Luminescent Organometallic Gold(I) Complexes. Structure and Photophysical Properties of Alkyl-, Aryl- and μ-Ethynylene Gold(I) Complexes†

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The complexes [Au(PPh$_3$)Ph] **1**, [Au$_2$(dppm)Me$_2$] **2**, [Au$_2$(dppm)Ph$_2$] **3** and [{Au[P(C$_6$H$_4$OMe-*p*)$_3$]}$_2$(μ-C≡C)] **4** were prepared by literature methods. The structures of **1**–**3** have been established by X-ray crystallography: **1**, triclinic, space group $P\bar{1}$, a = 8.524(2), b = 15.227(2), c = 15.525 Å, α = 91.07(1), β = 92.06(1), γ = 94.28(1)°; **2**, monoclinic, space group $P2_1/n$, a = 12.201(3), b = 13.014(5), c = 16.329(4) Å, β = 94.11(2)°; **3**, monoclinic, space group $C2/c$, a = 16.688(3), b = 10.468(1), c = 17.899(2) Å, β = 97.70(1)°. The intramolecular Au···Au distances in **2** and **3** are 3.251(1) and 3.154(1) Å respectively. Extended-Hückel molecular orbital calculations showed that the highest occupied molecular orbital of **3** is a combination of d_{σ^*} and d_{δ^*}, whereas its lowest unoccupied molecular orbital is the π* of the co-ordinated phenyl group. The UV/VIS absorption spectra of **2** and **3** show intense absorptions at around 290–300 nm, which are assigned as Au(d_{σ^*}, d_{δ^*}) $\longrightarrow$ π*(Ph, dppm) in nature. Both **2** and **3** show luminescence in fluid solution at room temperature. The emission properties of **3** have been examined in detail. Complex **4** shows a well resolved vibronic structured emission at 400–600 nm in dichloromethane at room temperature, arising from the ^{3}[ππ*] excited state of C_2^{2-}.

Recent studies by us[1] and others[2] have uncovered the rich photochemistry of gold(I) complexes, which are generally emissive and with long-lived excited states in fluid solution at room temperature. Depending on the structure and nuclearity of the complexes, both intraligand[1a–c] and metal-centred[1d–i] emissions have been observed. These excited states are highly energetic and are strongly reducing. In the case of [Au$_2$(dppm)$_2$]$^{2+}$ [dppm = bis(diphenylphosphino)methane][1h] its ^{3}[$d_{\delta^*}p_\sigma$] excited state is a powerful reductant with a $E°$ value of −1.6 V *vs.* standard calomel electrode (SCE). This gold complex has been shown to be an effective photocatalyst for C–C bond formation from alkyl halides.[1e] Our recent studies also established that the phosphorescence of an organic molecule is greatly enhanced through co-ordination to Au^I. Long-lived and emissive intraligand excited states have been observed for gold(I)–phenylacetylide[1a] and –amide[1b] complexes.

In order to make use of gold(I) complexes in photoinduced organic transformation reactions it is essential that they should be soluble in non-polar organic solvents. In this context, neutral organometallic gold(I) complexes have received our attention. Herein we describe the structure and photophysical properties of some alkyl-, aryl- and μ-ethynylene gold(I) complexes.

Experimental

Reagents and Materials.—The compound P(C$_6$H$_4$OMe-*p*)$_3$ was obtained from Strem Co. The complexes [Au(PPh$_3$)Ph] **1**,[3] [Au$_2$(dppm)Me$_2$] **2**[4] and [{Au[P(C$_6$H$_4$OMe-*p*)$_3$]}$_2$(μ-C≡C)] **3**[5] were prepared by published procedures. Acetonitrile and dichloromethane for photophysical measurements were of spectroscopic grade and distilled over calcium hydride prior to use. The complex [Au$_2$(dppm)Ph$_2$] was prepared by treating [Au$_2$(dppm)Cl$_2$] (0.3 g) with a diethyl solution of LiPh (50 cm^3, 0.04 mol dm^{-3} in diethyl ether) under a nitrogen atmosphere for 12 h at room temperature. After the reaction water was added, the diethyl ether layer was separated and upon addition of hexane the product precipitated. It was recrystallised by slow evaporation of a dichloromethane–methanol (10:1 v/v) solution. Yield (53%) (Found: C, 47.4; H, 3.60; P, 6.40. Calc: C, 47.6; H, 3.45; P, 6.65%).

Physical Measurements and Instrumentation.—The UV/VIS spectra were recorded on a Milton Roy Spectronic 3000 diode-array spectrophotometer and steady-state emission spectra on a SPEX Fluorolog-2 spectrofluorometer. Emission lifetime measurements were performed with a Quanta Ray DCR-3 Nd-YAG laser (pulse output 355 nm, 8 ns). The decay signal was recorded by a R928 photomultiplier tube (Hamamatsu) digitised with a Tektronix 2430 digital oscilloscope interfaced to an IBM PC/AT computer, equipped with single- and double-exponential fitting. Solutions for emission and lifetime measurements were degassed by at least four freeze–pump–thaw cycles. The ^{31}P, ^{13}C and ^{1}H NMR spectra were recorded on a JNM-GSX 270 FT spectrometer (270 MHz); ^{31}P chemical shifts were referenced to 85% H$_3$PO$_4$.

Molecular Orbital Calculations.—Extended-Hückel molecular orbital (EHMO) calculations were carried out by using the ARGUS program.[6] The geometric parameters were obtained from the X-ray diffraction data. A total of 206 orbitals were employed and the parameters of the Au atom were taken from ref. 6.

Crystal Structure Determinations.—*Crystal data.* C$_{24}$H$_{20}$AuP **1**, M = 536.37, triclinic, space group $P\bar{1}$, a = 8.524(2), b = 15.227(2), c = 15.525(2) Å, α = 91.07(1), β = 92.06(1), γ = 94.28(1)°, U = 2000.6(1.0) Å^3, Z = 4, D_c = 1.774 g cm^{-3}, μ(Mo-Kα) = 73.97 cm^{-1}, F(000) = 1032, dimensions 0.07 × 0.1 × 0.2 mm.

C$_{27}$H$_{28}$Au$_2$P$_2$ **2**, M = 808.41, monoclinic, space group $P2_1/n$, a = 12.201(3), b = 13.014(5), c = 16.329(4) Å, β = 94.11(2)°, U = 2586.1(1.0) Å^3, Z = 4, D_c = 2.076 g cm^{-3}, μ(Mo-Kα) = 114.5 cm^{-1}, F(000) = 1512, dimensions 0.3 × 0.3 × 0.5 mm.

C$_{37}$H$_{32}$Au$_2$P$_2$ **3**, M = 932.55, monoclinic, space group

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Non-SI unit employed: eV ≈ 1.60 × 10^{-19} J.

$C2/c$, $a = 16.688(3)$, $b = 10.468(1)$, $c = 17.899(2)$ Å, $\beta = 97.70(1)°$, $U = 3098.6(1.0)$ Å^3, $Z = 4$, $D_c = 1.999$ g cm^{-3}, μ(Mo-Kα) = 95.69 cm^{-1}, $F(000) = 1768$, dimensions 0.1 × 0.15 × 0.35 mm.

Intensities were measured at 24 °C on an Enraf–Nonius CAD4 diffractometer with graphite-monochromatized Mo-Kα radiation (λ = 0.710 73 Å) using ω–2θ scans with ω-scan angles at scan speeds 1.10–5.49° min^{-1} for complexes **1** and **3** and 1.48–8.24° min^{-1} for **2**. Intensity data (**1**, $2\theta_{max}$ = 48°, h 0–9, k −17 to 17, l −17 to 17; **2**, $2\theta_{max}$ = 50°, h 0–14, k 0–15, l −19 to 19; **3**, $2\theta_{max}$ = 46°, h 0–18, k 0–11, l −19 to 19) were corrected for decay, Lorentz and polarisation effects and empirical absorption based on the ψ scans of four strong reflections. The numbers of independent and observed reflections [$F_o > 6.0\sigma(F_o)$] are **1**, 6280, 4489; **2**, 4769, 3598; **3**, 2188, 1954. The space groups were determined from systematic absences, and the structures were solved by Patterson and Fourier methods and subsequent refinement by full-matrix least squares using the Enraf–Nonius SDP programs[7] on a MicroVAX II computer. All the non-H atoms were refined anisotropically; H atoms were placed at calculated positions with isotropic thermal parameters equal to 1.3 times that of the attached C atom and not refined. In complex **3** the two halves of the molecule are related by a two-fold axis at $0,0,\frac{1}{4}$ along which the methylene carbon atom lies. The numbers of variables used in the least-squares refinement were 469, 280 and 185 for **1**, **2** and **3** respectively. The weighting scheme was $w = 4F_o^2/\sigma^2(F_o^2)$ where $\sigma^2(F_o^2) = [\sigma^2(I) + (0.05F_o^2)^2]$. The final R, R' and S values were **1**, 0.027, 0.035, 0.966; **2**, 0.037, 0.049, 1.53; **3**, 0.036, 0.047, 1.701. Final atomic coordinates of **1**, **2** and **3** are given in Tables 1, 2 and 3 respectively, selected bond distances and angles in Table 4.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters, and remaining bond lengths and angles.

Results and Discussion

The synthesis of complexes [Au(PPh$_3$)Ph] **1**, [Au$_2$(dppm)Me$_2$] **2** and [Au$_2$(dppm)Ph$_2$] **3** followed the literature procedures in which the starting [Au(PPh$_3$)Cl] and [Au$_2$(dppm)Cl$_2$] were allowed to react with the appropriate LiR (R = Me or Ph) in diethyl ether at room temperature. Their spectroscopic data are in agreement with the literature values. As expected, the ^{31}P NMR spectrum of **3** shows only one sharp peak at δ 33.82. Its ^{1}H NMR spectrum shows the phenyl protons as multiplets at δ 6.9–7.8 and the methylene protons as a triplet centred at δ 3.62. Their structures have been determined by X-ray crystallography.

Fig. 1 shows a perspective drawing of complex **1**. There are two independent molecules per unit cell. The Au^I has a two-

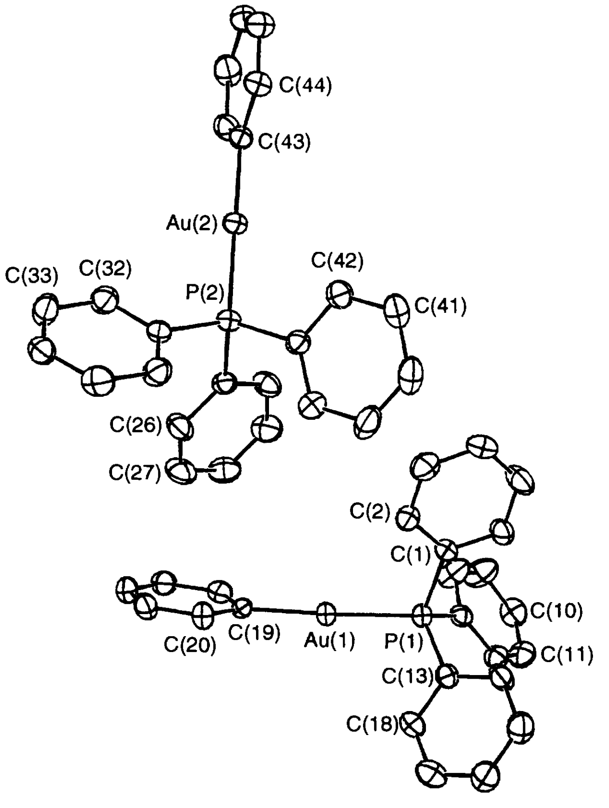

Fig. 1 Perspective drawing of complex **1**

Table 1 Positional parameters and their estimated standard deviations (e.s.d.s) for non-hydrogen atoms of complex **1**

Atom	x	y	z	Atom	x	y	z
Au(1)	−0.408 02(3)	0.380 99(2)	0.125 11(2)	Au(2)	0.158 51(3)	0.135 92(2)	0.619 23(2)
P(1)	−0.317 3(2)	0.525 7(1)	0.147 4(1)	P(2)	0.213 5(2)	0.149 1(1)	0.476 2(1)
C(1)	−0.192 5(8)	0.539 6(4)	0.245 7(4)	C(25)	0.042 3(7)	0.159 6(4)	0.404 1(4)
C(2)	−0.120 7(8)	0.467 7(4)	0.276 8(4)	C(26)	0.009 2(9)	0.106 6(5)	0.331 7(5)
C(3)	−0.024 5(9)	0.475 7(5)	0.350 1(5)	C(27)	−0.121 6(9)	0.118 6(5)	0.278 5(5)
C(4)	0.001 8(9)	0.555 6(5)	0.394 1(5)	C(28)	−0.218 6(9)	0.183 5(5)	0.299 1(5)
C(5)	−0.068(1)	0.627 3(5)	0.362 9(5)	C(29)	−0.187 9(9)	0.236 2(5)	0.370 5(5)
C(6)	−0.166 9(9)	0.620 0(4)	0.288 4(5)	C(30)	−0.058 6(8)	0.222 8(5)	0.424 3(4)
C(7)	−0.468 1(7)	0.600 2(4)	0.165 4(4)	C(31)	0.307 7(7)	0.056 0(4)	0.431 5(4)
C(8)	−0.565(1)	0.585 5(5)	0.234 4(5)	C(32)	0.264 8(8)	−0.025 7(4)	0.462 2(5)
C(9)	−0.682(1)	0.639 5(6)	0.250 3(6)	C(33)	0.322 3(9)	−0.101 0(4)	0.426 5(5)
C(10)	−0.709 3(9)	0.707 7(5)	0.198 5(6)	C(34)	0.427 6(8)	−0.092 6(4)	0.361 8(4)
C(11)	−0.616 1(9)	0.724 2(5)	0.130 1(5)	C(35)	0.474 4(8)	−0.011 1(5)	0.333 4(5)
C(12)	−0.495 0(8)	0.670 2(4)	0.113 5(4)	C(36)	0.413 2(9)	0.063 4(4)	0.367 2(5)
C(13)	−0.203 1(8)	0.571 6(4)	0.060 5(4)	C(37)	0.337 6(7)	0.248 0(4)	0.453 4(4)
C(14)	−0.102 0(9)	0.647 2(5)	0.070 9(5)	C(38)	0.346 1(9)	0.282 1(5)	0.371 4(5)
C(15)	−0.022 5(9)	0.680 6(5)	0.001 8(5)	C(39)	0.442(1)	0.357 4(4)	0.356 0(5)
C(16)	−0.041 0(9)	0.639 2(5)	−0.077 7(5)	C(40)	0.525 1(9)	0.401 0(5)	0.422 6(6)
C(17)	−0.137(1)	0.564 5(6)	−0.087 7(5)	C(41)	0.520 1(9)	0.368 6(5)	0.504 2(5)
C(18)	−0.219 5(9)	0.530 2(5)	−0.020 1(5)	C(42)	0.426 0(8)	0.292 3(4)	0.520 6(4)
C(19)	−0.475 5(8)	0.249 6(4)	0.112 0(4)	C(43)	0.119 2(8)	0.124 1(4)	0.748 4(4)
C(20)	−0.371 0(9)	0.189 6(4)	0.085 8(5)	C(44)	0.245 0(8)	0.134 8(4)	0.809 7(4)
C(21)	−0.409(1)	0.100 2(5)	0.084 2(5)	C(45)	0.223 3(9)	0.123 3(5)	0.895 8(5)
C(22)	−0.554(1)	0.067 0(5)	0.107 9(5)	C(46)	0.079(1)	0.100 0(5)	0.925 4(5)
C(23)	−0.661(1)	0.122 8(5)	0.133 4(5)	C(47)	−0.048 9(9)	0.089 4(5)	0.867 2(5)
C(24)	−0.622 3(9)	0.213 8(5)	0.135 8(4)	C(48)	−0.027 4(8)	0.101 8(4)	0.780 4(4)

Table 2 Positional parameters and their e.s.d.s for non-hydrogen atoms of complex **2**

Atom	x	y	z
Au(1)	0.007 52(3)	0.296 33(3)	0.404 48(2)
Au(2)	0.108 96(3)	0.669 6(3)	0.387 64(2)
P(1)	0.048 1(2)	0.293 5(2)	0.543 0(1)
P(2)	0.204 6(2)	0.121 7(2)	0.505 0(1)
C(1)	0.118 5(7)	0.176 1(6)	0.581 1(5)
C(2)	0.469(1)	0.193 6(9)	0.777 2(6)
C(3)	0.529 9(8)	0.487(1)	0.779 7(6)
C(4)	0.140 0(6)	0.398 2(6)	0.580 3(5)
C(5)	0.172 3(7)	0.469 2(6)	0.523 7(6)
C(6)	0.242 6(8)	0.549 3(7)	0.551 2(7)
C(7)	0.279 6(8)	0.553 9(7)	0.632 5(7)
C(8)	0.247 1(8)	0.484 4(8)	0.686 4(6)
C(9)	0.177 5(7)	0.404 2(8)	0.661 7(5)
C(10)	−0.070 9(7)	0.302 6(6)	0.605 3(5)
C(11)	−0.147 5(8)	0.225 5(7)	0.597 7(7)
C(12)	−0.241 2(8)	0.231 6(9)	0.641 7(7)
C(13)	−0.258 0(8)	0.312 4(9)	0.690 0(6)
C(14)	−0.184 3(8)	0.390 2(9)	0.696 0(6)
C(15)	−0.088 7(7)	0.384 8(8)	0.654 6(5)
C(16)	0.304 1(6)	0.220 1(6)	0.488 8(5)
C(17)	0.310 9(8)	0.255 9(7)	0.412 0(6)
C(18)	0.388 4(8)	0.333 2(8)	0.395 1(6)
C(19)	0.455 1(9)	0.372 2(8)	0.460 4(8)
C(20)	0.446 6(8)	0.336 8(8)	0.539 7(8)
C(21)	0.372 0(8)	0.262 7(8)	0.554 0(6)
C(22)	0.277 5(6)	0.017 2(6)	0.558 5(5)
C(23)	0.390 0(7)	0.012 8(8)	0.571 4(6)
C(24)	0.439 6(9)	−0.074 2(9)	0.608 3(7)
C(25)	0.377 6(8)	−0.156 5(8)	0.629 6(7)
C(26)	0.267 8(8)	−0.152 4(7)	0.619 4(6)
C(27)	0.213 9(8)	−0.066 2(7)	0.582 3(6)

Table 3 Positional parameters and their e.s.d.s for non-hydrogen atoms of complex **3**

Atom	x	y	z
Au	0.004 33(3)	0.194 91(4)	0.162 65(3)
P	0.063 7(2)	0.387 9(2)	0.196 9(2)
C(1)	0	0.5	0.25
C(2)	0.085 8(6)	0.486 6(9)	0.119 9(5)
C(3)	0.151 2(6)	0.450(1)	0.082 5(6)
C(4)	0.169 0(7)	0.517(1)	0.020 0(6)
C(5)	0.121 2(8)	0.618(1)	−0.005 2(6)
C(6)	0.058 4(7)	0.655(1)	0.027 5(7)
C(7)	0.038 6(7)	0.590(1)	0.090 3(6)
C(8)	0.158 1(6)	0.384(1)	0.259 9(6)
C(9)	0.190 6(7)	0.273 9(9)	0.292 5(6)
C(10)	0.260 1(8)	0.274(1)	0.342 0(7)
C(11)	0.300 9(8)	0.386(1)	0.359 5(7)
C(12)	0.270 6(8)	0.498(1)	0.327 1(7)
C(13)	0.200 8(6)	0.498(1)	0.278 8(6)
C(14)	−0.056 9(7)	0.029(1)	0.129 5(7)
C(15)	−0.086 7(7)	−0.052(1)	0.181 6(8)
C(16)	−0.130 5(8)	−0.160(1)	0.159 3(9)
C(17)	−0.144 1(8)	−0.196(1)	0.087 9(9)
C(18)	−0.117 0(9)	−0.121(1)	0.033 6(9)
C(19)	−0.074 3(8)	−0.008(1)	0.056 3(8)

co-ordinated linear geometry with P–Au–C angles 175.5(2) and 176.8(4)°. In the crystal lattice two of the $[Au(PPh_3)Ph]$ molecules are orientated as a pair but *anti* to each other. Nevertheless, there is no intermolecular Au ⋯ Au interaction.

The structure of complex **2** is quite similar to that of $[Au_2(dppm)Cl_2]$.[4] A perspective view of the molecule is shown in Fig. 2. The P–Au–C (CH_3) angle is essentially 180°. The two P–Au–CH_3 normal planes are twisted with respect to each other and with a dihedral angle of 94.9(4)°. The intramolecular Au ⋯ Au separation of 3.251(1) Å is about 0.1 Å shorter than that of 3.351(2) Å in the isostructural $[Au_2(dppm)Cl_2]$ complex.[4]

Table 4 Selected bond distances (Å) and angles (°)

Complex **1**			
Au(1)–P(1)	2.296(2)	Au(1)–C(19)	2.045(6)
P(1)–Au(1)–C(19)	175.5(2)		
Complex **2**			
Au(1)–P(1)	2.281(3)	Au(2)–C(3)	2.07(1)
Au(1)–C(2)	2.100(9)	Au(1) ⋯ Au(2)	3.251(1)
Au(2)–P(2)	2.285(2)	P(1) ⋯ P(2)	3.034(3)
C(2)–Au(1)–P(1)	177.3(4)	P(1)–C(1)–P(2)	111.7(5)
C(3)–Au(2)–P(2)	176.8(4)		
Complex **3**			
Au–P	2.300(2)	Au ⋯ Au*	3.154(1)
Au–C(14)	2.07(2)	P ⋯ P*	3.039(4)
P–Au–C(14)	175.8(4)	Au–P–C(1)	115.0(1)

* Atoms at $-x, y, \frac{1}{2} - z$.

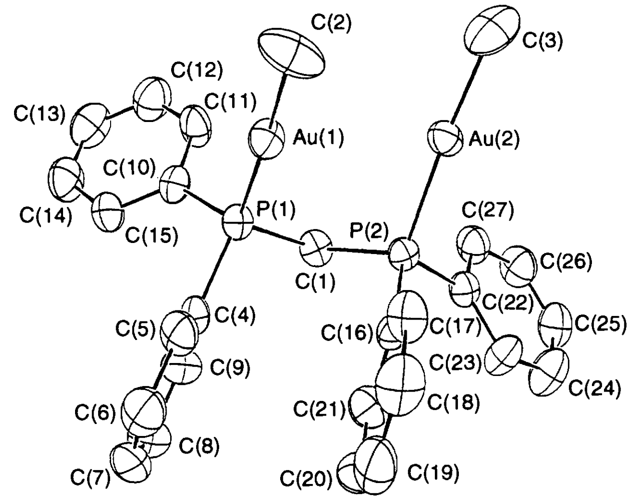

Fig. 2 Perspective drawing of complex **2**

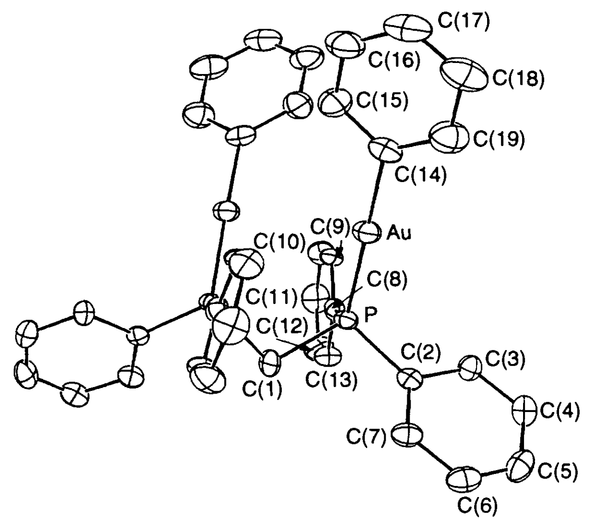

Fig. 3 Perspective drawing of complex **3**

Replacing the Me by the Ph group results in a similar structure, as shown by the perspective drawing in Fig. 3. The P–Au–C(Ph) angle of 175.8(4)° still conforms to a linear geometry. However the dihedral angle between the mean planes defined by the atoms Au, P, C(14), C(15) and C(19) becomes 57.14°. The intramolecular Au ⋯ Au distance is 3.154(1) Å,

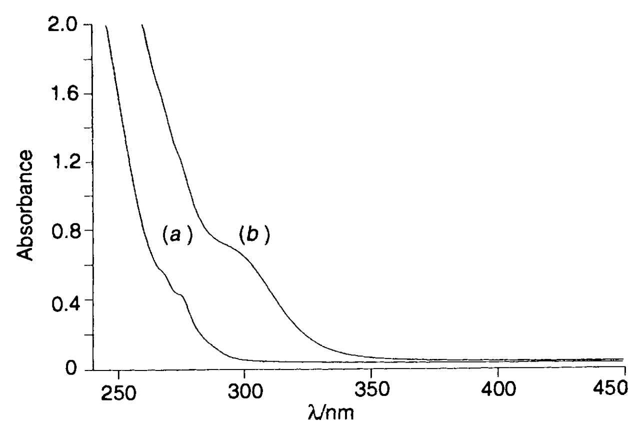

Fig. 4 The UV/VIS absorption spectra of complexes **1** (2.12×10^{-5} mol dm^{-3}) (*a*) and **3** (5.6×10^{-5} mol dm^{-3}) (*b*) in dichloromethane. Path length 1 cm

which is shorter than that of 3.251(1) Å in **2**. A similar structure with a Au···Au distance of 3.163(1) Å has previously been reported for $[Au_2(dppm)(C_6F_5)_2]$.[4] The intramolecular Au···Au separations in both complexes **2** and **3** are longer than that of 2.931(1) Å in $[Au_2(dppm)_2][BF_4]_2$.[8] In the crystal lattices of both **2** and **3** there is no intermolecular Au···Au contact. All the Au–C distances of **1**–**3** are similar to those of $[Au_2(dppm)(C_6F_5)_2]$ [Au–C 2.063(12) and 2.058(12) Å] but are longer than that of Au–C(C≡CPh) found in [Au$_2$(dppe)(C≡CPh)$_2$] [dppe = 1,2-bis(diphenylphosphino)ethane].[1a]

Spectroscopic and Photophysical Properties of Complexes **2** *and* **3**.—The UV/VIS absorption spectrum of complexes **1** and **3** are depicted in Fig. 4 and that of **2** in Fig. 5. While **1** [$\lambda_{max}(\varepsilon_{max})$ = 275 nm (2.0×10^4 dm^3 mol^{-1} cm^{-1})] displays no significant absorptions at wavelengths greater than 300 nm, both **2** and **3** have low-energy intense absorptions which appear as a shoulder at around 290–300 nm [λ_{max}/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}): **2**, 290 (8.92×10^4); **3**, 294 (1.25×10^4)]. There are also absorptions tailing from 290 to 350 nm. The red-shift in the low-energy absorption from mono- to di- and poly-nuclear gold(I) complexes has previously been noted in several cases[1d,g,h,2a,d,e] and ascribed to weak gold–gold interactions. For $[Au_2(dppm)_2]^{2+}$, the lowest-energy dipole-allowed transition at 290 nm has been assigned to the $d_{\sigma^*} \longrightarrow p_\sigma$ transition.[1h,2a,9] To assign the absorption bands of **2** and **3** at 290–300 nm to similar electronic transitions seems to be appealing at first glance. However, there is a problem. One would expect that the $d_{\sigma^*} \longrightarrow p_\sigma$ transition energy should decrease with the intramolecular Au···Au distance. The crystallographic data revealed that the intramolecular Au···Au distances of **2** and **3** are significantly longer than that of $[Au_2(dppm)_2]^{2+}$. However, the lowest-energy dipole-allowed transitions of these three complexes are at similar energies.

Extended-Hückel molecular-orbital calculations were performed on complex **3**. The net charge on the Au atom is 0.72e. The electron lost by Au is mostly located on the carbon atom of the phenyl ring which carries a charge of −0.77e. The calculated overlap population between the two Au atoms is 0.0412, which mostly arises from the interaction of the 6s, 6p and 5d orbitals of Au. As in previous studies, our calculation does provide support for a weak Au···Au bonding interaction, which has been termed 'aurophilicity' by Schmidbaur.[10]

The highest occupied molecular orbital (HOMO) at −10.305 eV of complex **3** has been found to consist of both d_{σ^*} (33) and d_{δ^*} (45%) and some σ_{Au-C} (22%). Here d_{σ^*} refers to a combination of 6s (15) and $5d_{z^2}$ (18%), and d_{δ^*} to a combination of $d_{x^2-y^2}$ (16) and d_{xy} (29%). We denote the HOMO as Au(d_{σ^*},d_{δ^*}). However, unlike $[Au_2(dppm)_2]^{2+}$,[2a] the lowest unoccupied molecular orbital (LUMO) at −8.359 eV is not p_σ in origin but rather is the π* orbital of the phenyl group. It should be mentioned that the 3d orbitals of dppm, which are at −8.295 eV, are at similar energies to those of the LUMO. Thus the lowest-energy allowed transition of **3** at 298 nm could be assigned to either Au(d_{σ^*},d_{δ^*}) ⟶ π*(Ph) or π*(dppm) or a hybrid of these two. In the case of **2**, the transition would be Au(d_{σ^*},d_{δ^*}) ⟶ π*(dppm). Our calculation also revealed that the p_σ orbital of **3** is 3.5 eV higher than the LUMO. This can be rationalised by the strong inductive effect of the Ph groups, which destabilise the p_σ orbitals.

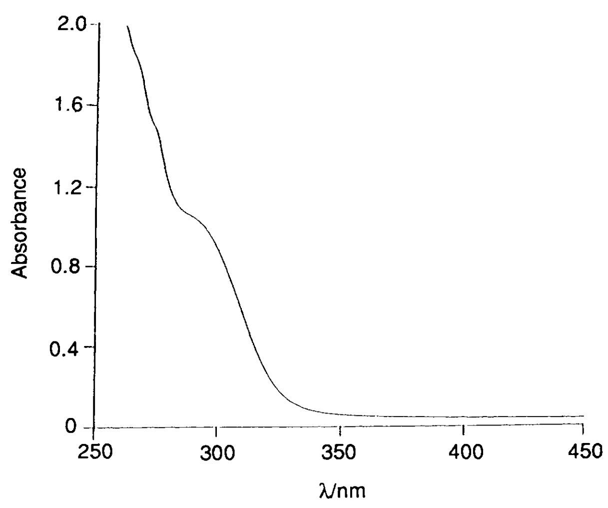

Fig. 5 The UV/VIS absorption spectrum of complex **2** (1.13×10^{-4} mol dm^{-3}) in dichloromethane. Path length 1 cm

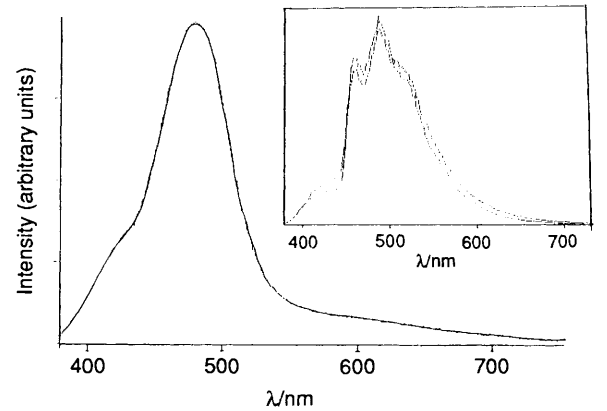

Fig. 6 Emission spectrum of complex **3** in a butyl nitrile glass at 77 K. The insert shows the emission spectrum recorded in the solid state at 77 K. Excitation: 320–350 nm

Photoluminescence has been found to be a common property of gold(I) systems.[1,2a,f] Previous studies showed that, for those polynuclear phosphine complexes having weak metal–metal interaction, both the high-energy intraligand emission of the phosphine ligand and the low-energy metal-centred emission from the $^3[d_{\delta^*}p_\sigma]$ excited state could be observed. In this work we found that **1** is non-emissive. For **2** in dichloromethane at room temperature a broad and weak emission (lifetime < 1.0 μs at room temperature) ranging from 430 to 600 nm was recorded upon excitation of the sample at 320–350 nm. Since the emission is very weak no detailed study on its photophysical properties was undertaken. For **3** in dichloromethane a broad emission peaking at 480–490 and ranging from 450 to 600 nm was recorded. The emission lifetime, monitored at 500 nm, is 1.0 ± 0.1 μs and the emission quantum yield is 1.6×10^{-3} at room temperature. In a butyl nitrile glass at 77 K the emission spectrum (Fig. 6) is better resolved. As shown there are two emissions, one at 480 nm and the less intense at 600 nm. In the solid state and at 77 K the high-energy emission shows vibronic

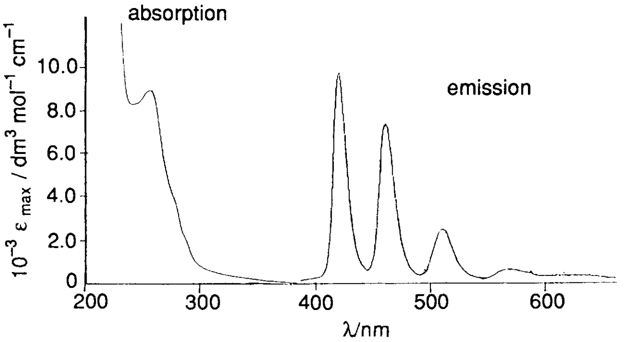

Fig. 7 The UV/VIS absorption and emission spectra of complex **4** in dichloromethane at room temperature. Absorption spectrum: concentration of **4** is 8.9×10^{-5} mol dm^{-3}. Emission spectrum: excitation at 320 nm

structure. The vibrational progression is around 1120 cm^{-1}, which corresponds to the skeletal vibration frequency of the phenyl ring (see Fig. 6). With this finding and the spectral assignment discussed above, the emission at 480 nm arises from $^3[\mathrm{Au}(d_{\sigma^*},d_{\delta^*}), \pi^*(\mathrm{Ph})]$ and the low-energy emission at around 600 nm from $^3[\mathrm{Au}(d_{\sigma^*},d_{\delta^*}), \pi^*(\mathrm{dppm})]$. Thus the emissions of **3** are metal-to-ligand charge transfer in origin.

Spectroscopic and Photophysical Properties of Complex **4**.—There has been a growing interest in μ-ethynylene metal complexes but studies on their physical and spectroscopic properties are sparse. Beck and co-workers[11] first reported the UV/VIS spectroscopic data, molecular orbital diagram *via* SCF-Xα-DV calculation and cyclic voltammetric studies of (μ-ethynylene)-bis(pentacarbonylrhenium). Our recent work showed that the phosphorescence of $\mathrm{PhC{\equiv}C^-}$ could be greatly enhanced through co-ordination to Au$^{\mathrm{I}}$.[1a] Thus co-ordination of the '$\mathrm{C_2}^{2-}$' unit to Au$^{\mathrm{I}}$ may provide a convenient entry to its photophysical properties. The complex $[\{\mathrm{Au}[\mathrm{P}(\mathrm{C_6H_4OMe}\text{-}p)_3]\}_2(\mu\text{-}\mathrm{C{\equiv}C})]$ **4** was prepared by the procedure reported by Cross and Davidson.[5] Its ^{13}C NMR spectrum shows a doublet centred at δ 89.95, which could be assigned to the μ-ethynylene carbon atoms with J(P–C) = 24.4 Hz. As expected, there is only one ^{31}P signal, which is at δ 38.28. The absorption spectrum (Fig. 7) is featureless. However, photoexcitation of a dichloromethane solution of **4** at 320 nm leads to a well resolved vibronic structured emission ranging from 400 to 600 nm. The emission spectrum is shown in Fig. 7. The observed vibrational spacing of 2100 cm^{-1} could be attributed to the ν(C≡C) stretch. The total emission quantum yield of 2.6×10^{-3} and the emission lifetime is 3.8, 4.2 and 3.0 μs measured at 510, 460 and 420 nm respectively. We suggest the emission of **4** arises from the intraligand $^3[\pi\pi^*]$ excited state of $\mathrm{C_2}^{2-}$.

Conclusion

Here we have shown with selected examples that neutral organometallic complexes of gold(I) also have long-lived and emissive excited states in fluid solution at room temperature. Since these complexes generally have a high solubility in non-polar organic solvents, their photochemistry should be rich but yet is relatively unexplored.

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