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Photophysical properties and crystal structures of luminescent phenylethynylgold(I) complexes of alkyl and aryl isocyanides

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Several phenylethynylgold(I) complexes were prepared by treating $[\{Au(C\equiv C{-}Ph)\}_\infty]$ with 2,5-diisocyano-2,5-dimethylhexane (L^1), (1,8-diisocyano-*p*-menthane (L^2) and 2,6-dimethylphenyl isocyanide in dichloromethane. The intermolecular Au ··· Au separations established by X-ray crystal analyses are 3.329(4), 3.565(2) and 3.485(3) Å for the crystals of $[(Au(C\equiv CPh)(CNC_6H_3Me_2\text{-}2,6)]$, $[\{Au(C\equiv CPh)\}_2L^1]$ and $[\{Au(C\equiv CPh)\}_2L^2]$ respectively. These gold(I) complexes have long-lived and emissive $^3(\pi\pi^*)$ excited states in fluid solutions at room temperature. The photoredox properties of $[Au(C\equiv CPh)(CNC_6H_3Me_2\text{-}2,6)]$ have been studied by Stern–Volmer quenching experiments, and its excited-state redox potential $E^\circ(Au^+{-}Au^{0*})$ is $-1.62(1)$ V *vs.* saturated sodium chloride calomel electrode.

There is a considerable interest in organogold(I) complexes containing π-acid ligands such as phosphines and aryl and alkyl isocyanides.[1-3] Recent studies have revealed the intriguing structures and photoelectronic properties of alkynyl and phenylethynyl complexes.[1,2b] In particular, some of these complexes form novel polymeric structures *via* gold(I)–gold(I) interactions.[1f,3d] Luminescence has also been observed from this class of complexes.[1,2b] Most of the gold(I)–alkynyl and –phenylethynyl complexes which have been subjected to photochemical studies have phosphines as ancillary ligands. Puddephatt and co-workers[3a] recently reported that it is possible to prepare rigid rod materials with extended backbone conjugation using $[\{Au(C\equiv CR)\}_\infty]$ (R = aryl) and bridging isocyanide ligands. Thus it would be interesting to learn whether or not the building block $(RNC)Au(C\equiv CR)$ would display long-lived and emissive excited states.

Herein is described the synthesis and crystal structures of three phenylethynylgold(I) complexes containing alkyl and aryl isocyanide ligands, $[Au(C\equiv CPh)(CNC_6H_3Me_2\text{-}2,6)]$ and $[\{Au(C\equiv CPh)\}_2L]$ (L = 2,5-diisocyano-2,5-dimethylhexane or 1,8-diisocyano-*p*-menthane). Their photophysical properties are also reported.

Experimental

Materials

The salt $K[AuCl_4]$ (Johnson Matthey Chemicals), 2,2′-thiodiethanol (Strem), phenylacetylene, sodium acetate and starting materials for the preparation of the isocyanide ligands, 2,5-dimethylhexane-2,5-diamine and 1,8-diamino-*p*-menthane were obtained from Aldrich Chemicals. 2,6-Dimethylphenyl isocyanide was obtained from Fluka Chemicals. The compounds 2,5-diisocyano-2,5-dimethylhexane (L^1) and 1,8-diisocyano-*p*-menthane (L^2) were prepared according to the method of Weber *et al.*[4] The complex $[\{Au(C\equiv CPh)\}_\infty]$ was prepared by the literature method.[5] Solvents for emission studies and lifetime measurements were spectroscopic grade.

Syntheses

$[Au(C\equiv CPh)(CNC_6H_3Me_2\text{-}2,6)]$ 1. A solution of 2,6-$Me_2C_6H_3NC$ (0.07 g, 0.5 mmol) in dichloromethane (10 cm^3) was added dropwise with stirring to a suspension of $[\{Au(C\equiv CPh)\}_\infty]$ (0.1 g, 0.3 mmol) in the same solvent (20 cm^3) for 30 min at room temperature. A clear solution was obtained. Upon preconcentration of the solution to 5 cm^3 and diffusion of diethyl ether, pale yellow crystals of $[(Au(C\equiv CPh)(CN\text{-}C_6H_3Me_2\text{-}2,6)]$ were obtained (yield 80%). IR (KBr pellets): ν(C≡N) 2211, ν(C≡C) 2119 cm^{-1} (Found: C, 47.7; H, 3.4; N, 3.20. Calc. for $C_{17}H_{14}AuN$: C, 47.5; H, 3.25; N, 3.25%).

$[\{Au(C\equiv CPh)\}_2L^1]$ 2. A mixture of compound L^1 (0.04 g, 0.25 mmol) and $[\{Au(C\equiv CPh)\}_\infty]$ (0.1 g, 0.33 mol) in dichloromethane (20 cm^3) was stirred at room temperature for 20 min until a clear solution was obtained. The volume of the solution was reduced to 5 cm^3. Pale yellow crystals were obtained by diffusion of diethyl ether into the solution. Yield (60%). IR (KBr pellets): ν(C≡N) 2250, ν(C≡C) 2120cm^{-1} (Found: C, 41.5; H, 3.45; N, 3.70. Calc. for $C_{26}H_{26}Au_2N_2$: C, 41.05; H, 3.40; N, 3.70%).

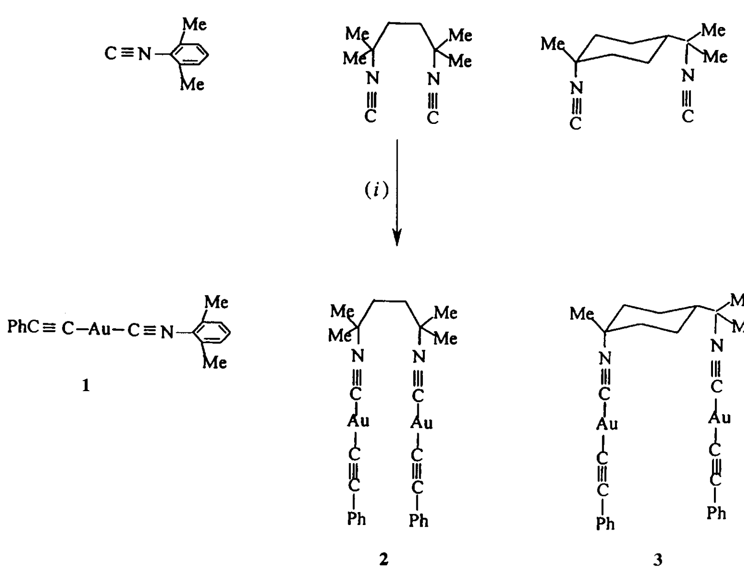
$[\{Au(C\equiv CPh)\}_2L^2]$ 3. A dichloromethane solution of compound L^2 (0.05 g, 0.25 mmol) was slowly added to a suspension of $[\{Au(C\equiv CPh)\}_\infty]$ (0.1 g, 0.33 mmol) in the same solvent (20 cm^3). After stirring for 20 min a clear solution was obtained and was preconcentrated to 5 cm^3. Pale yellow crystals were obtained by diffusion of diethyl ether into the solution. Yield (40%). IR (KBr pellets): ν(C≡N) 2250, ν(C≡C) 2118 cm^{-1} (Found: C, 43.1; H, 3.60; N, 3.60. Calc. for $C_{28}H_{28}Au_2N_2$: C, 42.75; H, 3.55; N, 3.55%).

Physical measurements and instrumentation

The UV/VIS absorption spectra were recorded on a Perkin-Elmer UV/VIS/NIR spectrophotometer, steady-state emission spectra on a SPEX Fluorolog-2 spectrofluorometer and IR spectra as KBr pellets on a Shimadzu IR-470 spectrophotometer. Emission-lifetime measurements were performed with a Quanta Ray DCR-3 Nd-YAG laser (pulse output 355 nm, 8 ns). The absolute emission quantum yield was measured by the method of Demas and Crosby.[6] Solutions for photochemical experiments were degassed by at least four freeze–pump–thaw cycles. Luminescence quenching experiments were performed by lifetime emission measurements, and the quenching rate constants were deduced from plots of $1/\tau$ *versus* [Q] according to the Stern–Volmer equation $\tau_0/\tau = 1 + k_q\tau_0[Q]$, where τ_0 and τ are the respective emission lifetimes in the absence and presence of quencher Q, k_q the quenching rate constant, and [Q] the quencher concentration.

Crystallography

X-Ray diffraction data for complexes **1**–**3** were collected on an Enraf-Nonius CAD-4 diffractometer with graphite-monochro-



Scheme 1 (*i*) [{Au(C≡CPh)}$_\infty$], CH$_2$Cl$_2$, room temperature

matized Mo-Kα radiation (λ = 0.7107 Å) using ω–2θ scan mode (2θ_{max}/°, scan speed/° min^{-1}: **1**, 54, 1.10–5.49; **2**, 50, 1.83–5.49; **3**, 48, 1.83–5.49, see Table 1. Three standard reflections measured every 2 h showed a decay of 4.2% for **1**, 4.1% for **2** and 3.2% for **3**. The intensity data were corrected for Lorentz-polarization effects, and empirically for absorption based on five strong reflections. The space groups were determined from systematic absences. The structures were solved by Patterson and Fourier methods and subsequently refined by full-matrix least squares on *F* using the Enraf-Nonius SDP programs[7] on a MicroVAX II computer. Unless otherwise stated, all 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. For **2**, the unit cell contains eight crystallographic asymmetric units and four molecules. The six methyl hydrogen atoms at C(16) and C(17) were not included in the refinement. The crystallinity of **3** was rather low and it was not possible to collect intensity data at 2θ > 48°. The number of $F_o > 6\sigma(F_o)$ is not large enough to refine the atomic parameters anisotropically. However, the least-squares refinement did converge and the refinement of the inverted structure led to a higher *R* factor of 0.085 and *R'* of 0.098. 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 are: **1**, 0.030, 0.038, 1.11; **2**, 0.030, 0.034, 1.12; **3**, 0.075, 0.083, 1.863.

Atomic coordinates, thermal parameters, and bond lengths and angles and have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/170.

Results and Discussion

Complexes **1**–**3** were synthesized by treating [{Au(C≡CPh)}$_\infty$] with the appropriate isocyanide ligands in dichloromethane (Scheme 1). These reactions are rapid at room temperature and the products are air-stable pale yellow solids. In the IR spectra strong ν(CN) stretching bands are observed at 2211 (**1**)[1] and 2250 cm^{-1} (**2** and **3**) comparable to that of 2215 cm^{-1} for [Au(C≡CBu^t)(CNC$_6$H$_4$C≡CH)].[3a] In addition, there is also one weak shoulder at around 2110 cm^{-1}. This is tentatively assigned to the C≡C stretching and a similar band at 2110 cm^{-1} has been reported for [Au(C≡CBu^t)(CNC$_6$H$_4$C≡CH)].[3a] The structures of **1**–**3** have been determined by X-ray crystal analyses.

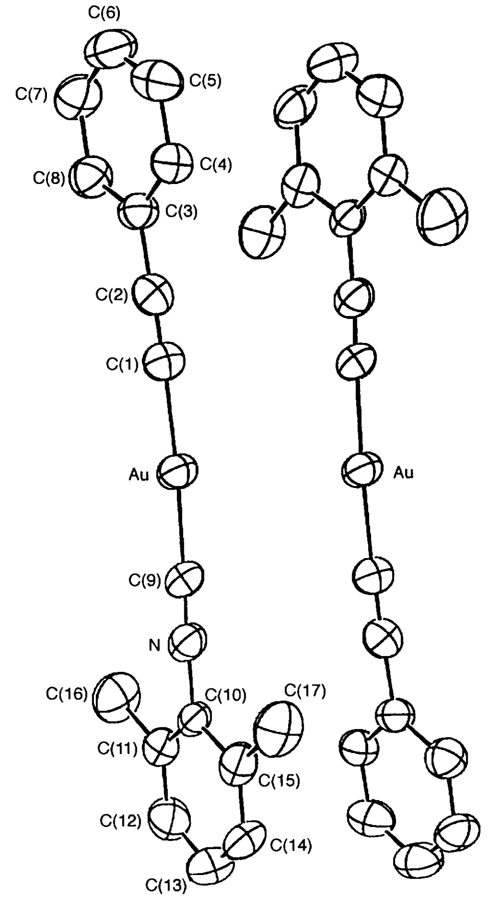


Fig. 1 Perspective view of complex **1**

Fig. 1 shows a perspective view of complex **1**. In the crystal lattice two weakly interacting molecules pair up in an *anti* configuration to allow an intermolecular Au ··· Au contact of 3.329(4) Å. This is similar to the separation of 3.379(1) Å in [Au(PPh$_3$)(C≡CPh)],[5] but shorter than those of 3.64 Å in K[Au(CN)$_2$],[8] 3.568 Å in [Au(MeNC)(CN)],[1b] 3.60 Å in [AuCl(CNC$_6$H$_4$C≡CH)][3a] and 3.479(2) Å in [Au(C≡CBu^t){CNC$_6$H$_3$(Me)C≡CH}][3a] suggesting weak intermolecular gold–gold interaction.[9] The co-ordination geometry of Au^I is almost linear with the C(9)–Au–C(1) angle 176.8(3)° (Table 2). The respective Au–C (CN) and Au–C (C≡C) distances of 1.957(7)

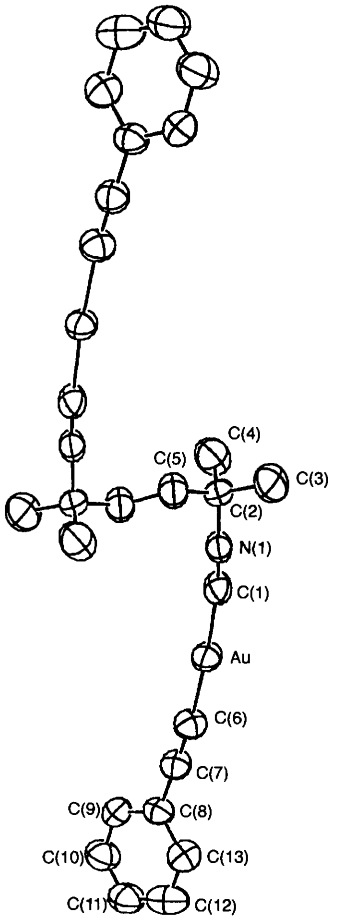


Fig. 2 Perspective view of complex 2

and 1.974(7) Å are nearly equal to those found in $[Au(RNC)(CN)]$[1b] analogues.

A perspective view of complex **2** is shown in Fig. 2. Similar to $[Au_2(L^1)(CN)_2]$,[1b] the L^1 ligand binds two Au(C≡CPh) units in an *anti* configuration. A molecule of $[Au_2(L^1)(C{\equiv}CPh)_2]$ is formed by two asymmetric units related by a centre of symmetry at $(-\frac{1}{2}, 0, 0)$. Two molecules of $[Au_2(L^1)(C{\equiv}CPh)_2]$ related by the centre of symmetry at (0, 0, 0) give an intermolecular non-bonding separation of 3.565(2) Å which is longer than the values of 3.3063(3) Å in $[Au_2(L^1)Cl_2]$,[10] 3.21(2) Å in $[Au_2(L^1)(CN)_2]$[1b] and 3.153(2) Å in $[\{Au(C{\equiv}CPh)\}_2(\mu\text{-dppe})]$[1d] [dppe = 1,2-bis(diphenylphosphino)ethane] respectively. The N≡C–Au–C≡C– chain is also linear with the C(1)–Au–C(6), Au–C(1)≡N(1), and Au–C(6)≡C(7) angles of 175.1(5), 172.8(8), and 173.3(9)° as in the case of $[\{Au(C{\equiv}CPh)\}_2(\mu\text{-dppe})]$[1d] [P–Au–C 176.6(7) and 172(1), Au–C≡C 177(2) and 168(3)°] and $[Au(PPh_3)(C{\equiv}CPh)]$ [P–Au–C 173.5(5) and 177.6(6); Au–C≡C 175.7(16) and 170.8(19); C≡C–C 176.5(18) and 174.0(20)°]. The Au–C (C≡C–Ph) and Au–C (C≡N) distances [1.971(9) and 1.952(8) Å] are similar to those of $[Au_2(L^1)Cl_2]$[10] [1.914(21)–1.921(22) Å] and $[Au_2(L^2)(CN)_2]$[1b] [1.96–1.98(1) Å].

Fig. 3 shows a perspective drawing of complex **3**. Owing to its low crystallinity the final *R* and *S* values are high. Nevertheless, its structures was found to be similar to that reported for $[Au_2(L^2)(CN)_2]$,[1a] with similar intramolecular Au···Au separation: $[Au_2(L^2)(CN)_2]$,[1a] 3.54(1); **3**, 3.485(3) Å.

Spectroscopic properties

The spectroscopic data for the three phenylethynylgold(I) complexes are summarized in Table 3. Fig. 4 depicts the UV/VIS absorption spectra measured in dichloromethane at room temperature. The three spectra are similar to each other showing intense absorption bands from 240 to 290 nm. There is an intense high-energy absorption around 240 nm, which is assigned to the $d_{z^2} \longrightarrow \pi^*(RNC)$ transition after the works of Chastain and Mason.[11] The two absorptions around 273 and 288 nm in each spectrum could arise from the intraligand π–π* transition(s) of the co-ordinated phenylacetylide, as similar transitions have previously been reported for the related complexes $[Au(PPh_3)(C{\equiv}CPh)]$[1d] and $[\{Au(C{\equiv}CPh)\}_2(\mu\text{-dppe})]$.[1d]

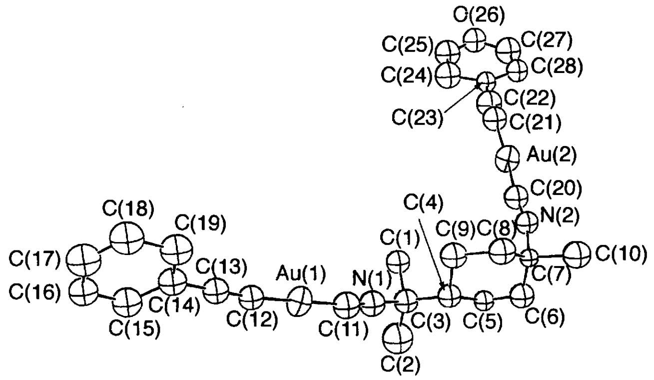


Fig. 3 Perspective view of complex 3

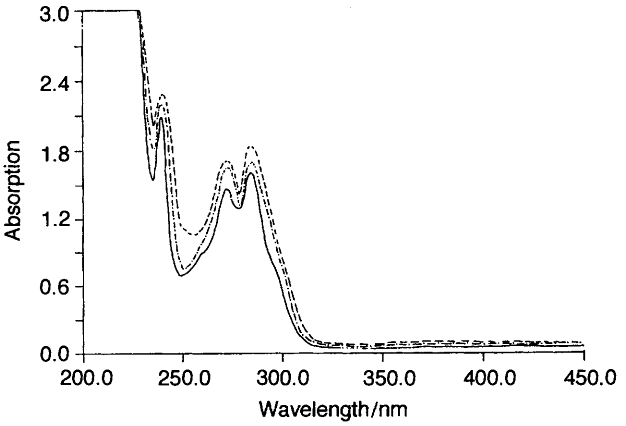


Fig. 4 The UV/VIS absorption spectra of $[Au(C{\equiv}CPh)(CNC_6H_3Me_2\text{-}2,6)]$ (——), $[\{Au(C{\equiv}CPh)\}_2L^1]$ (- · - · -) and $[\{Au(C{\equiv}CPh)\}_2L^2]$ (– – –) in dichloromethane at room temperature

Photophysical properties

Excitation of degassed dichloromethane solutions of complexes **1**–**3** at room temperature results in a long-lived emission with λ_{max} = 420 nm in each case. Fig. 5 shows the emission spectra of $[Au(C{\equiv}CPh)(CNC_6H_3Me_2\text{-}2,6)]$ measured in dichloromethane at room temperature and in a *n*-butyronitrile glass at 77 K. Both spectra show nice well resolved vibronic structure, and are similar to those of $[Pt(PEt_3)_2(C{\equiv}CPh)_2]$[12] and $[Au(PPh_3)(C{\equiv}CPh)]$[1d] which have been assigned to $^3(\pi\pi^*)$ transitions. In the solid state and at room temperature, a broad featureless emission band is observed for **1**–**3** and the emission maximum is red-shifted to around 550 nm. The emission energy is similar to that of the solid-state emission of $[\{Au(C{\equiv}CPh)\}_2(\mu\text{-dppe})]$[1d] ($\lambda_{max}$ = 570 nm), which has a relatively close $Au^I \cdots Au^I$ contact in the solid state [2.982(2) Å]. With reference to the crystal structures discussed above, the three complexes have intermolecular and/or intramolecular Au···Au contacts between 3.3 and 3.64 Å, suggesting the existence of weak gold–gold interaction in the solid state. With reference to previous works,[1d,e,13] such interaction would give rise to the low-energy $^3[d_\delta, p_\sigma]$ excited state, which is responsible for the solid-state emission. In fluid solution, the two molecules separate and the intraligand emission of the co-ordinated phenylacetylide

Table 1 Crystal data and summary of data collection and refinement for compounds **1**–**3**

	1	**2**	**3**
Formula	$C_{17}H_{14}AuN$	$C_{26}H_{26}Au_2N_2$	$C_{28}H_{28}Au_2N_2$
M	429.27	760.44	786.44
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$C2/c$	$P2_12_12_1$
a/Å	7.444(2)	11.921(2)	9.081(4)
b/Å	14.277(2)	11.348(1)	16.443(5)
c/Å	13.805(1)	11.396(2)	17.729(9)
β/°	90.08(1)	97.90(1)	—
U/Å^3	1467.1(1.0)	2464.9(1.0)	2647.2(1.0)
Z	4	4	4
F(000)	808	1416	1472
D_c/g cm^{-3}	1.943	2.051	1.973
Crystal size/mm	0.1 × 0.15 × 0.25	0.15 × 0.15 × 0.25	0.1 × 0.15 × 0.45
μ(Mo-Kα)/cm^{-1}	99.9	118.8	110.7
Scan width/°	0.60	0.95	1.30
T/K	296	296	301
Collection range, $2\theta_{max}$/°	54	50	48
Transmission factors	0.539–0.993	0.863–0.999	0.442–0.997
No. reflections measured	3327	2409	2395
No. unique data	3075	2228	2395
R^a	0.030	0.030	0.075
R'^b	0.038	0.034	0.083
S^c	1.11	1.12	1.863
No. reflections with $F_o > 6\sigma(F_o)$	2036	1317	1102
No. parameters in least-squares refinement	172	136	133
Residual electron density/e Å^{-3}	+0.65, −1.69	+1.07, −0.47	+1.68–1.55 (near the Au atoms), +0.75–0.74 (elsewhere)

[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [b] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma|F_o|^2]^{\frac{1}{2}}$. [c] $S = [\Sigma w(|F_o| - |F_c|)^2/(n - p)]^{\frac{1}{2}}$.

Table 2 Selected bond distances (Å) and angles (°)

Compound **1**			
Au–C(1)	1.974(7)	Au–C(9)	1.957(7)
N–C(9)	1.144(9)	N–C(10)	1.406(8)
C(1)–Au–C(9)	176.8(3)	C(9)–N–C(10)	176.2(7)
Au–C(1)–C(2)	177.2(6)	Au–C(9)–N	177.4(6)
Compound **2**			
Au–C(1)	1.952(8)	Au–C(6)	1.971(9)
N(1)–C(1)	1.15(2)	N(1)–C(2)	1.47(2)
C(1)–Au–C(6)	175.1(5)	C(1)–N(1)–C(2)	177.9(9)
Au–C(6)–C(7)	173.3(9)	Au–C(1)–N(1)	172.8(8)
N(1)–C(2)–C(3)	108.1(7)	N(1)–C(2)–C(4)	105.1(7)
N(1)–C(2)–C(5)	106.9(8)		
Compound **3**			
Au(1)–C(11)	1.80(6)	Au(1)–C(12)	1.75(5)
Au(2)–C(20)	2.05(5)	Au(2)–C(21)	2.03(6)
N(1)–C(3)	1.55(7)	N(1)–C(11)	1.23(7)
N(2)–C(7)	1.45(6)	N(2)–C(20)	1.09(7)
C(11)–Au(1)–C(12)	179(3)	C(20)–Au(2)–C(21)	173(2)
Au(1)–C(11)–N(1)	167(5)	Au(1)–C(12)–C(13)	173(4)
Au(2)–C(20)–N(2)	163(5)	Au(2)–C(21)–C(22)	164(5)

Table 3 Spectroscopic and photophysical data for the phenylethynylgold(I) complexes in dichloromethane

Complex	λ_{max}^{abs}/nm (ε × 10^{-4}/dm^3 mol^{-1} cm^{-1})	λ_{max}^{em}/nm	τ/μs (φ_{em})
1	288 (3.33)	419	7.65 (1.4 × 10^{-2})
	274 (3.30)	422	5.40 (3.7 × 10^{-2})*
2	288 (4.41)	420	2.89 (3.1 × 10^{-3})
	277 (4.02)		
3	288 (5.42)	420	2.50 (9.2 × 10^{-3})
	277 (4.97)		

* In acetonitrile.

becomes dominant. On cooling the solid sample to 77 K the emission intensity increases but no vibrational fine structure has been observed.

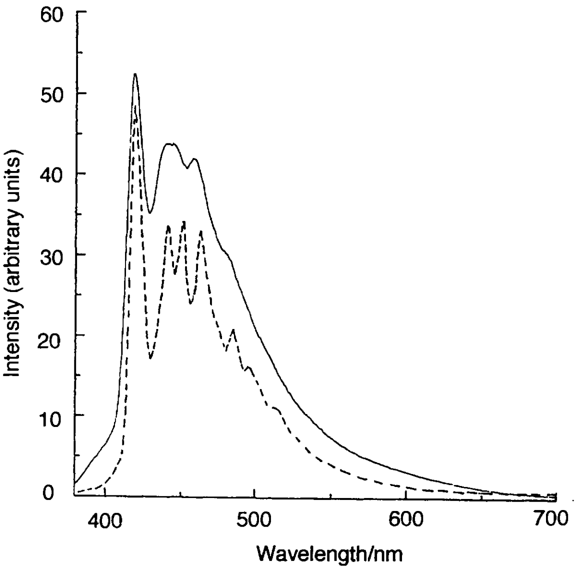


Fig. 5 Emission spectra of [Au(C≡CPh)(CN$C_6H_3Me_2$-2,6)] in dichloromethane at room temperature (——) and in a *n*-butyronitrile glass solution at 77 K (– – –). Excitation at 310 nm

Photoredox properties

With long emission lifetimes, these organogold(I) complexes should participate in photoinduced electron-transfer reactions. Since **1** can be considered as the building block for polymeric gold(I) phenylacetylide complexes with bridging isocyanide ligands, its photoredox properties have been studied. The emission was found to be quenched efficiently by methyl viologen (1,1′-dimethyl-4,4′-bipyridinium), mv^{2+}, in acetonitrile at room temperature. The quenching rate constant (k_q) is 1.63 × 10^{10} dm^3 mol^{-1} s^{-1}, which is higher than that of 5.1 × 10^8 dm^3 mol^{-1} s^{-1} in the case of [Au(PPh$_3$)(C≡CPh)].[1d] The quenching mechanism is electron transfer in nature, as represented by equation (1).

Table 4 Rate constants for quenching of the emission of complex **1** by pyridinium acceptors in acetonitrile at 298 K

Acceptor[a]	$E(A^{+/0})$/V *vs.* SSCE[b]	k_q/dm^3 mol^{-1} s^{-1}	$k_q'^c$/dm^3 mol^{-1} s^{-1}	ln k_q' (corrected)
N,*N*′-Dimethyl-4,4′-bipyridinium	−0.45	1.63×10^{10}	8.79×10^{10}	25.2
4-Cyano-*N*-methylpyridinium	−0.67	1.50×10^{10}	5.89×10^{10}	24.8
(*N*-Ethyl-4-pyridinio)amide	−0.93	6.45×10^9	9.53×10^9	23.0
(*N*-Benzyl-3-pyridinio)amide	−1.07	4.70×10^9	6.14×10^9	22.54
(*N*-Methyl-3-pyridinio)amide	−1.14	2.28×10^9	5.92×10^9	22.50
N-Ethylpyridinium	−1.36	1.13×10^9	1.16×10^9	20.51
4,*N*-Dimethylpyridinium	−1.49	4.33×10^7	4.34×10^7	17.58
2,6,*N*-Trimethylpyridinium	−1.52	3.30×10^7	3.31×10^7	17.31

[a] All are hexafluorophosphate salts. [b] From ref. 14. [c] Rate constant corrected for the diffusion rate constant of 2×10^{10} dm^3 mol^{-1} s^{-1}.

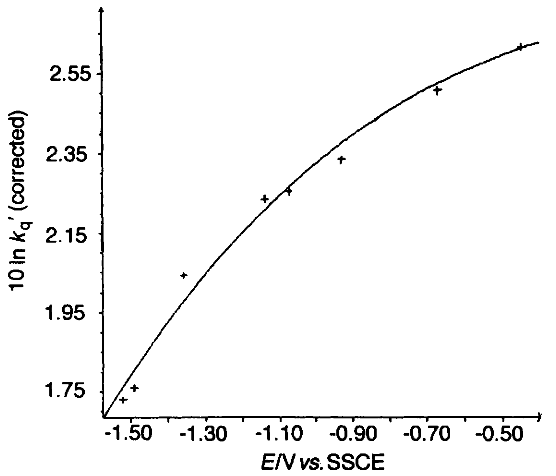


Fig. 6 Driving-force dependence of the rates of photoinduced electron-transfer reactions between complex **1** and pyridinium ions in acetonitrile at room temperature. The solid curve is a fit of the data by the Agmon–Levine equation. SSCE = Saturated sodium chloride calomel electrode

$$[Au(C{\equiv}CPh)(CNC_6H_3Me_2\text{-}2,6)]^* + mv^{2+} \longrightarrow [Au(C{\equiv}CPh)(CNC_6H_3Me_2\text{-}2,6)]^+ + mv^+ \quad (1)$$

In order to understand more about the excited-state reactivities, a study of the electron-transfer quenching of the emission of $[Au(C{\equiv}CPh)(CNC_6H_3Me_2\text{-}2,6)]^*$ by a series of pyridinium acceptors with different reduction potentials[14] was undertaken. Linear Stern–Volmer quenching kinetics within the concentration range of the quenchers (10^{-4}–10^{-5} mol dm^{-3}) was found. The experimental quenching rate constants were corrected for diffusion effects by using equation (2), where k_d is

$$\frac{1}{k_q'} = \frac{1}{k_q} - \frac{1}{k_d} \quad (2)$$

the diffusion-limited rate constant in acetonitrile and is taken to be 2.0×10^{10} dm^3 mol^{-1} s^{-1} and k_q' is the rate constant corrected for diffusional effects. The results are listed in Table 4. Non-linear least-square fits of ln k_q' *versus* $E°(Q^{0/+})$ using equation (3),[15] have been made. Here $K = k_d/k_{-d}$ which is

$$(RT/F) \ln k_{q'} = (RT/F) \ln K\kappa\nu - \lambda\,(1 + \Delta G/\lambda)^2/4 \quad (3)$$

approximately 1–2 dm^3 mol^{-1}, κ is the transmission coefficient, ν is the nuclear frequency, λ the reorganization energy for electron transfer, and ΔG the standard free-energy change of the reaction, and is given by equation (4). The work terms ω_p

$$\Delta G = E°(Au^{+/0*}) - E°(Q^{0/+}) + \omega_p - \omega_p \quad (4)$$

and ω_r associated with bringing the reactants or products to mean separation are small and are neglected in this case.

Fig. 6 shows the theoretical fit. The values of the parameters obtained in the fitting, namely the reduction potential of the excited state $E°(Au^+/Au^{0*})$, is −1.62(1) V *vs.* SSCE, and λ = 1.07 eV, *ca.* 1.7×10^{-19} J). The close agreement between the theoretical curve and the experimental data is in accord with the fact that the photoreactions are outer-sphere electron transfer in nature. The large negative value of $E°[Au(C{\equiv}CPh)(CNC_6H_3Me_2\text{-}2,6)^{+/0*}]$ is indicative of the strong reductive nature of the excited state, and is comparable to $E°[Au_2(dppm)_2{}^{3+/2+*}] = -1.6(1)$V *vs.* SSCE (dppm = $Ph_2PCH_2PPh_2$).[13]

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