Synthesis, structure and luminescence of 1,8-diaurionaphthalenes†‡§

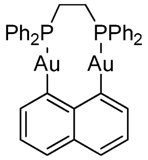
Casey R. Wade, Andrey A. Yakovenko and François P. Gabbaï*

Received (in Montpellier, France) 16th February 2010, Accepted 2nd April 2010
DOI: 10.1039/c0nj00128g

Reaction of 1,8-dilithionaphthalene with [AuCl(Et_3P)] or [Au_2Cl_2(μ-dppm)] (dppm = bis(diphenylphosphinomethane)) in Et_2O/THF leads to formation of bis(triethylphosphine)-1,8-diaurionaphthalene (**1**) and dppm-1,8-diaurionaphthalene (**2**), respectively. The dppm ligand present in complex **2** bridges the two gold centers leading to formation of short intramolecular Au–Au distances of av. 2.85 Å. Complex **2** reacts with $AgPF_6$ in THF/CH_2Cl_2 to afford a dicationic Au_4Ag_2 complex which has been isolated as the bis(hexafluorophosphate) salt (**3**). In this cluster, two molecules of **2** sandwich two Ag cations resulting in the formation of a Au_2AgAu_2Ag six-membered ring in which the metal centers are connected by Au–Au (av. 2.84 Å) and Au–Ag (av. 2.75 Å) metallophilic interactions. This cluster is further stabilized by short Ag–C interactions involving some of the naphthalene carbon atoms. The luminescence spectra of **2** and **3** have been recorded. Both complexes display relatively broad emission bands centered at 540 nm which result, at least in part, from the heavy atom induced phosphorescence of the naphthalene chromophore.

Introduction

Interest in bridged dinuclear gold(I) complexes containing short intramolecular Au–Au distances arises from their often rich optical properties[1,2] as well as unique structures which allow for study of the metal–metal interactions.[3] A number of bridging ligands such as diphosphines,[4–8] phosphine ylides,[9–14] and cyclometalating phosphines or arsines[15,16] have been used to scaffold both homo- and heterobridged molecules. Dinuclear gold(I) complexes bearing dianionic μ-C–C bridging ligands are more scarce, particularly those which allow short Au–Au contacts. Two examples of such structures include 1,1′-bis(triphenylphosphinegold)-biphenyl and 1,1′-bis(triphenylphosphinegold)-diphenylmethane in which, despite the flexibility of the bridging diaryl ligand, Au–Au distances of 3.169 Å and 3.012 Å, respectively, were reported.[17,18] Recently, Yam *et al.* have described the preparation of a 1,8-diaurionaphthalene complex (**I**) and examined its luminescence properties and reactivity with respect to oxidative addition.[19] Herein we describe the synthesis and structural characterization of two new 1,8-diaurionaphthalene complexes [$Au_2(\mu\text{-}C_{10}H_6)(Et_3P)_2$] (**1**) and [$Au_2(\mu\text{-}C_{10}H_6)$(μ-dppm)] (dppm = $Ph_2P(CH_2)PPh_2$) (**2**), the former being supported only by the naphthalenediyl ligand and the latter doubly bridged by both the naphthalenediyl and dppm ligands. In addition, we also describe the hexafluorophosphate salt of a novel $[Au_4Ag_2]^{2+}$ cluster (**3**) obtained by reaction of **2** with $AgPF_6$.



I

Results and discussion

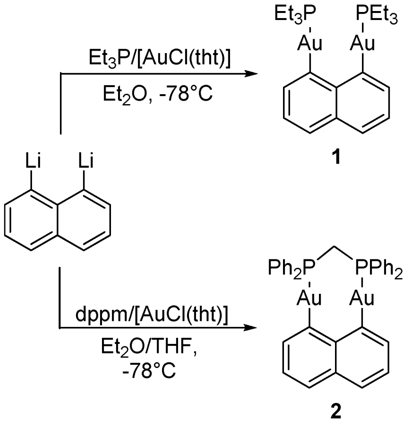
The synthesis described by Yam *et al.* for **I** involves the reaction of 1,8-bis(trimethylstannyl)naphthalene with [Au_2Cl_2(μ-dppe)] (dppe = 1,2-bis(diphenylphosphino)-ethane).[19] To avoid the use of toxic organotin reagents and additional synthetic steps, we decided to employ 1,8-dilithionaphthalene as a starting material.[20] Reaction of this dilithium reagent with *in situ* prepared [AuCl(Et_3P)] and [Au_2Cl_2(μ-dppm)] afforded **1** and **2**, respectively (Scheme 1). While **2** was obtained in up to 71% yield, only small amounts of **1** (≤10% yield) were isolated from the reaction mixtures. Both **1** and **2** have been fully characterized by multinuclear NMR and X-ray diffraction. The compounds are moderately soluble in CH_2Cl_2, C_6H_6, and THF but are insoluble in MeOH, Et_2O, and hydrocarbon solvents. The ^{31}P NMR spectra of **1** and **2** display single resonances at 38 ppm (CD_2Cl_2) and 29 ppm ($CDCl_3$), respectively, indicating the symmetrical nature of the structures in solution. Accordingly, the ^1H NMR spectrum of each complex displays all the expected resonances, including three sets of signals corresponding to the symmetrically substituted 1,8-naphthalene backbones.

Department of Chemistry, Texas A&M University, College Station, Texas 77843, USA. E-mail: francois@tamu.edu

† It is with an immense sadness that I learned about the passing of Pascal Le Floch on March 17, 2010. Although I had met Pascal only once, I felt that I knew him very well because of the similarities of our research interests as well as the many friends that we shared. In 2004, Pascal sent one of his students, Mohand Melaimi, for a postdoctoral stay in my group. It is largely through Mohand that I discovered Pascal's enthusiastic and rigorous approach to graduate education and research. I share my deepest sympathy with those who were personally close to him; I will continue to remember Pascal through his publications which serve as an immortal testament to his highly productive life. François P. Gabbaï, College Station, March 30, 2010.

‡ This article is part of a themed issue on Main Group chemistry.

§ CCDC 766215 (**1**), 766216 (**2**), and 766217 (**3**). For crystallographic data in CIF or other electronic format see DOI: 10.1039/c0nj00128g



Scheme 1

The X-ray crystal structure of **1** was determined using single crystals obtained by cooling a CH_2Cl_2/Et_2O solution of the compound (Fig. 1, Table 1). The complex crystallizes in the space group $P2_1/n$ and exhibits linearly coordinated gold atoms (C(1)–Au(1)–P(1), 166.89(12)°; C(8)–Au(2)–P(2), 163.89(11)°) with an intramolecular Au–Au contact (Au(1)–Au(2), 2.9982(5) Å).

Single crystals of **2** suitable for X-ray diffraction were obtained by cooling a solution of the compound in $CH_2Cl_2/MeOH$ (4 : 1). This compound crystallizes in the orthorhombic space group $P2_12_12_1$ with the unit cell containing three independent molecules (Table 1). One of these molecules (molecule **A**), which does not form any unusual intermolecular contacts, displays a relatively short intramolecular Au(1A)–Au(2A) distance of 2.8137(8) Å (Fig. 2). The other two independent molecules (molecules **B** and **C**) present in the asymmetric unit are associated end to end by an unsupported aurophilic Au(1B)–Au(1C) interaction of 3.0983(8) Å (Fig. 3). Interestingly, formation of this intermolecular aurophilic interaction induces a noticeable lengthening of the intramolecular Au–Au interactions in molecules **B** and **C** (Au(1B)–Au(2B) = 2.8693(8) Å and Au(1C)–Au(2C) 2.8658(8) Å) when compared to that observed in molecule **A** (2.8137(8) Å). The coordination environment of the gold(I) atoms in **2** is also more linear than observed for **1** with C–Au–P angles in the range 173.0(4)–178.5(4)° for the combined independent molecules.

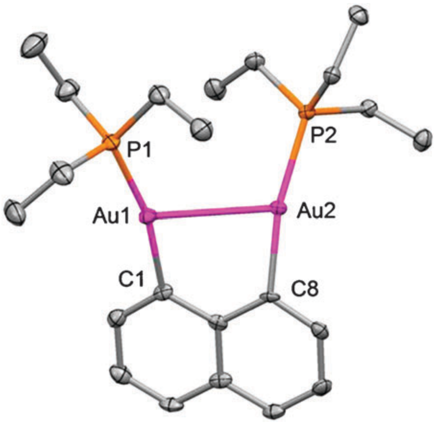


Fig. 1 Molecular structure of complex **1**. Ellipsoids are scaled to the 50% probability level and hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Au(1)–Au(2) 2.9982(5), Au(1)–P(1) 2.2855(11), Au(2)–P(2) 2.2893(11), Au(1)–C(1) 2.057(4), Au(2)–C(8) 2.055(4); C(1)–Au(1)–P(1) 166.89(12), C(8)–Au(2)–P(2) 163.89(11).

Comparison of the structures of **1** and **2** with the reported structure of **I** shows a trend in the intramolecular Au–Au distances with respect to the rigidity and bridging ability of the phosphine ligands. The longest of these distances is observed for **1** (2.9982(5) Å), indicating that the bulk of the monodentate Et_3P ligands impedes a close approach of the two Au atoms. A comparison of the intramolecular Au–Au distances in **2** (av. 2.85 Å) and **I** (av. 2.90 Å) suggests that the narrower dppm ligand promotes the formation of a shorter Au–Au contact. The short intramolecular Au–Au distances observed in **2** are also comparable to, or shorter than, those seen in the 8-membered cyclometalated gold(I) dimers $[Au_2(\mu\text{-}2\text{-}C_6H_4PPh_2)_2]$ (2.8594(3) Å) and $[Au_2(\mu\text{-}C_6H_3\text{-}2\text{-}PPh_2\text{-}6\text{-}Me)_2]$ (2.861(2) Å).[21,22]

The metallophilicity of gold(I) complexes often extends beyond inter- and intramolecular Au–Au interactions, and the presence of other heavy metal ions such as Cu(I), Ag(I), and Tl(I) may result in formation of intermetallic aggregates or polymeric materials supported by heterometallic closed shell interactions.[1,23] In the present case, we have found that upon layering a solution of **2** in CH_2Cl_2 with 1 eq. of $AgPF_6$ (THF), colorless crystals formed which were identified by X-ray diffraction as the hexafluorophosphate salt of a dicationic complex featuring a Au_2AgAu_2Ag six-membered ring (**3**) (Scheme 2). This salt crystallizes in the space group $P\bar{1}$ with two independent molecules, referred to as molecules **A** and **B**, two PF_6^- counteranions, and disordered THF/CH_2Cl_2 solvent molecules in the asymmetric unit (Table 1, Fig. 4). The independent molecules each consist of a single Ag atom and one $[Au_2(\mu\text{-}C_{10}H_6)(\mu\text{-dppm})]$ unit with the remainder of the hexanuclear "sandwich" structures and counteranions being generated by an inversion center located at the center of the 6-membered metalloring (Fig. 4). Restraints placed on the naphthalenediyl and phenyl rings to correct distortions, probably due to crystal twinning, limit detailed discussion of some aspects of the bonding in this complex. However, the distinguishing features of **3**, including the metal–metal and some metal–carbon bond distances, may be addressed. The presence of nearby Ag atoms do not induce any major distortions in the core structure of the $[Au_2(\mu\text{-}C_{10}H_6)(\mu\text{-dppm})]$ moiety. The observed intramolecular Au(1)–Au(2) distances of 2.8278(12) Å for molecule **A** and 2.8501(12) Å for molecule **B** are close to those observed in complex **2**. Similarly, the C–Au–P bond angles ranging from 176.5(2)° to 177.0(2)° in molecules **A** and **B** show little deviation from linearity. The Au(1′)–Ag(1) (2.740(2) Å for molecule **A** and 2.7646(19) Å for molecule **B**) and Au(2)–Ag(1) (2.783(2) Å for molecule **A** and 2.802(2) Å for molecule **B**) distances are close to one another and commensurate with the presence of metallophilic contacts such as those observed in the cationic aryl bridged heterometallic complexes $[\{Au(\mu\text{-Mes})(Ph_3As)\}_2Ag]ClO_4$ (Au–Ag = 2.7758(8) Å)[24] and $[\{Au(\mu\text{-Mes})(Ph_3P)\text{-}Ag(tht)\}_2]^{2+}$ (Au–Ag = 2.8245(6) Å).[25] Cohesion of the hexanuclear cluster also benefits from π-interactions involving

Table 1 Crystal data for complexes **1**, **2**, and **3**

Crystal data	**1**	**2**	**3**
Formula	$C_{22}H_{36}Au_2P_2$	$C_{35}H_{28}Au_2P_2\cdot 0.66(CH_2Cl_2)$	$C_{74}H_{64}Ag_2Au_4F_{12}OP_6$[a]
M_r	756.38	961.08	2386.68
Crystal size/mm	0.12 × 0.08 × 0.004	0.10 × 0.10 × 0.03	0.33 × 0.05 × 0.03
Crystal system	Monoclinic	Orthorhombic	Triclinic
Space group	$P2(1)/n$	$P2(1)2(1)2(1)$	$P\bar{1}$
a/Å	14.589(2)	15.312(3)	13.721(3)
b/Å	11.7417(17)	20.213(3)	15.084(4)
c/Å	15.155(2)	30.189(5)	19.253(5)
α/°	90	90	84.974(2)
β/°	113.913(2)	90	69.611(2)
γ/°	90	90	84.399(3)
V/Å^3	2373.3(6)	9343(3)	3711.0(16)
Z	4	12	2
ρ_{calc}/g cm^{-3}	2.117	2.050	2.136
μ/mm^{-1}	12.488	9.652	8.597
$F(000)$	1424	5448	2248 (2461)[b]
T/K	110(2)	110(2)	110(2)
Scan mode	ω	ω	ω
hkl range	$-17 \rightarrow +17$	$-17 \rightarrow +17$	$-16 \rightarrow +16$
	$-13 \rightarrow +13$	$-23 \rightarrow +23$	$-16 \rightarrow +18$
	$-17 \rightarrow +17$	$-35 \rightarrow +35$	$-23 \rightarrow +23$
Measd reflns	21 290	85 668	37 102
Unique reflns [R_{int}]	3948 [0.0298]	15 533 [0.0817]	14 427 [0.0910]
Reflns used for refinement	3948	15 533	14 427
Refined parameters	235	1066	646
GooF	1.002	1.049	1.025
R_1,[c] wR_2[d] (all data)	0.0214, 0.0429	0.0472, 0.0795	0.1328, 0.1836
ρ_{fin} (max., min.)/e Å^{-3}	1.246, −0.491	1.576, −1.045	2.923, −1.898
Absolute structure parameter	N/A	−0.009(6)	N/A

[a] Interstitial solvent molecules were removed using the SQUEEZE program and not included in the formula. [b] The $F(000)$ value in parentheses includes the amount of electrons in the structure removed using the SQUEEZE program. [c] $R_1 = \sum\|F_o| - |F_c\|/\sum|F_o|$. [d] $wR_2 = ([\sum w(F_o^2 - F_c^2)^2]/[\sum w(F_o^2)^2])^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$ with $a = 0.0258$ for **1**, 0.0250 for **2**, and 0.0300 for **3**; and $b = 3.1624$ for **1**, 10 for **2**, and 130 for **3**.

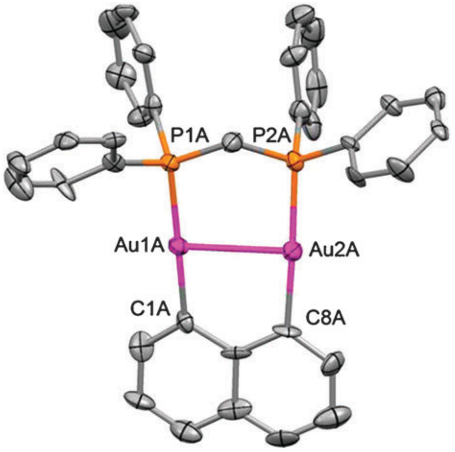


Fig. 2 Structure of independent molecule **A** present in the asymmetric unit of **2**. Ellipsoids are scaled to the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Au(1A)–Au(2A) 2.8137(8), Au(1A)–P(1A) 2.283(3), Au(1A)–C(1A) 2.044(13), Au(2A)–P(2A) 2.299(4), Au(2A)–C(8A) 2.052(12); C(1A)–Au(1A)–P(1A) 177.5(4), C(8A)–Au(2A)–P(2A) 177.8(4).

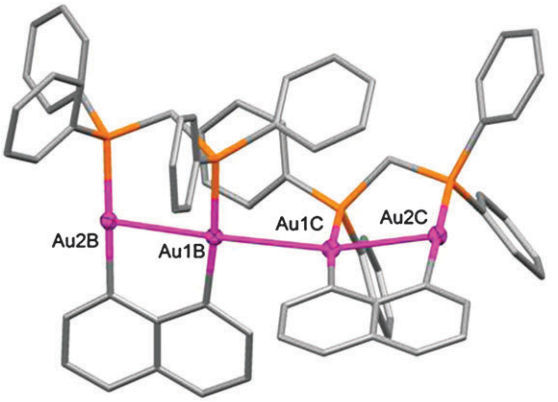
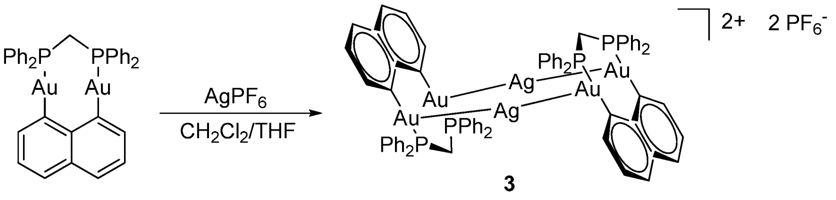


Fig. 3 Structure of independent molecules **B** and **C** present in the asymmetric unit of **2**. Ellipsoids are scaled to the 50% probability level. The ligands are represented using a stick model. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Au(1B)–Au(1C) 3.0983(8), Au(1B)–Au(2B) 2.8693(8), Au(1C)–Au(2C) 2.8658(8); Au(2B)–Au(1B)–Au(1C) 172.27(2), Au(2C)–Au(1C)–Au(1B) 166.10(2).

the naphthalene ligands and the silver cation (Ag(1)–C(8) = 2.434(7) Å for molecule **A** and 2.344(7) Å for molecule **B**, Ag(1)–C(7) = 2.482(9) Å for molecule **A** and 2.521(9) Å for molecule **B**, Ag(1)–C(1′) = 2.347(4) Å for molecule **A** and 2.321(5) Å for molecule **B**). Finally, we note that formation of this cluster results in a slight lengthening of the Au–C bonds (av. 2.13 Å *vs.* 2.06 Å in **2**).

The electronic spectra of complexes **2** and **3** in CH_2Cl_2 both display broad absorption bands around 310 nm, arising from a mixture of metal perturbed naphthalene and phenyl π–π*



Scheme 2

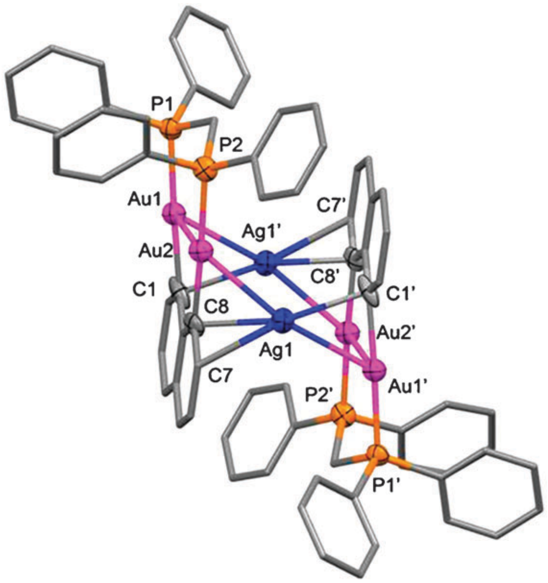


Fig. 4 Structure of independent molecule **A** of complex **3**. The symmetry equivalent half of the molecule is generated by inversion ((atom)(number)′ = $-x$, $-y$, $-z + 1$). Ellipsoids are scaled to the 50% probability level. Hydrogen atoms, PF_6^- counteranions, and solvent molecules have been omitted for clarity. Selected bond lengths (Å) and angles (°) for molecule **A**, with those for the independent molecule **B** given in brackets: Au(1)–Au(2) 2.8278(12) [2.8501(12)], Au(1)–P(1) 2.300(5) [2.286(6)], Au(1)–C(1) 2.125(6) [2.143(6)], Au(2)–P(2) 2.290(5) [2.304(5)], Au(2)–C(8) 2.099(7) [2.143(6)], Au(1′)–Ag(1) 2.740(2) [2.7647(19)], Au(2)–Ag(1) 2.783(2) [2.802(2)], Ag(1)–C(1′) 2.347(4) [2.321(5)], Ag(1)–C(8) 2.434(7) [2.344(7)], Ag(1)–C(7) 2.482(9) [2.521(9)]; C(1)–Au(1)–P(1) 176.8(2) [176.5(2)], C(8)–Au(2)–P(2) 177.0(2) [176.3(2)], Au(1′)–Ag(1)–Au(2) 164.09(9) [163.54(11)].

excitations and metal centered transitions (Fig. 5).[19,26,27] In deaerated CH_2Cl_2 solution, both complexes display emission bands in the 475–650 nm range (Fig. 6). The vibronic progression observed in these emission spectra are characteristic of the triplet state of naphthalene thus indicating the occurrence of an internal heavy atom effect.[19,28,29] Related heavy atom induced triplet emissions have been observed for other aurated polycyclic aromatics including naphthalene, anthracene, and pyrene.[30–34] Upon exposure to air, nearly complete loss of emission intensity was observed for both complexes thus confirming the triplet nature of the emissive state. Interestingly, the emission band of **3** is redshifted by *ca.* 20 nm *versus* that of **2** indicating that Au–Ag metallophilic interactions observed in the solid state might be retained in solution.

The solid state spectra of **2** and **3** also display relatively broad emission bands around 475–650 nm (Fig. 7). However, the emission band of **2** is distinctly broadened and more red-shifted. Since it has been previously shown that aggregation and aurophilic interactions play an important role in the luminescence of gold(I) complexes,[35] we assign the differences observed in the solution and solid state spectra of **2** to the presence of an aurophilic dimer in the solid state structure of **2**.

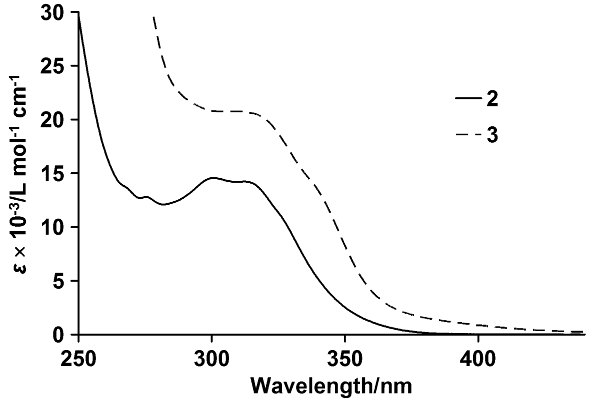


Fig. 5 UV-Vis absorption spectra of complexes **2** and **3** in CH_2Cl_2 solution under ambient conditions.

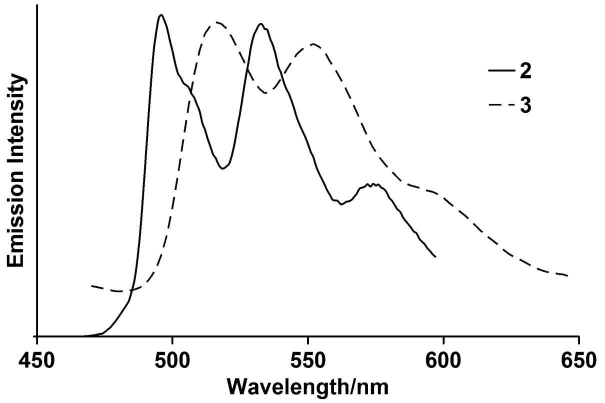


Fig. 6 Luminescence spectra of complexes **2** (λ_{exc} = 310 nm) and **3** (λ_{exc} = 350 nm) in deoxygenated CH_2Cl_2 solution (1 mM) at room temperature. The spectra have been corrected for the I *vs.* λ bias introduced by the PMT detector.

Conclusion

Here we report that 1,8-diaurionaphthalene complexes such as **2** can be readily prepared from 1,8-dilithionaphthalene and may be used as a building block for the construction of a larger complex such as **3** which contains a $[Au_4Ag_2]^{2+}$ metallocycle. The luminescence properties of **2** and **3** in CH_2Cl_2 solution arise from triplet state phosphorescence of the

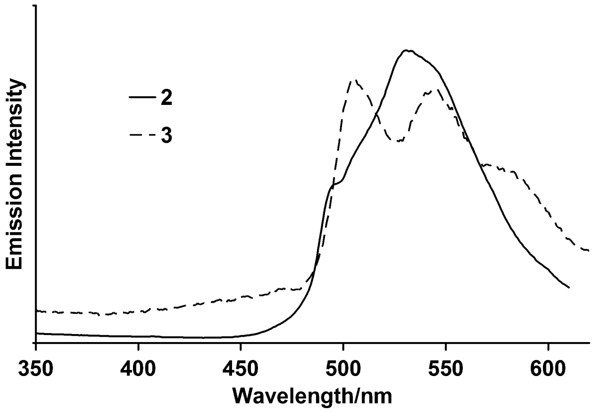


Fig. 7 Luminescence spectra of complexes **2** and **3** (λ_{exc} = 315 nm) in the solid state at room temperature. The spectra have been corrected for the *I vs.* λ bias introduced by the PMT detector.

naphthalene backbone thus indicating the occurrence of an internal heavy atom effect. A redshift (*ca.* 20 nm) in the emission spectrum of **3** *versus* that of **2** suggests that the Au–Ag metallophilic interactions remain in solution. Similarly, broadening of the solid state emission spectrum of **2** is attributed to the presence of an intramolecular aurophilic contact observed in the solid state structure of the complex.

Experimental

General considerations

1,8-Dilithionaphthalene[36] and [AuCl(tht)][37] were prepared according to the literature. Bis(diphenylphosphino)methane and triethylphosphine were purchased from Alfa Aesar and used as received. $AgPF_6$ was purchased from Sigma Aldrich and used as received. Solvents were dried by passing through an alumina column (*n*-hexane, CH_2Cl_2) or refluxing under N_2 over Na/K (Et_2O and THF). Air-sensitive compounds were handled under a N_2 atmosphere using standard Schlenk and glovebox techniques. Elemental analyses were performed at Atlantic Microlab (Norcross, GA). NMR spectra were recorded on a Varian Unity Inova 400 FT NMR (399.59 MHz for ^{1}H, 161.75 MHz for ^{31}P, and 100.45 MHz for ^{13}C) spectrometer at ambient temperature unless otherwise stated. Chemical shifts δ are given in ppm, and are referenced against external Me_4Si (^{1}H, ^{13}C) and H_3PO_4 (^{31}P). Electronic absorption spectra were recorded using an Ocean Optics USB4000 spectrometer with an Ocean Optics ISS light source. Steady state emission spectra were collected at room temperature using a PTI QuantaMaster 4 fluorescence spectrophotometer equipped with a Model 810 PMT detector. Solution based samples were prepared at *ca.* 1 mM concentrations under an atmosphere of N_2 using dry, degassed CH_2Cl_2. Solid samples were loaded as powders in 0.7 mm glass capillaries and suspended in the sample cavity to sit at the intersection of excitation and emission optical paths.

Single-crystal X-ray diffraction analysis

Crystal data, details of data collection and structure refinement parameters for compounds **1**, **2**, and **3**, are presented in Table 1. The X-ray diffraction experiments were carried out with a Bruker SMART APEX II diffractometer with a CCD area detector (graphite monochromated MoKα radiation, λ = 0.71073 Å, ω-scans with a 0.5° step in ω) at 110 K. The semiempirical method SADABS[38] was applied for absorption correction. The structures were solved by direct methods and refined by the full-matrix least-square technique against F^2 with the anisotropic temperature parameters for all non-hydrogen atoms. All H atoms were geometrically placed and refined in riding model approximation. Data reduction and further calculations were performed using the Bruker SAINT+[39] and SHELXTL NT[40] program packages.

During the structure refinement of complex **3**, we found large planarity, bond length and bond angle distortions in the phenyl and naphthyl rings in both molecules of complex. This effect is probably due to twinning of the crystal which could however not be resolved using the CELL NOW,[41] ROTAX[42] or APEX2[43] software. To correct this distortion, we restrained the structure parameters of these rings to the ideal geometries (C–C bond length 1.390(1) Å and C–C–C bond angles 120.0(1)°). In addition, the PF_6^- counter-anions were found to be highly disordered. Attempts to solve this disorder were not successful. Since these anions do not bring any new structural information to our research, after restraining their geometry to the ideal (P–F bond length 1.581(1) Å and F–P–F bond angle 90.0(1)°) they were left as is.

There are large channel-like volumes permeating the crystal which are occupied by heavily disordered solvent molecules. Modeling attempts indicate a mixture of CH_2Cl_2 and THF. No satisfactory disorder model could be achieved, and therefore the Squeeze program implemented in PLATON was used to model this electron density.[44] The program calculated a solvent-accessible volume of 272.1 Å^3 (7.33% of the total unit cell volume), which was then removed from subsequent structure factor calculations.

Synthesis

$[Au_2(\mu\text{-}C_{10}H_6)(Et_3P)_2]$ (1). A mixture of [AuCl(tht)] (0.200 g, 0.62 mmol) and Et_3P (0.074 g, 0.62 mmol) in Et_2O (10 mL) was added to a solution of 1,8-dilithionaphthalene·1.5TMEDA (0.099 g, 0.31 mmol) in Et_2O (5 mL) at −78 °C. The yellow suspension was stirred for 15 min at reduced temperature then 3 h at room temperature. The solvent was removed *in vacuo* and the residue extracted with 15 mL of CH_2Cl_2 and filtered over Celite. The extract was then concentrated and a yellow precipitate was obtained by addition of hexanes. Recrystallization of the crude material from CH_2Cl_2/Et_2O (3 mL/5 mL) gave the pure product as bright yellow blocks (0.020 g, 10% yield). Attempts to obtain more product from the recrystallization supernatant resulted only in the isolation of decomposition products. ^{1}H NMR (399.9 MHz, $CDCl_3$): δ 1.29 (dt, 18H, P-CH_2-CH_3, $^{3}J_{H\text{-}H}$ = 7.60 Hz, $^{3}J_{H\text{-}P}$ = 16.8 Hz), 1.84 (dq, 12H, P-CH_2-CH_3, $^{3}J_{H\text{-}H}$ = 7.60 Hz, $^{2}J_{H\text{-}P}$ = 8.80 Hz), 7.32 (t, 2H, Naph-*CH*, $^{3}J_{H\text{-}H}$ = 7.20 Hz), 7.60 (d, 2H, Naph-*CH*, $^{3}J_{H\text{-}H}$ = 8.00 Hz), 7.67 (t, 2H, Naph-*CH*, $^{3}J_{H\text{-}H}$ = 7.20 Hz). ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 9.12 (s, P-CH_2-CH_3), 18.67 (d, P-CH_2-CH_3, $^{1}J_{C\text{-}P}$ = 26.7 Hz), 123.94, 125.54, 135.39

(*ipso* C1, C8, C9, and C10 not observed). $^{31}P\{^1H\}$ NMR (161.75 MHz, $CDCl_3$): δ 38.04. Anal. calcd for $C_{22}H_{36}Au_2P_2$: C, 34.93; H, 4.80%. Found: C, 34.69; H, 4.77%.

$[Au_2(\mu\text{-}C_{10}H_6)(\mu\text{-dppm})]$ (2). A mixture of [AuCl(tht)] (0.834 g, 2.60 mmol) and dppm (0.500 g, 1.30 mmol) in THF/Et_2O (5 mL/5 mL) was added dropwise to a solution of 1,8-dilithionaphthalene·1.5TMEDA (0.413 g, 1.30 mmol) in Et_2O (10 mL) at −78 °C. The yellow suspension was stirred for 15 min at reduced temperature then overnight at room temperature. The solvent was removed *in vacuo* and the residue extracted with 15 mL of CH_2Cl_2 and filtered over Celite. The extract was then concentrated and a yellow precipitate was obtained by addition of Et_2O. The solid was filtered and washed copiously with Et_2O. The resulting crude product was recrystallized from CH_2Cl_2 : MeOH (4 : 1) to give the pure product as bright yellow blocks (840 mg, 71% yield). ^1H NMR (399.9 MHz, C_6D_6): δ 2.83 (t, 2H, P-CH_2, $^2J_{H\text{-}P}$ = 10.8 Hz), 6.75–6.86 (m, 12H, *m*-, *p*-Ph-*CH*), 7.33 (dd, 8H, *o*-Ph-*CH*, $^3J_{H\text{-}P}$ = 12.1 Hz), 7.65 (t, 2H, Naph-*CH*, $^3J_{H\text{-}H}$ = 7.14 Hz), 7.97 (t, 2H, Naph-*CH*, $^3J_{H\text{-}H}$ = 7.87 Hz), 8.49 (br, 2H, Naph-*CH*). ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 30.19 (t, P-CH_2-P, $^1J_{C\text{-}P}$ = 22.1 Hz), 124.22, 126.42, 128.92, 130.53, 131.29, 133.44, 135.87, 135.99, 154.73, 174.25. $^{31}P\{^1H\}$ NMR (161.75 MHz, CD_2Cl_2): δ 29.09 (s). Anal. calcd for $C_{35}H_{28}Au_2P_2{\cdot}0.66CH_2Cl_2$: C, 44.57; H, 3.08%. Found: C, 44.61; H, 2.99%.

$[\{Au_2(\mu\text{-}C_{10}H_6)(\mu\text{-dppm})\}_2Ag_2](PF_6)_2$ (3). Colorless crystals of **3** suitable for X-ray diffraction were obtained by layering a solution of **2** (0.060 g, 0.066 mmol) in 3 mL CH_2Cl_2 with a solution of $AgPF_6$ (0.017 g, 0.067 mmol) in 3 mL THF. ^1H NMR (399.9 MHz, CD_2Cl_2): δ 2.53 (br, 1H, dppm-CH_2), 4.06(br, 1H, dppm-CH_2), 7.03 (br, 4H), 7.16–7.36 (t, br, 12H), 7.53–7.75 (d, br, 8H), 8.05 (br, 2H). $^{31}P\{^1H\}$ NMR (161.75 MHz, CD_2Cl_2): δ −144.38 (sept., PF_6, $^1J_{F\text{-}P}$ = 711 Hz), 31.03 (s, dppm-*P*). Anal. calcd for $C_{70}H_{56}F_{12}Au_4Ag_2P_6$: C, 36.32; H, 2.44%. Found: C, 36.09; H, 2.41%.

Acknowledgements

This work was supported by the National Science Foundation (CHE-0646916) and the Welch Foundation (A-1423).

References

1 E. J. Fernandez, A. Laguna and J. M. Lopez-de-Luzuriaga, *Dalton Trans.*, 2007, 1969–1981.
2 V. W.-W. Yam and E. C.-C. Cheng, *Chem. Soc. Rev.*, 2008, **37**, 1806–1813.
3 H. Schmidbaur and A. Schier, *Chem. Soc. Rev.*, 2008, **37**, 1931–1951.
4 H. Schmidbaur, A. Wohlleben, U. Schubert, A. Frank and G. Huttner, *Chem. Ber.*, 1977, **110**, 2751–2757.
5 M. N. I. Khan, C. King, D. D. Heinrich, J. P. Fackler, Jr. and L. C. Porter, *Inorg. Chem.*, 1989, **28**, 2150–2154.
6 R. M. Davila, A. Elduque, T. Grant, R. J. Staples and J. P. Fackler, Jr., *Inorg. Chem.*, 1993, **32**, 1749–1755.
7 R. M. Davila, A. Elduque, R. J. Staples, M. Harlass and J. P. Fackler, Jr., *Inorg. Chim. Acta*, 1994, **217**, 45–49.
8 S. S. Tang, C.-P. Chang, I. J. B. Lin, L.-S. Liou and J.-C. Wang, *Inorg. Chem.*, 1997, **36**, 2294–2300.
9 H. Schmidbaur, J. R. Mandl, J. M. Bassett, G. Blaschke and B. Zimmer-Gasser, *Chem. Ber.*, 1981, **114**, 433–440.
10 M. Bardaji, N. G. Connelly, M. C. Gimeno, J. Jimenez, P. G. Jones, A. Laguna and M. Laguna, *J. Chem. Soc., Dalton Trans.*, 1994, 1163–1167.
11 M. Bardaji, M. C. Gimeno, P. G. Jones, A. Laguna and M. Laguna, *Organometallics*, 1994, **13**, 3415–3419.
12 M. Bardaji, N. G. Connelly, M. C. Gimeno, P. G. Jones, A. Laguna and M. Laguna, *J. Chem. Soc., Dalton Trans.*, 1995, 2245–2250.
13 M. Bardaji, P. G. Jones, A. Laguna and M. Laguna, *Organometallics*, 1995, **14**, 1310–1315.
14 M. Bardaji, A. Laguna and M. Laguna, *J. Organomet. Chem.*, 1995, **496**, 245–248.
15 F. Mohr, S. H. Priver, S. K. Bhargava and M. A. Bennett, *Coord. Chem. Rev.*, 2006, **250**, 1851–1888.
16 S. K. Bhargava, F. Mohr, M. A. Bennett, L. L. Welling and A. C. Willis, *Inorg. Chem.*, 2001, **40**, 4271–4275.
17 T. y. V. Baukova, L. G. Kuz'mina, N. y. A. Oleinikova, D. A. Lemenovskii and A. L. Blumenfel'd, *J. Organomet. Chem.*, 1997, **530**, 27–38.
18 L. G. Kuz'mina, A. V. Churakov and J. A. K. Howard, *Russ. J. Coord. Chem.*, 1998, **24**, 435–440.
19 N. Meyer, C. W. Lehmann, T. K. M. Lee, J. Rust, V. W. W. Yam and F. Mohr, *Organometallics*, 2009, **28**, 2931–2934.
20 W. Neugebauer, A. J. Kos and P. v. R. Schleyer, *J. Organomet. Chem.*, 1982, **228**, 107–118.
21 M. A. Bennett, S. K. Bhargava, K. D. Griffiths, G. B. Robertson, W. A. Wickramasinghe and A. C. Willis, *Angew. Chem.*, 1987, **99**, 261–262.
22 S. K. Bhargava, F. Mohr, M. A. Bennett, L. L. Welling and A. C. Willis, *Organometallics*, 2000, **19**, 5628–5635.
23 M. J. Katz, K. Sakai and D. B. Leznoff, *Chem. Soc. Rev.*, 2008, **37**, 1884–1895.
24 M. Contel, J. Garrido, M. C. Gimeno, P. G. Jones, A. Laguna and M. Laguna, *Organometallics*, 1996, **15**, 4939–4943.
25 M. Contel, J. Jimenez, P. G. Jones, A. Laguna and M. Laguna, *J. Chem. Soc., Dalton Trans.*, 1994, 2515–2518.
26 D. V. Partyka, M. Zeller, A. D. Hunter and T. G. Gray, *Angew. Chem., Int. Ed.*, 2006, **45**, 8188–8191.
27 C. M. Che, H. L. Kwong, V. W. W. Yam and K. C. Cho, *J. Chem. Soc., Chem. Commun.*, 1989, 885–886.
28 T. J. Taylor, C. N. Burress and F. P. Gabbaï, *Organometallics*, 2007, **26**, 5252–5263.
29 M. R. Haneline, M. Tsunoda and F. P. Gabbaï, *J. Am. Chem. Soc.*, 2002, **124**, 3737–3742.
30 W. Y. Heng, J. Hu and J. H. K. Yip, *Organometallics*, 2007, **26**, 6760–6768.
31 M. Osawa, M. Hoshino and D. Hashizume, *Dalton Trans.*, 2008, 2248–2252.
32 V. W.-W. Yam, K.-L. Cheung, S.-K. Yip and N. Zhu, *Photochem. Photobiol. Sci.*, 2005, **4**, 149–153.
33 D. V. Partyka, A. J. Esswein, M. Zeller, A. D. Hunter and T. G. Gray, *Organometallics*, 2007, **26**, 3279–3282.
34 L. Gao, M. A. Peay, D. V. Partyka, J. B. Updegraff, III, T. S. Teets, A. J. Esswein, M. Zeller, A. D. Hunter and T. G. Gray, *Organometallics*, 2009, **28**, 5669–5681.
35 A. L. Balch, *Struct. Bonding*, 2007, **123**, 1–40.
36 W. Neugebauer, T. Clark and P. v. R. Schleyer, *Chem. Ber.*, 1983, **116**, 3283–3292.
37 R. Uson, A. Laguna and M. Laguna, *Inorg. Synth.*, 1989, **26**, 85–91.
38 G. M. Sheldrick, *SADABS, Version 2007/4*, Bruker Analytical X-ray Systems, Inc., Madison, Wisconsin, USA, 2007.
39 Bruker, *SAINTPlus. Data Reduction and Correction Program v. 6.2*, Bruker AXS, Madison, Wisconsin, USA, 2001.
40 G. M. Sheldrick, *SHELXTL-2008/2004, Structure Determination Software Suite*, Bruker AXS, Madison, Wisconsin, USA, 2008.
41 G. M. Sheldrick, *CELL_NOW*, University of Gottingen, Germany, 2006.
42 R. I. Cooper, R. O. Gould, S. Parsons and D. J. Watkin, *J. Appl. Crystallogr.*, 2002, **35**, 168.
43 APEX2, *Bruker Molecular Analysis Research Tool, v. 1.27*, Bruker AXS, Madison, Wisconsin, USA, 2005.
44 A. L. Spek, *PLATON, A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands, 1998.