at the apical vertices. All the dicoordinated gold(I) complexes are photoluminescent in the solid state, whereas the tetracoordinated gold(I) and gold(III) complexes are not emissive.

2. Results and discussion

2.1. Synthesis and characterization

As stated in the introduction, complex **1** had been synthesized in a different way [9]. The reaction of bis(diphenylphosphano)acetylene with the corresponding gold(I) or gold(III) tht (tht = tetrahydrothiophene) derivative, in molar ratio 1:2, proceeds by displacing the tht ligand to give complexes **1**–**3**. Treatment of complex **1** with sodium dithiocarbamate or thiolate leads to derivatives **4**–**5**, by means of a substitution reaction. The reaction of the diphosphane with AuCl(tht) in a 3:2 molar ratio affords complex **6**, which can be also synthesized by reaction of diphosphane and complex **1** (see Scheme 1). The addition of an excess of diphosphane and work-up, as described in the Section 4, leads to the isolation of derivative **6**. However, in situ addition of diphosphane to [AuCl(tht)], monitored by phosphorus NMR at low temperature, leads to complex **6**, but when more diphosphane is added the spectrum shows complicated mixtures containing free phosphane arms coupled to coordinated phosphane arms. The reaction of diphosphane and [AuCl(tht)] in molar ratio 1:1 allows the isolation of a product with stoichiometry $[(AuCl)_2(\mu\text{-dppa})_2]$, but the phosphorus NMR spectrum at low temperature shows a mixture of **1** and **6**.

These complexes are air- and moisture-stable white or yellow (**4**) solids at room temperature. They were readily characterized by elemental analysis, IR and NMR spectroscopies. IR spectra show the presence of Au–Cl bonds for derivative **1**, but not for derivative **6**. The ^{19}F NMR spectra show the presence of one type of pentafluorophenyl gold(I) or tris(pentafluorophenyl)gold(III) units for complexes **2** or **3**, respectively. A singlet is always observed in the phosphorus spectra, the chemical displacement following the sequence: $C_6F_5 > SC_6F_5 > Cl > S_2CN(CH_2Ph)_2 > (C_6F_5)_3 > Cl(dppa)_3$.



Scheme 1. (i) +2[AuX(tht)] − 2tht; (ii) +2NaX′ − 2NaX; (iii) $+2PPh_2CCPPh_2$; (iv) +2/3[AuCl(tht)] − 2/3tht.

2.2. Crystal structures

The molecular structures of $[(AuX)_2(\mu\text{-dppa})]$, where $X = Cl$ (**1**), C_6F_5 (**2**), SC_6F_5 (**5**), were determined by X-ray diffraction studies. Compound **5** is a chloroform solvate. Structural parameters are set out in Table 1. Despite the similarities in molecular structures, complex **1** displays a more complicated intermolecular organization. The three dinuclear molecules display crystallographic inversion symmetry, with the inversion centre lying at the midpoint of the acetylenic C≡C bond. The gold(I) centres display an almost linear coordination with P–Au–X angles around 176° (see Fig. 1). There are no short intramolecular gold–gold contacts, the intramolecular gold–gold distance being 7.792 (**1**), 7.639 (**2**) and 7.412 Å (**5**) because of the *trans* conformation of the diphosphane, which is preferred to minimize steric hindrance; besides, a *cis* conformation would not lead to gold–gold interactions because of the long and rigid bridge. The Au–P distance displays a *trans* influence in the sequence $Cl < SC_6F_5 < C_6F_5$. The Au–Cl distance in **1** of 2.2928(11) Å compares well with those reported in $[AuCl(PPh_2CH_2SiMe_3)]$ (2.292(2) Å) [10] or in $[AuCl(PPh_2CCH)]$ (2.2892(12) Å) [11]. The Au–C bond length in **2** is 2.045(8) Å, similar to those found in $[Au(C_6F_5)(PPh_2CCH)]$ [11] or in $[(AuC_6F_5)_2(\mu\text{-dppm})]$

Table 1
Selected bond lengths (Å) and angles (°) for compound **1**, **2** and **5**

Compound **1**			
Au–P	2.2354(10)	P–Au–Cl	175.20(4)
Au–Cl	2.2928(11)	P–Au–Au#1	107.32(3)
Au–Au#1	3.0694(4)	Cl–Au–Au#1	77.47(3)
C(1)–C(1)#2	1.200(8)	C(1)#2–C(1)–P	177.8(5)
Compound **2**			
Au–C(31)	2.045(8)	C(1)–C(1)#1	1.200(16)
Au–P	2.2713(19)		
C(31)–Au–P	175.8(2)	C(1)#1–C(1)–P	176.1(10)
Compound **5**			
Au–P	2.2483(7)		
Au–S	2.3193(7)		
C(1)–C(1)#1	1.209(5)		
P–Au–S	175.94(2)		
C(11)–S–Au	107.62(10)		
C(1)#1–C(1)–P	174.0(3)		

Symmetry transformations used to generate equivalent atoms: #1 $-x+1, y, -z+1/2$; #2 $-x+1, -y+2, -z+1$ (compound **1**), #1 $-x+1, -y+1, -z+2$ (compound **2**), #1 $-x+1, -y+1, -z$ (compound **5**).

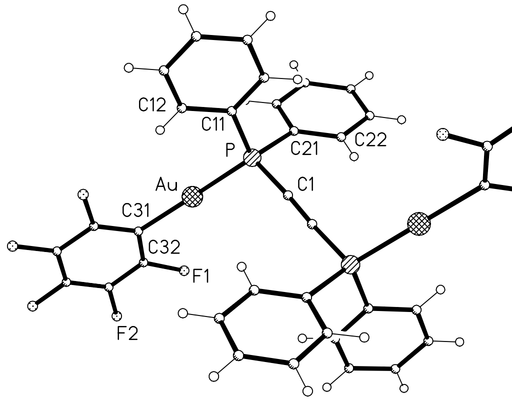


Fig. 1. Molecular structure of complex **2**.

[12]. The Au–S bond length in **5** is 2.3193(7) Å, close to those reported in thiolato-phosphano gold(I) complexes. The acetylenephosphano ligand shows almost linear angles P–C–C, from 174.0(3)° in complex **5** to 177.8(5)° in complex **1**. The central C–C distances of around 1.200 Å are consistent with a triple bond.

As stated above, derivatives **2** and **5** are discrete molecules whilst derivative **1** shows intermolecular gold(I)–gold(I) interactions of 3.0694(4) Å via a twofold axis, leading to an infinite twisted chain with a ladder-like form in projection (Fig. 2). The existence of intermolecular gold–gold contacts in the absence of intramolecular gold-gold contacts is less common in diphosphanogold(I) derivatives and has usually been observed for diphosphanes bridged by longer carbon chains, such as $PPh_2(CH_2)_nPPh_2$ $n = 3$ [13], 5 [6c,14], 8 [15], and for bis(diphenylphosphano)ethene [6d,16]. A similar infinite chain, arising from aurophilic interactions, has been observed for $[(AuSPh)_2(\mu\text{-}PPh_2CH{=}CHPPh_2)]$ and $[(AuCl)\,(AuSPh)(\mu\text{-}PPh_2CH{=}CHPPh_2)]$ [16]. In addition, complex **1** displays several C–H···Cl contacts, one particularly short, that could be interpreted as hydrogen bonds (Table 2). These interactions connect the chains. This is an example of a cooperative effect of aurophilic interactions and hydrogen bonds to give a supramolecular structure. In compound **5**, the chloroform molecule, although disordered over an inversion centre, is hydrogen bonded to one or the other of two sulfur atoms, with H···S 2.87 Å, C–H···S 168°.

The crystal structure of complex **6** $[(AuCl)_2(\mu\text{-dppa})_3]$ is shown in Fig. 3, with selected bond lengths and angles in Table 3. Compound **6** is a monohydrate. The structure shows a cage capped by two chlorine atoms and two gold atoms triply bridged by the dppa ligands. The gold(I) centres are four-coordinate and display a distorted tetrahedral environment with P–Au–P and P–Au–Cl angles lying in the range 102.87(3)–122.99(3)°.

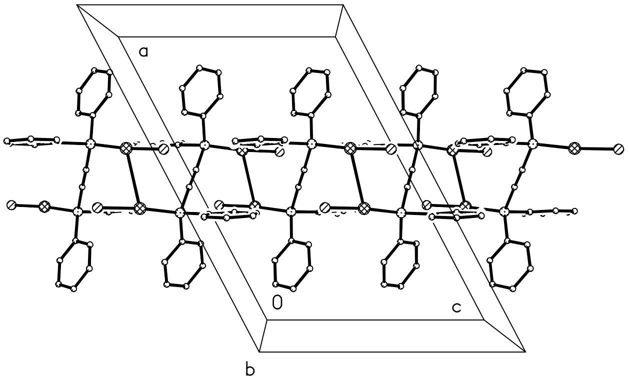


Fig. 2. View of the chain of complex **1**.

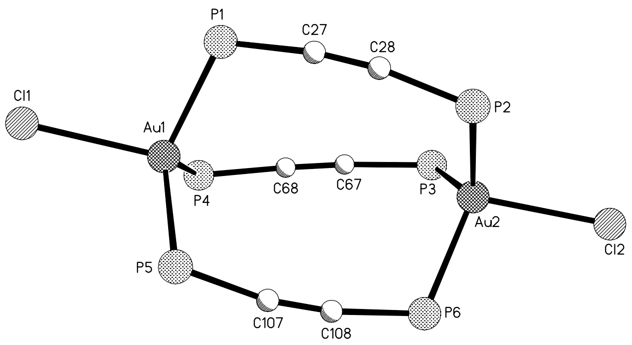


Fig. 3. Molecular structure of complex **6**. Phenyl rings and hydrogen atoms have been omitted for clarity.

Table 2
Hydrogen bonds for compound **1** and **6** (Å) and (°)

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠(DHA)
Compound **1**				
C(25)–H(25)···Cl#3	0.95	2.76	3.664(5)	160.1
C(14)–H(14)···Cl#4	0.95	2.92	3.563(5)	126.5
C(15)–H(15)···Cl#4	0.95	2.95	3.577(5)	124.5
Compound **6**				
C(43)–H(43)···Cl(1)#1	0.93	2.86	3.551(3)	131.9
C(84)–H(84) Cl(2)#2	0.93	2.80	3.580(3)	142.5
O(1)–H(1)···Cl(1)	1.077(4)	2.42(4)	3.330(3)	141.8(3)
O(1)–H(2)···Cl(2)#3	0.903(4)	2.38(4)	3.239(3)	158.6(4)

Symmetry transformations used to generate equivalent atoms: #3 $-x+1/2, y+1/2, -z+1/2$; #4 $x, y, z+1$ (compound **1**), #1 $x-1/2, -y+3/2, z-1/2$; #2 $x+1/2, -y+3/2, z+1/2$; #3 $x-1/2, -y+3/2, z+1/2$ (compound **6**).

Table 3
Selected bond lengths (Å) and angles (°) for compound **6**

Au(1)–P(5)	2.3424(8)	Au(2)–P(3)	2.3660(8)
Au(1)–P(1)	2.3721(8)	Au(2)–Cl(2)	2.6378(8)
Au(1)–P(4)	2.4068(8)	C(27)–C(28)	1.191(4)
Au(1)–Cl(1)	2.6399(8)	C(67)–C(68)	1.194(4)
Au(2)–P(2)	2.3412(8)	C(107)–C(108)	1.200(4)
Au(2)–P(6)	2.3659(8)		
P(5)–Au(1)–P(1)	122.99(3)	P(2)–Au(2)–Cl(2)	105.09(3)
P(5)–Au(1)–P(4)	112.36(3)	P(6)–Au(2)–Cl(2)	102.87(3)
P(1)–Au(1)–P(4)	103.76(3)	P(3)–Au(2)–Cl(2)	103.48(3)
P(5)–Au(1)–Cl(1)	107.45(3)	C(28)–C(27)–P(1)	172.1(3)
P(1)–Au(1)–Cl(1)	103.36(3)	C(27)–C(28)–P(2)	170.2(3)
P(4)–Au(1)–Cl(1)	105.38(3)	C(68)–C(67)–P(3)	171.1(3)
P(2)–Au(2)–P(6)	117.34(3)	C(67)–C(68)–P(4)	173.1(3)
P(2)–Au(2)–P(3)	118.58(3)	C(108)–C(107)–P(5)	170.0(3)
P(6)–Au(2)–P(3)	107.30(3)	C(107)–C(108)–P(6)	171.7(3)

The intramolecular gold–gold distance is 5.769 Å and the tetracoordination prevents any intermolecular gold–gold interaction. The three acetylenephosphane bridges display P–C–C angles lying in the range 170.0(3)–173.1(3)°, slightly bent compared to those of complexes **1**, **2** and **5** and C–C triple bond lengths in the range 1.191(4)–1.200(4) Å, similar to the above structures. The cage shows a helical twist of 26.2°, about the Au···Au axis, calculated as the average of the torsion angles P(1)–Au(1)–Au(2)–P(2), P(3)–Au(2)–Au(1)–P(4) and P(5)–Au(1)–Au(2)–P(6). This structure is close to those reported for silver(I) complexes with the same diphosphane, namely [Ag_2(μ-dppa)$_3$(anion)$_2$] (anion = SbF_6, BF_4, O_3SCF_3 or NO_3), where silver centres have a trigonal geometry but tetrahedrically distorted because of Ag–anion contacts and a helical twist of 33°, 27°, 35.3° and 28.6°, respectively [17]. The related copper complex [(CuTe^{n}Bu)$_2$(μ-dppa)$_3$] also presents a helical twist of 23.6° and a similar structure to complex **6** [18]. However, the related structure [(AuI)$_2$(μ-P_2pz)$_3$] (P_2pz = 3,6-bis(diphenylphosphano)pyridazine) does not show this helical twist and crystallizes in a hexagonal space group with only one-sixth of the molecule being crystallographically unique [6g].

The Au–P bond lengths range from 2.3412(8) to 2.4068(8) Å, much longer than those found in the two-coordinate complexes **1**, **2** and **5**, but in a similar range to those reported in other four-coordinate complexes such as [AuCl(PPh_3)$_3$] (2.395(2)–2.431(2) Å) [19], [{(AuCl)$_2$(μ-L)}$_n$] (L = *p-tert*-butyl-calix[4]-(OCH_2PPh_2)$_4$; 2.371(2)–2.384(2) Å) [20], [{(AuCl)$_2$(μ-P_2pz)$_3$}$_n$] (2.3683(6) Å) [6g] and in the similar cage structure [(AuI)$_2$(μ-P_2pz)$_3$] (2.417(4) Å) [6g]. The Au–Cl distances of 2.6378(8) and 2.6399(8) Å are clearly longer than standard covalent Au(I)–Cl bond lengths in two-coordinate derivatives, as found in complex **1** (2.2928(11) Å), although slightly shorter than reported in [AuCl(PPh_3)$_3$] (2.710(2) Å) [19], [{(AuCl)$_2$(μ-P_2pz)$_3$}$_n$] (2.7026(10) Å) [6g] and shorter than in [{(AuCl)$_2$(μ-L)}$_n$] (3.012(6) Å) [20]. This long (and presumably weak) bond should explain why the Au–Cl vibration is not observed by IR spectroscopy. Additionally, complex **6** displays two classical hydrogen bonds of the form Cl···H–O (water) (H···Cl1 2.42 Å and O–H···Cl1 142°; H···Cl2 2.38 Å and O–H···Cl2 159°).

2.3. Photophysical studies

The absorption spectra in dichloromethane were measured in the range 200–600 nm and the results are summarized in Table 4. All the spectra are dominated by an absorption around 230 nm from the phenyl phosphane rings [21]. There is also an absorption around 277 nm, which is already observed in the diphosphane ligand, and it could be assigned to a π–π^* transition, although this could be complicated by transitions of the pentafluorophenyl or thiolate ligands in derivatives **2**–**5**. The thiolato derivatives **4**–**5** also display an intense absorption at 300 nm, which could be related to sulfur to gold charge transfer transitions [22].

We have studied the photoluminescence of these products in the solid state and the results are summarized in Table 5. Emission spectra of derivatives **1**, **4** and **5** at low temperature are plotted in Fig. 4. Derivatives **1**, **2** and **4** emit weakly at room temperature, whereas they and derivative **5** emit intensely at 77K; the diphosphane does not emit under the same conditions. The cooling produces a 701 cm^{-1} blue shift in the emission of complex **1**, a 476 cm^{-1} red shift for **2** and a 141 cm^{-1} blue shift in the emission of complex **4**. Only complex **1** has gold–gold interactions in the solid state and therefore, to explain the luminescence of complexes **1** and **2**, a ligand-centred transition modified by the anionic ligands and the gold(I) centres can be suggested, as has been already proposed for the series [{AuXPPhMe$_2$}$_n$] (X = Cl, Br, I; n = 2, 3) or [AuX(ER_3)] (X = Cl, Br; E = P, As) [23]; however, a metal–metal centred transition, as suggested for most luminescent diphosphane gold(I) complexes, could also be possible for complex **1** [24]. The emission observed for thiolato derivatives **4**–**5** is usually assigned to a thiolato to gold charge transfer transition, which is changed by varying the nature of the substituents of the thiolate ligand [25].

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

Complex	λ (nm) (ε/M^{-1} cm^{-1})
PPh_2CCPPh_2	230 (31800), 244 (30100), 277 (sh, 9500)
1	230 (51600), 270 (sh, 8170), 277 (sh, 5840)
2	233 (70100), 258 (sh, 71410), 277 (sh, 7400)
3	229 (71800), 277 (34560)
4	231 (66400), 277 (48140), 295 (sh, 37640)
5	233 (79550), 268 (sh, 31440), 301 (sh, 13570)
6	234 (117660), 267 (sh, 42250), 276 (sh, 31080)

[a] In CH_2Cl_2 solution, 5×10^{-5} M.

Table 5
Excitation and emission data in the solid state for luminescent complexes **1**–**2** and **4**–**5**

Complex	298 K		77 K	
	λ_{exc} (nm)	λ_{emis} (nm)	λ_{exc} (nm)	λ_{emis} (nm)
1	309	470	304	455
2	370	516	355	529
4	457, 467	598	458, 465	593
5			355, 393	551

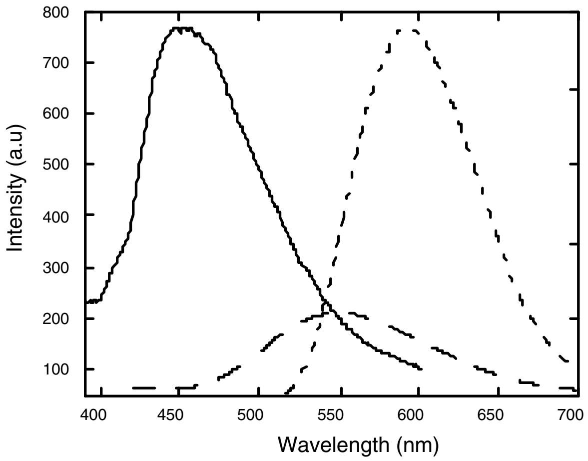


Fig. 4. Emission spectra of derivatives **1** (—), **4** (- -) and **5** (– –) at low temperature in the solid state.

3. Conclusions

We have shown that dinuclear derivatives [(AuX)$_2$(μ-dppa)] (X = Cl, C_6F_5, $S_2CN(CH_2Ph)_2$, SC_6F_5) containing a rigid PCCP unit can be found as monomers without any obvious intra- or intermolecular interactions, but also be linked to a chain and then to a three-dimensional structure by intermolecular gold(I)–gold(I) and hydrogen bonding interactions, as has been reported for diphosphano-gold(I) derivatives with long alkyl chain bridges. Additionally, the use of this rigid diphosphane allows us to prepare [(AuCl)$_2$(μ-dppa)$_3$] as a helical twisted cage, with two tetrahedrically coordinated gold(I) centres at the apical positions bridged by three diphosphane ligands. Most of these complexes are photoluminescent.

4. Experimental

4.1. General procedures

All the reactions were carried out under an argon atmosphere at room temperature. IR spectra were recorded on a Perkin–Elmer Spectrum One and a Brücker Equinox 55 spectrophotometers, over the range 4000–200 cm^{-1}, by using Nujol mulls between polyethylene sheets or KBr pellets. ^{1}H, ^{19}F and ^{31}P{^{1}H} NMR spectra were recorded on a Bruker ARX · 300 or GEMINI 2000 apparatus; chemical shifts are quoted relative to $SiMe_4$ (external, ^{1}H), $CFCl_3$ (external, ^{19}F) and 85% H_3PO_4 (external, ^{31}P). C, H, N and S analyses were performed with a Perkin–Elmer 2400 microanalyzer. The luminescence spectra were recorded on a Perkin–Elmer LS-55 spectrofluorometer. UV–Vis absorption spectra in dichloromethane solution were recorded at 298 K on a Shimadzu UV-1603.

*4.2. Preparation of [(AuX)$_2$(μ-dppa)] X = Cl (**1**), C_6F_5 (**2**), $(C_6F_5)_3$ (**3**)*

To a 30 mL dichloromethane solution of [AuX(tht)] (tht = tetrahydrothiophene; X = Cl, 0.4 mmol 128 mg; C_6F_5 0.2 mmol, 90 mg) [26,27] or [Au(C_6F_5)$_3$(tht)] (157 mg, 0.2 mmol) [26] was added bis(diphenylphosphane)acetylene (78 mg, 0.2 mmol for X = Cl; 39 mg, 0.1 mmol). After stirring for 1 h, derivative **1** was filtered off as a white powder. The solution was concentrated to ca. 3 mL and further addition of hexane afforded complexes **1** (second fraction), **2** and **3** as white solids. Yield of **1**: 90%. ^{1}H NMR (300 MHz, $CDCl_3$, 21 °C): δ 7.47–7.79 (m, Ph); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, 21 °C): δ 5.5 (s). ^{31}P{^{1}H} NMR (−50 °C): δ 5.1 (s). IR: 326 (m, ν(Au–Cl)) cm^{-1}. Found: C, 36.1; H, 2.25%. $C_{26}H_{20}Au_2Cl_2P_2$ requires: C, 36.35; H, 2.35%. Yield of **2**: 83%. IR: 955, 785 (s, C_6F_5) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, 21 °C): δ 7.29–7.79 (m, Ph); ^{1}F NMR (282 MHz, $CDCl_3$, 21 °C): δ-117.1 (m, 2F$_o$), −158.7 (t, $^3J_{FF}$ = 20.0 Hz, 1F$_p$), −163.2 (m, 2F$_m$); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, 21 °C): δ 18.4 (s). Found: C, 40.35; H, 2.0%. $C_{38}H_{20}Au_2F_{10}P_2$ requires: C, 40.65; H, 1.8%. Yield of **3**: 76%. IR: 969, 793 (s, C_6F_5) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, 21 °C): δ 7.43–7.79 (m, Ph); ^{1}F NMR (282 MHz, $CDCl_3$, 21 °C): δ −121.4 (m, 4F$_o$), −122.8 (m, 2F$_o$), −156.2 (t, $^3J_{FF}$ = 20.1 Hz, 2F$_p$), −157.2 (t, $^3J_{FF}$ = 20.1 Hz, 1F$_p$), −161.0 (m, 4F$_m$), −161.7 (m, 2F$_m$); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, 21 °C): δ −1.1 (s). Found: C, 41.75; H, 1.25%. $C_{62}H_{20}Au_2F_{30}P_2$ requires: C, 41.6; H, 1.15%.

*4.3. Preparation of [{Au($S_2CN(CH_2Ph)_2$)}$_2$(μ-dppa)] (**4**)*

To a dichloromethane suspension (20 mL) of **1** (86 mg, 0.1 mmol) was added $NaS_2CN(CH_2Ph)_2$ (0.2 mmol, 59 mg). The mixture was stirred for about 2 h, then filtered through celite. Concentration to ca. 2 mL and addition of hexane (20 mL) afforded complex **4** as a yellow solid. Yield: 67%. IR: 1494 (s, C=N) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, 21 °C): δ 7.37–7.86 (m, 40H, Ph), 5.15 (s, 8H, CH_2–N); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, 21 °C): δ 3.1 (s). Found: C, 50.25; H, 3.55; N, 2.0; S, 9.3%. $C_{56}H_{48}Au_2N_2P_2S_4$ requires: C, 50.45; H, 3.65; N, 2.1; S, 9.6%.

*4.4. Preparation of [{Au(SC$_6$F$_5$)}$_2$(μ-dppa)] (**5**)*

To a dichloromethane suspension (20 mL) of **1** (86 mg, 0.1 mmol) was added a methanol solution (10 mL) of $NaSC_6F_5$ (0.2 mmol, prepared in situ with HSC_6F_5 and NaOMe). The mixture was stirred for about 2 h, then evaporated to dryness. Extraction with dichloromethane, concentration to ca. 3 mL and addition of hexane (20 mL) afforded complex **5** as a white solid. Yield: 67%. ^{1}H NMR (300 MHz, $CDCl_3$, 21 °C): δ 7.49–7.79 (m, Ph); ^{1}F NMR (282 MHz, $CDCl_3$, 21 °C): δ −132.7 (m, $2F_o$), −162.2 (t, $^{3}J_{FF} = 20.3$ Hz, $1F_p$), −164.2 (m, $2F_m$); $^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$, 21 °C): δ 11.1 (s). Found: C, 38.15; H, 1.7; S, 5.0%. $C_{38}H_{20}Au_2F_{10}P_2S_2$ requires: C, 38.45; H, 1.7; S, 5.4%.

*4.5. Preparation of [(AuCl)$_2$(μ-dppa)$_3$] (**6**)*

This derivative has been obtained by two ways: (a) to a 40 mL dichloromethane solution of [AuCl(tht)] (100 mg, 0.31 mmol) was added bis(diphenylphosphane)acetylene (185 mg, 0.47 mmol). After stirring for 1 h, the solution was concentrated to ca. 5 mL and addition of hexane afforded complex **6** as a white solid. (b) To a 20 mL dichloromethane suspension of **1** (86 mg, 0.1 mmol) was added bis(diphenylphosphane)acetylene (79 mg, 0.2 mmol). The solid dissolved rapidly and the

Table 6
Details of crystal data and structure refinement for complexes **1**, **2**, **5** and **6**

Compound	**1**	**2**	**5** · $CHCl_3$	**6** · H_2O
Empirical formula	$C_{26}H_{20}Au_2Cl_2P_2$	$C_{38}H_{20}Au_2F_{10}P_2$	$C_{39}H_{21}Au_2Cl_3F_{10}P_2S_2$	$C_{78}H_{62}Au_2Cl_2OP_6$
Formula weight	859.19	1122.41	1305.90	1665.93
Temperature (K)	133(2)	143(2)	133(2)	100(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	triclinic	triclinic	monoclinic
Space group	$C2/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
Unit cell dimensions				
a (Å)	16.4410(11)	8.123(2)	8.2842(6)	12.9807(7)
b (Å)	15.4767(11)	10.452(2)	11.2977(8)	22.1607(11)
c (Å)	11.1496(8)	11.939(3)	11.9184(8)	24.0781(12)
α (°)	90	67.509(6)	73.955(4)	
β (°)	117.694(4)	73.321(6)	69.751(4)	96. 8070(10)
γ (°)	90	75.263(6)	76.611(4)	
Volume (Å^3)	2512.0(3)	885.1(4)	994.28(12)	6877.5(6)
Z	4	1	1	4
D_{calc} (mg m^{-3})	2.272	2.106	2.181	1.609
Absorption coefficient (mm^{-1})	12.020	8.449	7.834	4.524
$F(000)$	1592	526	616	3280
Crystal size (mm)	0.20 × 0.09 × 0.09	0.25 × 0.18 × 0.03	0.2 × 0.2 × 0.1	0.24 × 0.24 × 0.20
Diffractometer	Bruker SMART 1000 CCD	Bruker SMART 1000 CCD	Bruker SMART 1000 CCD	Bruker SMART APEX CCD
θ Range data collection	1.92–30.01°	1.89–28.28°	1.86–30.03°	1.25–28.46°
Index ranges	$-22 \le h \le 23$, $-21 \le k \le 21$, $-15 \le l \le 15$	$-10 \le h \le 10$, $-13 \le k \le 13$, $-15 \le l \le 15$	$-11 \le h \le 11$, $-15 \le k \le 15$, $-16 \le l \le 16$	$-17 \le h \le 17$ $-28 \le k \le 29$ $-31 \le l \le 31$
Reflections collected	22565	8772	19847	62275
Independent reflections [R_{int}]	3662 [0.0389]	4313 [0.0709]	5785 [0.0238]	16175 [0.0376]
Completeness to θ (max) (%)	99.9	98.2	99.4	93.1
Absorption correction	semi-empirical from equivalents	semi-empirical from equivalents	semi-empirical from equivalents	semi-empirical from equivalents
Maximum and minimum transmission	0.604 and 0.293	0.962 and 0.485	0.584 and 0.391	1.00000 and 0.876101
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Data/restraints/parameters	3662/40/145	4313/72/235	5785/6/275	16175/0/808
Goodness-of-fit on F^2	1.223	0.972	1.040	0.866
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0257$[a], $wR_2 = 0.0643$[b]	$R_1 = 0.0520$[a], $wR_2 = 0.1192$[b]	$R_1 = 0.0214$[a], $wR_2 = 0.0554$[b]	$R_1 = 0.0271$[a], $wR_2 = 0.0472$[b]
R indices (all data)	$R_1 = 0.0288$[a], $wR_2 = 0.0651$[b]	$R_1 = 0.0683$[a], $wR_2 = 0.1254$[b]	$R_1 = 0.0242$[a], $wR_2 = 0.0562$[b]	$R_1 = 0.0362$[a], $wR_2 = 0.0485$[b]
Largest difference peak and hole (e Å^3)	1.670 and −2.023	4.418 and −4.492	1.759 and −0.821	1.403 and −0.644

[a] $R_1(F) = \sum |F_o| - |F_c| / \sum |F_o|$.

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

resulting solution was stirred for 1 h, concentrated to ca. 3 mL and precipitated with hexane. Yield: 90%. ^{1}H NMR (300 MHz, $CDCl_3$, 21 °C): δ 7.12–7.71 (m, Ph); $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$, 21 °C): δ −7.3 (br). $^{31}P\{^1H\}$ NMR (−50 °C): δ −5.55 (s). Found: C, 56.65; H, 3.65%. $C_{78}H_{60}Au_2Cl_2P_6$ requires: C, 56.85; H, 3.65%.

4.6. Crystal structure determinations

Crystal data and refinement details are given in Table 6. Single crystals of $[(AuCl)_2(\mu\text{-dppa})]$, $[(AuC_6F_5)_2(\mu\text{-dppa})]$, $[(Au(SC_6F_5))_2(\mu\text{-dppa})]$ and $[(AuCl)_2(\mu\text{-dppa})_3]$ were obtained by slow diffusion at −18 °C, of hexane/ethanol into a dichloromethane/chloroform solution, of diethyl ether into a dichloromethane solution, of petroleum ether into a dichloromethane/chloroform solution, of hexane into a dichloromethane solution, respectively. The structures were refined anisotropically on F^2 (program SHELXL 97) [28] using a system of restraints (to light-atom U values and local ring symmetry). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included using a riding model. Special features of refinement: the chloroform molecule of **5** is disordered over an inversion centre. The water molecule of **6** (O(1), H(1) and H(2)) was located from difference Fourier maps. Oxygen atom was refined with anisotropic displacement parameters and hydrogen atoms were refined with isotropic displacement parameters 1.2 times the isotropic equivalent of oxygen atom.

5. Supplementary material

Complete X-ray data (excluding structure factors) for complexes **1**, **2**, **5** and **6** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-231716-231719. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.htlm [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk].

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.

References

[1] M.C. Gimeno, A. Laguna, Chem. Rev. 97 (1997) 511.
[2] H. Schmidbaur, Gold Bull. 33 (2000) 3.
[3] B. Ahrens, S. Friedrichs, R. Herbst-Irmer, P.G. Jones, Eur. J. Inorg. Chem. (2000) 2017, and references therein.
[4] (a) W.J. Hunks, M.C. Jennings, R.J. Puddephatt, Inorg. Chem. 41 (2002) 4590;
(b) B.-C. Tzeng, A. Schier, H. Schmidbaur, Inorg. Chem. 38 (1999) 3978;
(c) C. Hollatz, A. Schier, H. Schmidbaur, J. Am. Chem. Soc. 119 (1997) 8115.
[5] A. Laguna, in: H. Schmidbaur (Ed.), Gold: Progress in Chemistry, Biochemistry and Technology, Wiley, Chichester, 1999, pp. 349–427.
[6] (a) Z. Qin, M.C. Jennings, R.J. Puddephatt, Chem. Eur. J. 8 (2002) 723;
(b) C.P. McArdle, M.J. Irwin, M.C. Jennings, J.J. Vittal, R.J. Puddephatt, Chem. Eur. J. 8 (2002) 735;
(c) M.C. Brandys, R.J. Puddephatt, Chem. Commun. (2001) 1280;
(d) W.J. Hunks, J. Lapierre, H.A. Jenkins, R.J. Puddephatt, J. Chem. Soc., Dalton Trans. (2002) 2885;
(e) M.C. Brandys, R.J. Puddephatt, J. Am. Chem. Soc. 123 (2001) 4839;
(f) J.H.K. Yip, J. Prabhavathy, Angew. Chem. Int. Ed. 40 (2001) 2159;
(g) V.J. Catalano, M.A. Malwitz, S.J. Horner, J. Vasquez, Inorg. Chem. 42 (2003) 2141, and its reference 4;
(h) R.-H. Uang, C.-K. Chan, S.-M. Peng, C.-M. Che, J. Chem. Soc., Chem. Commun. (1994) 2561.
[7] I.D. Salter, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry, vol. 10, Pergamon, Oxford, 1995, pp. 255–317.
[8] (a) A. Amoroso, B. Johnson, J. Lewis, A. Massey, P. Raithby, W. Wong, J. Organomet. Chem. 440 (1992) 219–231;
(b) C. Housecroft, A. Rheingold, A. Waller, G. Yap, J. Organomet. Chem. 565 (1999) 105;
(c) J. Galsworthy, C. Housecroft, A. Rheingold, J. Chem. Soc., Dalton Trans. (1995) 2639.
[9] A.J. Carty, A. Efraty, Inorg. Chem. 8 (1969) 543.
[10] M. Bardají, P.G. Jones, A. Laguna, Eur. J. Inorg. Chem. (1998) 989.
[11] M. Bardají, P.G. Jones, A. Laguna, J. Chem. Soc., Dalton Trans. (2002) 3624.
[12] P.G. Jones, C. Thöne, Acta Crystallogr., Sect. C 48 (1992) 1312.
[13] J.W.A. Van der Velden, J.J. Bour, J.J. Steggerda, P.T. Beurskens, M. Roseboom, J.H. Nordik, Inorg. Chem. 21 (1982) 4321.
[14] H. Schmidbaur, P. Bissinger, J. Lachamann, O. Steigelmann, Z. Naturfosch, Teil B 47 (1992) 1711.
[15] P.M. Van Calcar, M.M. Olmstead, A.L. Balch, Inorg. Chem. 36 (1997) 5231.
[16] (a) S. Onaka, Y. Katsukawa, M. Yamashita, Chem. Lett. (1998) 525;
(b) S. Onaka, Y. Katsukawa, M. Shiotsuka, O. Kanegawa, M. Yamashita, Inorg. Chim. Acta 312 (2001) 100.
[17] E. Lozano, M. Nieuwenhuyzen, S.L. James, Chem. Eur. J. 7 (2001) 2644.
[18] M. Semmelmann, D. Fenske, J.F. Corrigan, J. Chem. Soc., Dalton Trans. (1998) 2541.
[19] P.G. Jones, G.M. Sheldrick, J.A. Muir, M.M. Muir, L.B. Pulgar, J. Chem. Soc., Dalton Trans. (1982) 2123.
[20] C.B. Dieleman, D. Matt, A. Harriman, Eur. J. Inorg. Chem. (2000) 831.
[21] C. King, J.-C. Wang, M.N.I. Khan, J.P. Fackler Jr., Inorg. Chem. 28 (1989) 2145.
[22] (a) R. Narayanaswamy, M.A. Young, E. Parkhurst, M. Ouellette, M.E. Kerr, D.M. Ho, R.C. Elder, A.E. Bruce, M.R.M. Bruce, Inorg. Chem. 32 (1993) 2506;
(b) V.W.W. Yam, E.C.C. Cheng, N. Zhu, Angew. Chem. Int. Ed. 40 (2001) 1763.

[23] (a) B. Weissbart, D.V. Toronto, A.L. Balch, D.S. Tinti, Inorg. Chem. 35 (1996) 2490;
(b) L.J. Larson, E.M. McCauley, B. Weissbart, D.S. Tinti, J. Phys. Chem. 99 (1995) 7218.
[24] (a) H. Xiao, Y. Weng, W. Wong, T.C.W. Mak, C. Che, J. Chem. Soc., Dalton Trans. (1997) 221;
(b) J.S. Field, J. Grieve, R.J. Haines, N. May, M.M. Zulu, Polyhedron 17 (1998) 3021.
[25] (a) W.B. Jones, J. Yuan, R. Narayanaswamy, M.A. Young, R.C. Elder, A.E. Bruce, M.R.M. Bruce, Inorg. Chem. 34 (1995) 1996;
(b) J.M. Forward, D. Bohmann, J.P. Fackler, R.J. Staples, Inorg. Chem. 34 (1995) 6330;
(c) V.W.W. Yam, C.L. Chan, C.K. Li, K.M.C. Wong, Coord. Chem. Rev. 216-217 (2001) 173.
[26] R. Usón, A. Laguna, M. Laguna, Inorg. Synth. 26 (1989) 85.
[27] R. Usón, A. Laguna, J. Vicente, Chem. Commun. (1976) 353.
[28] G.M. Sheldrick, SHELXL 97: A Program for Crystal Structure Refinement, University of Göttingen, Göttingen, Germany, 1997.