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Synthesis, photophysics and photochemistry of alkynylgold(I) phosphine complexes†

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A series of alkynylgold(I) phosphine complexes with various bridging phosphines and acetylide ligands have been synthesized. All complexes have been shown to exhibit rich photophysical and photochemical behaviour. A systematic comparative study on their spectroscopy and photophysics has been attempted. The complexes undergo facile electron-transfer reactions with pyridinium electron acceptors. The redox nature of the quenching reactions has been established by time-resolved transient absorption spectroscopy.

Since the first study of the photoluminescence of d^{10} gold(I) phosphine complexes by Dori and co-workers,[1] a number of reports on the spectroscopic and photochemical studies of such complexes have emerged.[2–5] By using mono-, di- and polydentate phosphines as ligands, the respective mono-, di- and poly-nuclear complexes could be obtained and their spectroscopic properties studied. However, despite the wide and selective applications of alkynylcopper(I) complexes in organic chemistry, the chemistry of the heavier gold congener has not been as extensively studied. In fact, gold(I) ethynyls are amongst the most stable organogold(I) compounds.[6] Nevertheless, such compounds containing tertiary phosphines appear to be limited to $[Au(PR_3)(C{\equiv}CR)]$.[7] Only recently is there growing interest in the synthesis of ethynylgold(I) compounds with bidentate phosphines.[4a,5a,c,8,9] For most of the complexes concerned, the distances between the gold(I) centres have been studied and discussed extensively.[2,3,4a,5b,9–11] Such weak Au···Au interaction, which has a bond energy comparable to that of hydrogen bonding, is important in determining the molecular conformations and packing within the complexes.[12,13] Besides, such interactions have been suggested to be the origins of the luminescent properties of a number of gold(I) complexes.[2,3]

In this work a series of alkynylgold(I) phosphine complexes with phosphine ligands such as PMe_3, bis(dimethylphosphino)methane (dmpm) and bis(dimethylphosphinomethyl)methylphosphine (dmmp), 1,8-bis(dicyclohexylphosphino)naphthalene (dcpn) and 1,8-bis(diphenylphosphino)naphthalene (dppn) have been synthesized and their photophysical and photochemical properties investigated.

Experimental

Materials and reagents

Potassium tetrachloroaurate(III), trimethylphosphine, oct-1-yne and phenylacetylene were obtained from Aldrich Chemical Co., dmpm and dmmp from Strem Chemical Ltd. and 4-methoxyphenylacetylene and 4-biphenylacetylene from Maybridge Chemical Co. Ltd. The compounds $[\{Au(C{\equiv}CR)\}_n]$,[7] $[\{Au(deb)Au\}_n]$ (H_2deb = 1,4-diethynylbenzene),[8] dppn[14] and dcpn[14] were prepared by published methods; $[\{Au(dea)Au\}_n]$ (H_2dea = 9,10-diethynylanthracene) was prepared by modification of the published method for [Au(deb)Au].[8] All the mononuclear $[Au(PR_3)(C{\equiv}CR')]$ complexes were prepared by modification of a published procedure.[7] All solvents were purified and distilled by standard procedures before use. All other reagents were of analytical grade and used as received.

Preparation of complexes

All reactions were carried out under a stream of dry nitrogen at room temperature.

$[\{(p\text{-}MeC_6H_4)_3P\}Au(deb)Au\{P(C_6H_4Me\text{-}p)_3\}]$ 1. To a suspension of $[\{Au(deb)Au\}_n]$ (100 mg, 0.19 mmol) in CH_2Cl_2 (10 cm^3) was added a solid sample of $P(C_6H_4Me\text{-}p)_3$ (115 mg, 0.38 mmol). A clear yellow solution was obtained at once. After stirring for 30 min the solution was concentrated and addition of hexane precipitated the product, which was subsequently recrystallized from dichloromethane–hexane. Yield 130 mg (60%). ^1H NMR (CD_2Cl_2): δ 2.39 (s, 18 H, Me) and 7.27–7.52 (m, 4 H, C_6H_4; 24 H, PPh). Positive-ion FAB mass spectrum: *m/z* 1128 (M^+). IR(Nujol): $\tilde{\nu}/cm^{-1}$ 2094vw (C≡C) (Found: C, 55.40; H, 4.15. Calc. for $C_{52}H_{46}Au_2P_2{\cdot}(CH_3CH_2)_2O$: C, 56.00; H, 4.70%).

$[\{(p\text{-}MeC_6H_4)_3P\}Au(dea)Au\{P(C_6H_4Me\text{-}p)_3\}]$ 2. The procedure was similar to that above except that $[\{Au(dea)Au\}_n]$ (117 mg, 0.19 mmol) was used instead of $[\{Au(deb)Au\}_n]$. Yield 130 mg (55%). ^1H NMR [$(CD_3)_2CO$]: δ 2.44 (s, 18 H, Me), 7.44–7.6 (m, 24 H, PPh; 6 H, anthracene) and 8.80 (dd, 2 H, anthracene). Positive-ion FAB mass spectrum: *m/z* 1228 (M^+). IR(Nujol): $\tilde{\nu}/cm^{-1}$ 2100vw (C≡C) (Found: C, 58.40; H, 3.85. Calc. for $C_{60}H_{50}Au_2P_2$: C, 58.75; H, 4.10%).

$[Au_2(dppn)(C{\equiv}CC_6H_4Ph\text{-}p)_2]$ 3. To a yellow suspension of $[\{Au(C{\equiv}CC_6H_4Ph\text{-}p)\}_n]$ (100 mg, 0.27 mmol) in dichloromethane (10 cm^3) was added a solid sample of dppn (67 mg, 0.14 mmol). A dull yellow suspension resulted and the mixture was allowed to stir for 18 h. The solid was filtered off and the filtrate concentrated and chromatographed on Al_2O_3 using dichloromethane–acetone (9 : 1) as eluent. After evaporation of the solvent the residue was recrystallized by slow diffusion of diethyl ether vapour into a dichloromethane solution of the solid. Yellow crystals were obtained. Yield 34 mg (20%). ^1H NMR (CD_2Cl_2): δ 7.11–7.57 (m, 20 H, PPh_2; 4 H, naphthyl) and 8.13 (d, 2 H, naphthyl). Positive-ion FAB mass spectrum: *m/z* 1067 ($[M - C{\equiv}CC_6H_4Ph\text{-}p]^+$). IR(Nujol): $\tilde{\nu}/cm^{-1}$ 2110w (C≡C) (Found: C, 59.85; H, 3.20. Calc. for $C_{66}H_{44}Au_2P_2$: C, 59.80; H, 3.55%).

$[Au_2(dcpn)(C{\equiv}CC_6H_4Ph\text{-}p)_2]$ 4. To a dichloromethane solution of $[\{Au(C{\equiv}CC_6H_4Ph\text{-}p)\}_n]$ (100 mg, 0.27 mmol) was added a solid sample of dcpn (70 mg, 0.14 mmol). A clear yellow solution resulted after stirring for 1 h. It was concentrated, hexane added and then filtered. Subsequent recrystallization

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

using CH_2Cl_2–hexane gave air-stable yellow crystals of $[Au_2(dcpn)(C\equiv CC_6H_4Ph\text{-}p)_2]$. Yield 69 mg (40%). ^1H NMR (CD_2Cl_2): δ 0.99–2.68 (m, 44 H, cyclohexyl) and 7.30–8.08 (m, 6 H, naphthyl; 18 H, biphenyl). Positive-ion FAB mass spectrum: *m/z* 1268 (M^+) and 1091 ($[M - C\equiv CC_6H_4Ph\text{-}p]^+$). IR(Nujol): $\tilde{\nu}$/cm^{-1} 2110w (C≡C) (Found: C, 58.85; H, 5.30. Calc. for $C_{62}H_{68}Au_2P_2$: C, 58.70; H, 5.35%).

$[Au_2(dppn)(C\equiv CC_6H_4OMe\text{-}p)_2]$ 5. A suspension of $[Au_2(dppn)Cl_2]$ (100 mg, 0.11 mmol) in ethanol (10 cm^3) was treated with an ethanolic solution of a mixture of *p*-methoxyphenylacetylene (29 mg, 0.22 mmol) and sodium ethoxide (5.1 mg Na in 5 cm^3 EtOH). The dull yellow suspension gradually turned pale yellow. After stirring for 5 h, the dull yellow solid was filtered off and recrystallized by slow diffusion of diethyl ether vapour into a dichloromethane solution of the crude product. Yield 38 mg (30%). ^1H NMR [$(CD_3)_2CO$]: δ 3.75 (s, 6 H, OMe), 7.13–7.68 (m, 4 H, naphthyl; 8 H, $C\equiv CC_6H_4OMe\text{-}p$; 20 H, PPh_2) and 8.35 (m, 2 H, naphthyl). Positive-ion FAB mass spectrum: *m/z* 1153 (M^+) and 1022 ($[M - C\equiv CC_6H_4OMe\text{-}p]^+$). IR(Nujol): $\tilde{\nu}$/cm^{-1} 2110w (C≡C) (Found: C, 54.25; H, 3.40. Calc. for $C_{52}H_{40}Au_2O_2P_2$: C, 54.20, H, 3.45%).

$[Au_2(dppn)(C\equiv CC_6H_{13})_2]$ 6. To a benzene solution of $[\{Au(C\equiv CC_6H_{13})\}_n]$ (100 mg, 0.33 mmol) was added a solid sample of dppn (81 mg, 0.16 mmol). A clear yellow solution resulted after stirring for 1 h. It was concentrated, hexane added and then filtered. Subsequent recrystallization from benzene–hexane gave air-stable yellow crystals of $[Au_2(dppn)(C\equiv CC_6H_{13})_2]$. Yield 40 mg (22%). ^1H NMR (CD_2Cl_2): δ 0.88 (m, 6 H, CH_3), 1.16 (m, 16 H, CH_2), 2.67 (m, 4 H, $C\equiv CCH_2$) and 6.80–7.27 (m, 26 H, dppn). Positive-ion FAB mass spectrum: *m/z* 1000 ($[M - C\equiv CC_6H_{13}]^+$). IR(Nujol): $\tilde{\nu}$/cm^{-1} 2110w (C≡C) (Found: C, 52.30; H, 4.55. Calc. for $C_{50}H_{52}Au_2P_2\cdot 0.5CH_2Cl_2$: C, 52.70; H, 4.60%).

$[Au_2(dmpm)(C\equiv CPh)_2]$ 7. A suspension of $[Au_2(dmpm)Cl_2]$ (100 mg, 0.17 mmol) in ethanol (10 cm^3) was treated with an ethanolic solution of a mixture of phenylacetylene (36 cm^3, 0.33 mmol) and sodium ethoxide (7.6 mg Na in 5 cm^3 ethanol). The mixture was stirred at room temperature for 4 h and the white suspension slowly turned yellow. The yellow solid was then filtered off and washed successively with water, methanol and diethyl ether. Analytically pure samples were obtained by slow diffusion of diethyl ether vapour into a dichloromethane solution to give yellow crystals. Yield 73 mg (60%). ^1H NMR (CD_2Cl_2): δ 1.64 (m, 6 H, PMe), 2.10 (m, 6 H, PMe), 2.89 (br m, 2 H, CH_2) and 7.11–7.45 (m, 10 H, Ph). Positive-ion FAB mass spectrum: *m/z* 632 ($[M - C\equiv CPh]^+$). IR(Nujol): $\tilde{\nu}$/cm^{-1} 2101s (C≡C) (Found: C, 34.55; H, 3.20. Calc. for $C_{21}H_{24}Au_2P_2$: C, 34.45; H, 3.25%).

$[Au_2(dmpm)(C\equiv CC_6H_4OMe\text{-}p)_2]$ 8. The procedure was similar to that for $[Au_2(dmpm)(C\equiv CPh)_2]$ except that *p*-methoxyphenylacetylene (44 mg, 0.33 mmol) was used instead of phenylacetylene. Yield 72 mg (55%). ^1H NMR (CD_2Cl_2): δ 1.77–1.92 (m, 6 H, PMe), 2.09 (m, 6 H, PMe), 2.89 (br m, 2 H, CH_2), 3.75 (s, 6 H, OMe) and 6.74–7.41 (m, 8 H, C_6H_4). Positive-ion FAB mass spectrum: *m/z* 661 ($[M - C\equiv CC_6H_4OMe\text{-}p]^+$). IR(Nujol): $\tilde{\nu}$/cm^{-1} 2101w (C≡C) (Found: C, 34.85; H, 3.45. Calc. for $C_{23}H_{28}Au_2O_2P_2$: C, 34.85; H, 3.55%).

$[Au_3(dmmp)(C\equiv CPh)_3]$ 9. A suspension of $[Au_3(dmmp)Cl_3]$ (100 mg, 0.11 mmol) in ethanol was treated with an ethanolic solution of phenylacetylene (37 cm^3, 0.34 mmol) and sodium ethoxide (7.7 mg sodium in 5 cm^3 EtOH). After stirring for 18 h the yellow solid was filtered off and washed successively with water, methanol and diethyl ether. Analytically pure samples were obtained by recrystallization from dichloromethane–hexane. Yield 73 mg (60%). ^1H NMR (CD_2Cl_2): δ 1.50–1.90 (m, 15 H, Me_2P and MeP), 2.30–2.98 (m, 4 H, CH_2) and 7.02–7.60 (m, 15 H, Ph). Positive-ion FAB mass spectrum: *m/z* 991 ($[M - C\equiv CPh]^+$). IR(Nujol): $\tilde{\nu}$/cm^{-1} 2102w (C≡C) (Found: C, 33.90; H, 2.90. Calc. for $C_{31}H_{34}Au_3P_3$: C, 34.15; H, 3.10%).

$[Au_3(dmmp)(C\equiv CC_6H_4OMe\text{-}p)_3]$ 10. The procedure was similar to that for $[Au_3(dmmp)(C\equiv CPh)_3]$, except that *p*-methoxyphenylacetylene (44 mg, 0.33 mmol) was used in place of phenylacetylene. Yield 73 mg (55%). ^1H NMR (CD_2Cl_2): δ 1.53–2.00 (m, 15 H, Me_2P and MeP), 2.30–2.95 (m, 4 H, CH_2), 3.75 (s, 9 H, OMe) and 6.77–7.38 (m, 12 H, C_6H_4). Positive-ion FAB mass spectrum: *m/z* 1051 ($[M - C\equiv CC_6H_4OMe\text{-}p]^+$). IR(Nujol): $\tilde{\nu}$/cm^{-1} 2102vw (C≡C) (Found: C, 34.30; H, 3.10. Calc. for $C_{34}H_{40}Au_3O_3P_3$: C, 34.60; H, 3.40%).

Physical measurements and instrumentation

The UV/VIS spectra were obtained on a Hewlett-Packard 8452A diode-array spectrophotometer, IR spectra as Nujol mulls on a Bio-Rad FTS-7 Fourier-transform spectrophotometer (4000–400 cm^{-1}), and steady-state excitation and emission spectra on a Spex Fluorolog-2 111 spectrofluorometer. Low-temperature (77 K) spectra were recorded by using an optical Dewar sample holder. Proton NMR spectra were recorded on a JEOL JNM-GSX270 Fourier-transform spectrometer with chemical shifts reported relative to $SiMe_4$, positive-ion FAB mass spectra on a Finnigan MAT95 spectrometer. Elemental analyses of the new complexes were performed by Butterworth Laboratories Ltd.

Emission-lifetime measurements were performed using a conventional laser system. The excitation source was the 355 nm output (third harmonic) of a Quanta-Ray Q-switched GCR-150 pulsed Nd-YAG laser. Luminescence decay signals were recorded on a Tektronix model TDS 620A digital oscilloscope and analysed using a program for exponential fits. All solutions for photophysical studies were prepared under vacuum in a round-bottomed flask (10 cm^3) equipped with a side-arm 1 cm fluorescence cuvette and sealed from the atmosphere by a Kontes quick-release Teflon stopper. Solutions were rigorously degassed with no fewer than four freeze–pump–thaw cycles.

Time-resolved transient absorption spectroscopy was performed using the 355 nm output of a Quanta-Ray GCR-150 pulsed Nd-YAG laser as the excitation source, with the monitoring light beam generated from a 250 W quartz–tungsten–halogen lamp placed perpendicular to the excitation beam. The transient absorption signals were amplified using a Tektronix AM502 differential amplifier, and digitized on a Tektronix TDS 620A digital oscilloscope, interfaced to an IBM-compatible personal computer for data acquisition and analysis. The transient absorption difference spectra were generated using the point-to-point method. The back electron-transfer rate constants (k_b) were obtained from a knowledge of the slope (m) of a plot of the reciprocal of absorbance change at 605 nm ($1/\Delta A$) *versus* time (t) for the transient signal with $k_b = (\Delta\varepsilon)bm$ where $\Delta\varepsilon$ is the difference in absorption coefficient between products and reactants at the monitored wavelength of 605 nm, which is taken to approximate $\varepsilon = 13\,900$ dm^3 mol^{-1} cm^{-1} for methyl viologen (1,1′-dimethyl-4,4′-bipyridinium) radical cation[15] and b is the pathlength of the cell. The plot was linear over at least 2.5 half-lives, indicative of second-order kinetics.

Results and Discussion

The alkynylgold(I) phosphine complexes were prepared either by the reaction of RC≡CH with the corresponding chlorogold(I) phosphine precursor in the presence of a base or by depolymerization of $[\{Au(C\equiv CR)\}_n]$ with the phosphine. In

Table 1 Photophysical data for complexes **1**–**18**

Complex	Absorption* λ/nm (ε/dm^3 mol^{-1} cm^{-1})	Medium (T/K)	Emission λ/nm (τ_0/μs)
1 $[\{(p\text{-MeC}_6H_4)_3P\}Au(deb)Au\{P(C_6H_4Me\text{-}p)_3\}]$	242 (sh) (70 650), 294 (29 535), 308 (62 020), 328 (86 450)	Solid (298)	533 (82 ± 2)
		Solid (77)	520
		CH_2Cl_2 (298)	489, 521 (2.5 ± 0.3)
2 $[\{(p\text{-MeC}_6H_4)_3P\}Au(dea)Au\{P(C_6H_4Me\text{-}p)_3\}]$	242 (sh) (107 375), 276 (109 185), 300 (25 920), 324 (sh) (7335), 410 (19 550), 436 (48 360), 464 (65 775)	Solid (298)	580 (< 0.1)
		Solid (77)	498, 528, 561
		CH_2Cl_2 (298)	479, 500, 529 (0.40 ± 0.04)
3 $[Au_2(dppn)(C{\equiv}CC_6H_4Ph\text{-}p)_2]$	309 (95 250), 394 (sh) (6100)	Solid (298)	655 (6.2 ± 0.6)
		Solid (77)	571
		CH_2Cl_2 (298)	434, 704 (0.14 ± 0.01)
4 $[Au_2(dcpn)(C{\equiv}CC_6H_4Ph\text{-}p)_2]$	310 (77 520)	Solid (298)	707 (4.8 ± 0.5)
		Solid (77)	569
		CH_2Cl_2 (298)	753 (2.8 ± 0.3)
5 $[Au_2(dppn)(C{\equiv}CC_6H_4OMe\text{-}p)_2]$	292 (65 720), 394 (sh) (3565)	Solid (298)	571 (132 ± 3)
		Solid (77)	561
		CH_2Cl_2 (298)	714 (2.3 ± 0.2)
6 $[Au_2(dppn)(C{\equiv}CC_6H_{13})_2]$	293 (74 895), 396 (sh) (9825)	Solid (298)	644 (2.0 ± 0.2)
		Solid (77)	604
		CH_2Cl_2 (298)	677 (sh), 704 (1.50 ± 0.15)
7 $[Au_2(dmpm)(C{\equiv}CPh)_2]$	274 (34 015), 284 (35 635), 320 (sh) (14 335)	Solid (298)	490 (0.42 ± 0.04)
		Solid (77)	489
		CH_2Cl_2 (298)	528 (0.46 ± 0.05)
8 $[Au_2(dmpm)(C{\equiv}CC_6H_4OMe\text{-}p)_2]$	290 (35 045), 326 (sh) (14 195)	Solid (298)	521 (0.95 ± 0.09)
		Solid (77)	502
		CH_2Cl_2 (298)	438, 530 (3.43 ± 0.35)
9 $[Au_3(dmmp)(C{\equiv}CPh)_3]$	272 (36 060), 284 (36 330), 324 (sh) (16 545)	Solid (298)	538 (1.29 ± 0.13)
		Solid (77)	529
		CH_2Cl_2 (298)	539 (1.05 ± 0.10)
10 $[Au_3(dmmp)(C{\equiv}CC_6H_4OMe\text{-}p)_3]$	252 (sh) (35 135), 290 (35 765), 332 (sh) (18 970)	Solid (298)	539 (1.16 ± 0.12)
		Solid (77)	524
		CH_2Cl_2 (298)	530 (0.55 ± 0.06)
11 $[Au(PMe_3)(C{\equiv}CPh)]$	258 (sh) (14 115), 268 (24 100), 282 (24 460)	Solid (298)	455 (0.70 ± 0.07)
		Solid (77)	478
		CH_2Cl_2 (298)	424, 450, 504 (0.51 ± 0.05)
12 $[Au(PMe_3)(C{\equiv}CC_6H_4OMe\text{-}p)]$	262 (sh) (12 725), 270 (20 650), 282 (26 960), 296 (20 615)	Solid (298)	532 (0.82 ± 0.08)
		Solid (77)	577
		CH_2Cl_2 (298)	536 (3.0 ± 0.3)
13 $[Au(PPh_3)(C{\equiv}CPh)]$	271 (19 400), 284 (19 300), 291 (sh) (11 400)	Solid (298)	459 (33.4 ± 3.3)
		Solid (77)	457
		CH_2Cl_2 (298)	410, 454 (sh) (6.6 ± 0.6)
14 $[Au(PPh_3)(C{\equiv}CC_6H_4OMe\text{-}p)]$	238 (52 440), 276 (27 775), 286 (32 420), 298 (27 690)	Solid (298)	427, 468 (15.0 ± 1.5)
		Solid (77)	439, 465
		CH_2Cl_2 (298)	426, 438 (7.0 ± 0.7)
15 $[Au(PPh_3)(C{\equiv}CC_6H_4Ph\text{-}p)]$	242 (sh) (33 650), 280 (26 410), 298 (42 470), 308 (43 955)	Solid (298)	495, 526 (427 ± 5)
		Solid (77)	503
		CH_2Cl_2 (298)	398, 418, 499, 532, 534 (35.4 ± 3.5)
16 $[Au(PPh_3)(C{\equiv}CC_{10}H_7)]$	302 (16 700), 314 (25 400), 332 (29 275)	Solid (298)	422 (2.5 ± 0.3), 545, 574 (3.6 ± 0.04)
		Solid (77)	412, 425, 554, 594
		CH_2Cl_2 (298)	414, 531, 575, 621 (6.6 ± 0.7)
17 $[Au(PPh_3)(C{\equiv}CC_{14}H_9)]$	260 (sh) (73 300), 266 (96 500), 286 (sh) (11 400), 358 (4590), 376 (10 490), 398 (19 810), 420 (23 620)	Solid (298)	488, 518, 545 (< 0.1)
		Solid (77)	487, 518, 545
		CH_2Cl_2 (298)	428, 449, 476 (< 0.1)
18 $[Au\{PPh_2(C_{14}H_9)\}(C{\equiv}CPh)]$	264 (72 240), 280 (27 830), 356 (4180), 370 (7000), 390 (8510), 410 (6600)	Solid (298)	511 (2.1 ± 0.2)
		Solid (77)	512
		CH_2Cl_2 (298)	455 (9.0 ± 0.9)

* All spectra were recorded in CH_2Cl_2.

the synthesis of complexes **1** and **2**, tri-*p*-tolylphosphine is employed. The triphenylphosphine analogues are insoluble in most common organic solvents, which renders their characterization difficult. All the newly synthesized complexes gave satisfactory elemental analyses and have been characterized by ^1H NMR, IR and FAB mass spectrometry. All the complexes display a weak IR absorption band at *ca.* 2100 cm^{-1} corresponding to the terminal ν(C≡C) stretch.

The electronic absorption spectral data for the newly synthesized alkynylgold(I) phosphine complexes together with some related complexes for comparative studies are summarized in Table 1. In the series of mononuclear $[Au(PR_3)(C{\equiv}CR')]$ complexes **11** and **13** absorb at similar energies as those of a related $[Au(PPh_2Me)(C{\equiv}CPh)]$ complex.[4b] On the other hand, $[Au(PPh_3)(C{\equiv}CR')]$ complexes with different acetylides absorb at different energies, with the order **13** > **14** > **15** > **16** > **17**. Fig. 1 depicts the electronic absorption spectra of complexes **13**, **16** and **17** in dichloromethane. The dependence of the absorption energies on the nature of the acetylides and their relative insensitivity to the nature of the phosphine ligands suggest that the transitions are most likely dominated by intraligand $\pi \longrightarrow \pi^*(C{\equiv}CR')$ transitions. However, the involvement of a $\sigma \longrightarrow \pi^*(\text{aryl})$ transition should not be overlooked in some cases. An example involves complex **18** where the electronic absorption exhibits vibronically structured bands with progressional spacings of *ca.* 1300 cm^{-1}, characteristic of

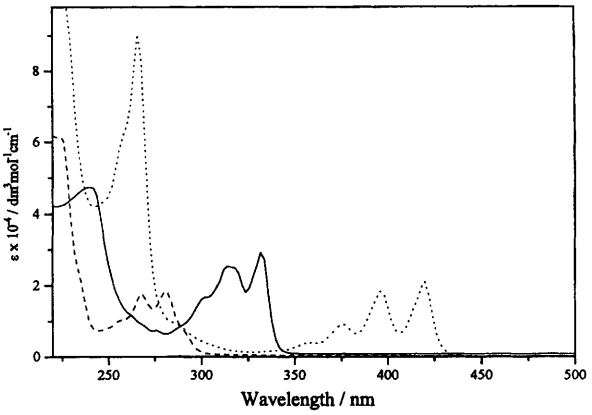


Fig. 1 Electronic absorption spectra of complexes **13** (——), **16** (– – –) and **17** (· · ·) in CH_2Cl_2 at 298 K

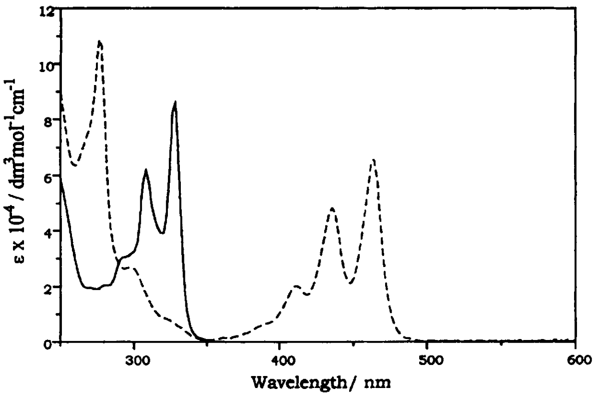


Fig. 2 Electronic absorption spectra of complexes **1** (——) and **2** (– – –) in CH_2Cl_2 at 298 K

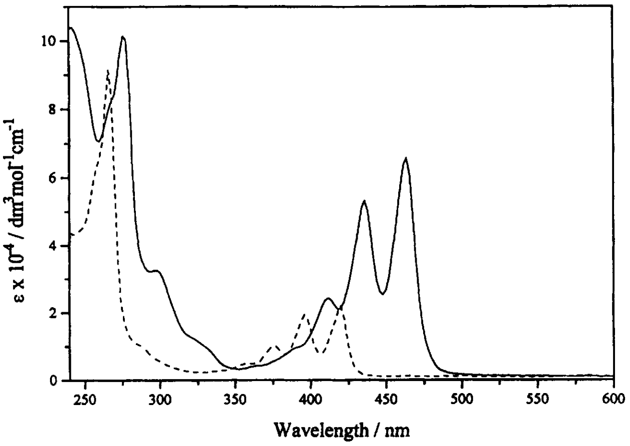


Fig. 3 Electronic absorption spectra of complexes **2** (——) and **17** (– – –) in CH_2Cl_2 at 298 K

the anthryl-substituted phosphine moiety. Similar vibrational progressions have also been observed for complex **17**, typical of the C=C stretch of the anthryl ring. It is likely that with the presence of the anthryl substituent on the phosphine ligand in **18**, the lowest-lying absorption is dominated by the $\sigma \longrightarrow \pi^*$(anthryl) transition. Similar assignments have been made for related alkynylgold(I) naphthyl-substituted phosphine systems.[4b]

Fig. 2 shows the electronic absorption spectra of complexes **1** and **2** in dichloromethane and Fig. 3 a comparison between the absorption of complexes **2** and **17**. Complexes **1** and **2** exhibit intense vibronically structured absorption bands at 294–328 nm with progressional spacings of 1980 cm^{-1} and at 410–464 nm with spacings of *ca.* 1400 cm^{-1}, respectively. The absorption bands of **1** probably arise from the intraligand $\pi \longrightarrow \pi^*(C{\equiv}C)$ or $\sigma(Au\text{–}P) \longrightarrow \pi^*(C{\equiv}C)$ transition, while those of **2** probably arise from an intraligand $\pi \longrightarrow \pi^*$(anthryl) or $\sigma(Au\text{–}P) \longrightarrow \pi^*$(anthryl) transition. On account of the more extensive electron delocalization in the deb ligand, the red shift in the absorption of **1** relative to **13** is understandable. Another view of rationalizing the results is that the $C{\equiv}CAuP(C_6H_4Me\text{-}p)_3$ moiety in the dimer can be regarded as an electron-withdrawing substituent on the phenylacetylide unit, which renders the acetylide more electron deficient, resulting in a lowering of the π^* energy of the acetylide unit. A similar red shift is also observable on going from complex **17** to **2**. It is also interesting that the absorption coefficients for the vibronic band of complex **2** are almost twice that found for **17**, in line with the presence of two chromophoric units in the dinuclear complex.

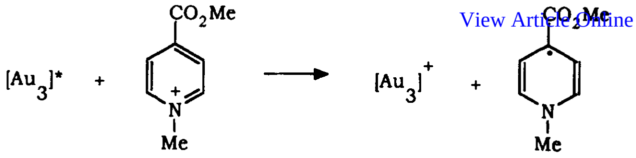
On the other hand, complexes **3**, **5** and **6** exhibit very similar absorption bands at *ca.* 290–310 nm and a weaker absorption at *ca.* 400 nm with tails extending to *ca.* 500 nm. Similar absorption patterns and energies are also found for the free dppn ligand. It is likely that the absorptions are $\sigma(Au\text{–}P) \longrightarrow \pi^*$(dppn) in origin. With complex **4** a similar assignment of $\sigma(Au\text{–}P) \longrightarrow \pi^*$(dcpn) is postulated.

For the series of complexes **7**–**12** the electronic absorption spectra are characterized by a strong absorption band at *ca.* 268–296 nm, while in the case of the dinuclear **7** and **8** and trinuclear **9** and **10** an additional shoulder appears at 320–332 nm, which tails off to *ca.* 380 nm for the former and *ca.* 430 nm for the latter. With reference to spectroscopic studies on the mononuclear analogues **11** and **12**, the bands at 268–296 nm of the di- and tri-nuclear species, which are also present for complexes **11** and **12**, are assigned as $\pi \longrightarrow \pi^*(C{\equiv}CR')$ or $\sigma \longrightarrow \pi^*(C{\equiv}CR')$. With reference to the well established spectroscopic pattern in d^8–d^8 species[16] and previous work on related d^{10}–d^{10} systems,[2,3,17] the low-energy absorption shoulders found for the di- and tri-nuclear complexes, which are absent in the absorption spectra of the mononuclear complexes, are attributed to the spin-allowed $d_{\sigma^*} \longrightarrow p_\sigma$ transition. The red shift of the transition energy from di- to tri-nuclear species (0.20 eV) is in accordance with the assignment of the $d_{\sigma^*} \longrightarrow p_\sigma$ transition, since increasing the number of gold units would cause an increase in the energy of the d_{σ^*} orbital, and hence narrowing of the $d_{\sigma^*} \longrightarrow p_\sigma$ gap. Similar red shifts in the $d_{\sigma^*} \longrightarrow p_\sigma$ transition have also been observed for two- and three-co-ordinate polynuclear d^{10} gold(I) systems[2a–c] and other polynuclear d^8 systems.[16c] For comparison, the red shift of the $^1(d_{\sigma^*} \longrightarrow p_\sigma)$ transition energy from $[Au_2(dmpm)_2]^{2+}$ to $[Au_3(dmmp)_2]^{3+}$ is 0.67 eV and from $[Au_2(dmpm)_3]^{2+}$ to $[Au_3(dmmp)_3]^{3+}$ is 0.69 eV.[2a,b] The smaller magnitude of red shift observed for gold(I) acetylides (0.20 eV) as compared with polynuclear gold(I) phosphines is probably attributed to the greater Au···Au distance in the former. On the other hand, when the shift of the absorption is compared with that of $[Au_2(dmpm)R_2]$ and $[Au_3(dmmp)R_3]$ (0.10 eV) (R = Me, $C_6H_4OMe\text{-}p$),[2c] a larger red shift is observed for these gold(I) acetylide complexes. It is likely that with the acetylides the Au···Au interaction is slightly stronger as a result of the stacking interactions of the C≡C π system, which are absent in the organogold(I) systems. An alternative assignment of the low-energy absorptions as metal–metal bond-to-ligand charge transfer [m.m.l.c.t. $d_{\sigma^*}(Au\cdots Au) \longrightarrow \pi^*(C{\equiv}C)$] is also likely, where a red shift in absorption energy is also anticipated on going from the mono- to the tri-nuclear system. On the other hand, an assignment as $\sigma(Au\text{–}P) \longrightarrow \pi^*(PR_3)$ is unlikely given the absence of a low-lying π^* orbital in the tertiary alkylphosphines PMe_3, dmpm and dmmp.

Excitation of solid sample and dichloromethane solutions of all the complexes at $\lambda > 350$ nm at both room temperature and 77 K produced long-lived intense luminescence. The photophysical data are summarized in Table 1. The luminescence lifetimes in the microsecond range are suggestive of a triplet parentage. The solid-state emission spectrum of complex **1** shows well resolved vibrational fine structures centred at *ca.* 533 nm. Similar absorption fine structures were observed for **13** except that **1** is red-shifted relative to **13**. An origin derived from states arising from a $\pi \longrightarrow \pi^*(C{\equiv}C)$ or $\sigma(Au{-}P) \longrightarrow \pi^*(C{\equiv}C)$ transition is assigned accordingly. The red shift is again attributed to the more extensive electron delocalization in the deb ligand as well as the electron-withdrawing properties of the $C{\equiv}CAuP(C_6H_4Me\text{-}p)_3$ moiety. Similarly, the solid-state emission of **2**, which is likely to be intraligand $\pi \longrightarrow \pi^*$(anthryl) or $\sigma(Au{-}P) \longrightarrow \pi^*$(anthryl) in origin, is at lower energy than that of complex **17**. On the other hand, the solid-state emission spectra of complexes **3**, **5** and **6** show a broad structureless band centred at *ca.* 655, 571 and 644 nm, respectively, while **4** emits at *ca.* 707 nm. In solution, the emission maxima are slightly red-shifted relative to their respective solid-state spectra. The similarity in the emission energies of the dppn-containing complexes to that of a mononuclear $[Au(dppn)_2]^+$ complex at room temperature (solid, 640; CH_2Cl_2, 693 nm)[18] is probably suggestive of an assignment originating from a $\sigma(Au{-}P) \longrightarrow \pi^*$(naphthyl) origin. This is further supported by the observation that the emission energy in the solid and solution state of **4** is of lower energy than that of the dppn-containing complexes. As dcpn contains four cyclohexyl groups, the electron-donating power of these groups would increase the electron density around P and render the Au–P σ-electron pair more readily available for donation. Thus a red shift in the emission energy may result. Another possible assignment for the emissive origin in complex **4** may involve states derived from a $\sigma(Au{-}P) \longrightarrow \pi^*(C{\equiv}CPh)$ origin as a result of the raising of the Au–P σ-orbital energy and the availability of low-lying $\pi^*(C{\equiv}CPh)$ orbitals. Nevertheless, it is interesting that, with the presence of low-lying dppn and dcpn ligand π^* orbitals, Au $\cdots$ Au interactions no longer play a significant role in governing the lowest excited-state properties of these complexes.

For the series of complexes **7**–**12** emissions from the mononuclear **11** and **12** are essentially derived from $\pi \longrightarrow \pi^*(C{\equiv}CR')$ or $\sigma \longrightarrow \pi^*(C{\equiv}CR')$ transitions. In the room-temperature solid-state emission spectra, complex **7** is found to emit at 490 nm and **9** at 538 nm, while **8** and **10** emit at 521 and 539 nm, respectively. It is interesting that the difference in emission energies between **11** and **12** with C≡CPh and $C{\equiv}CC_6H_4OMe\text{-}p$ ligands (0.40 eV) is larger than that of the dinuclear **7** and **8** (0.15 eV), and in turn larger than that of the trinuclear **9** and **10** (0.004 eV). Apparently, the involvement of the $\pi^*(C{\equiv}CR')$ character diminishes on going from the mono- to the di- and tri-nuclear system and other emission origins may be involved. With reference to previous spectroscopic findings on the luminescent properties of complexes with weak Au $\cdots$ Au interactions,[2,3] the solid-state emission of complexes **7**–**10** could be derived from states arising from a $d_{\delta^*} \longrightarrow p_\sigma$ transition. This is supported by the finding that the emission energy of the trinuclear species is slightly red-shifted from that of the dinuclear counterparts and that the emission energy is almost insensitive to the introduction of OMe groups on the acetylide. The relatively small difference in emission energies upon changing the number of gold units (0.05 eV) from **7** to **9** and **8** to **10**, and the large Stokes shift between the $d_{\sigma^*} \longrightarrow p_\sigma$ transition energies and the emission energies, suggest that the lowest emitting states are unlikely to be derived from the $(d_{\sigma^*})^1(p_\sigma)^1$ triplet, but rather from the $(d_{\delta^*})^1(p_\sigma)^1$ triplet. Similar assignments have been made for the emission of $[Au_2(dmpm)_2]^{2+}$ *vs.* $[Au_3(dmmp)_2]^{3+}$ and $[Au_2(dmpm)_3]^{2+}$ *vs.* $[Au_3(dmmp)_3]^{3+}$.[2a,b] With the absence of a low-lying π^* orbital in the tertiary alkylphosphines PMe_3, dmpm and dmmp, an assignment of the emission as originating from states derived from a $\sigma(Au{-}P) \longrightarrow \pi^*(PR_3)$ transition is also unlikely.

The alkynylgold(I) phosphine complexes have been shown to exhibit rich photochemical reactivities. In order to obtain further insights into the photoredox behaviour of this class of complexes selected alkynylgold(I) phosphine complexes have been investigated in detail. A bimolecular diffusion-controlled corrected quenching rate constant k_q' of 4.98×10^9 dm^3 mol^{-1} s^{-1} has been obtained from Stern–Volmer quenching studies of the reaction of **9*** with 4-(methoxycarbonyl)-*N*-methylpyridinium ion in acetonitrile. As the triplet-state energy of the pyridinium ion is too high for any appreciable energy transfer between the excited state of the complex and the quencher, the quenching of the excited state is electron transfer in nature. Nanosecond laser flash transient absorption spectroscopy was employed to provide direct spectroscopic evidence for the mechanism. The transient absorption difference spectrum of a degassed MeCN solution of **9** (9.6×10^{-5} mol dm^{-3}) and 4-(methoxycarbonyl)-*N*-methylpyridinium hexafluorophosphate (0.12 mol dm^{-3}) recorded 10 μs after the laser flash shows an absorption centred at *ca.* 400 nm, characteristic of the pyridinyl radical and matched well with the literature spectrum.[19] The reaction mechanism is shown in Scheme 1. No bands due to the oxidized species $\mathbf{9}^+$ can be observed in the difference spectrum, which may be a result of the strong absorption of the pyridinyl radical which masks the absorption of $\mathbf{9}^+$. Similarly, laser flash photolysis of a degassed acetonitrile solution of **5** (1.85×10^{-4} mol dm^{-3}) and methyl viologen (MV^{2+}) hexafluorophosphate (1.86×10^{-2} mol dm^{-3}) recorded 10 μs after the laser flash gave transient absorptions consisting of a sharp band at *ca.* 400 nm and a broad one at *ca.* 600 nm, typical of the $MV^{\bullet+}$ cation radical.[15] The electron-transfer mechanism is likely to be as in equation (1). A back electron-transfer rate constant for reaction (2) has been determined from a plot of $1/\Delta A$ *vs.* time and a knowledge of the absorption coefficient of $MV^{\bullet+}$, to be 1.30×10^{10} dm^3 mol^{-1} s^{-1}, which is near diffusion-controlled. Transient absorption studies on the reaction of a related tetranuclear alkynylgold(I) phosphine complex, $[Au_4(tppb)(C{\equiv}CC_6H_4OMe\text{-}p)_4]$ [tppb = 1,2,4,5-tetrakis(diphenylphosphino)benzene],[4a] with methyl viologen in degassed MeCN also produced transient signals typical of the methyl viologen cation radical. Fig. 4 shows a representative transient absorption difference spectrum recorded 10 μs after the laser flash. The spectrum exhibits no discernible absorption that could be attributed to the oxidized $[Au_4(tppb)(C{\equiv}CC_6H_4OMe\text{-}p)_4]^+$, probably as a result of the strong absorption of the methyl viologen cation radical which obscures it. A back electron-transfer rate constant for reaction (3) has also been determined from a plot of $1/\Delta A$ *vs.* time (see Fig. 4 insert) to be 1.94×10^{10} dm^3 mol^{-1} s^{-1}.



Scheme 1

$$[Au_2(dppn)(C{\equiv}CC_6H_4OMe\text{-}p)_2]^* + MV^{2+} \longrightarrow [Au_2(dppn)(C{\equiv}CC_6H_4OMe\text{-}p)_2]^+ + MV^{\bullet+} \quad (1)$$

$$[Au_2(dppn)(C{\equiv}CC_6H_4OMe\text{-}p)_2]^+ + MV^{\bullet+} \longrightarrow [Au_2(dppn)(C{\equiv}CC_6H_4OMe\text{-}p)_2] + MV^{2+} \quad (2)$$

$$[Au_4(tppb)(C{\equiv}CC_6H_4OMe\text{-}p)_2]^+ + MV^{\bullet+} \longrightarrow [Au_4(tppb)(C{\equiv}CC_6H_4OMe\text{-}p)_2] + MV^{2+} \quad (3)$$

Conclusion

Alkynylgold(I) phosphine complexes have been shown to exhibit rich luminescent behaviour with long-lived excited states. The

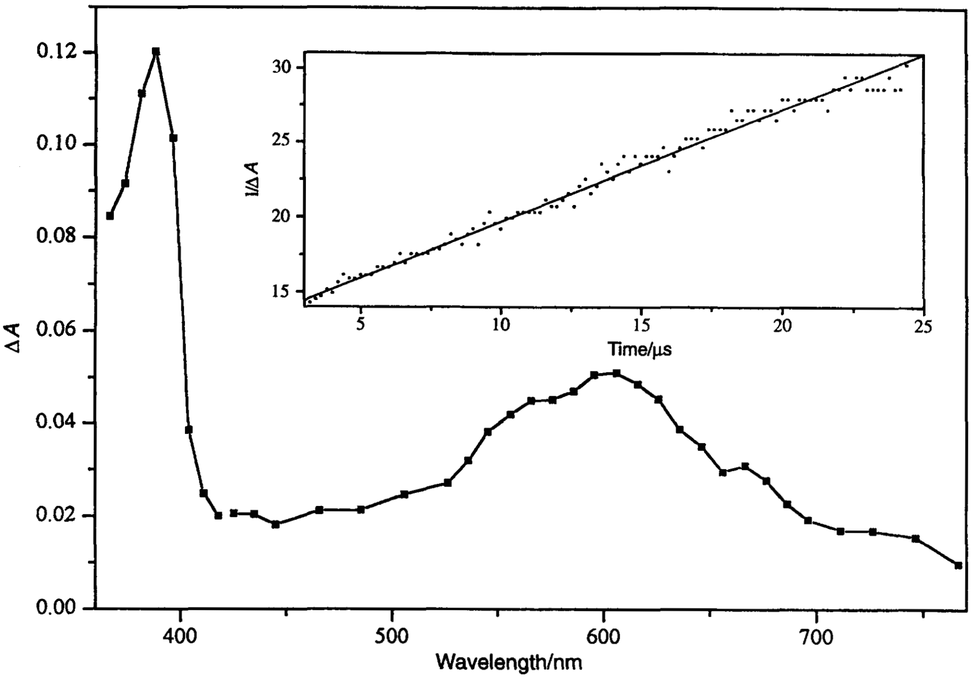


Fig. 4 Transient absorption difference spectrum recorded 10 μs after laser flash for a degassed MeCN solution of $[\mathrm{Au_4(tppb)(C{\equiv}CC_6H_4OMe}\text{-}p)_4]$ (1.9×10^{-4} mol dm^{-3}) and methyl viologen hexafluorophosphate (9.4×10^{-3} mol dm^{-3}). The inset shows the plot of $1/\Delta A$ *versus* time monitored at 605 nm

origin of their emissive behaviour is strongly dependent on the nature of the phosphine ligands and the acetylide units involved. Nevertheless, all the complexes are strong reducing agents in the excited state, capable of undergoing facile electron-transfer reactions with pyridinium acceptors, which has been confirmed by laser flash transient absorption studies.

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