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Syntheses and luminescence studies of mixed-metal gold(I)–copper(I) and –silver(I) alkynyl complexes. The “turning-on” of emission upon d^{10} metal ion encapsulation

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Reaction of the gold(I) alkynyl precursor complexes, [(R$_3$P)Au{C≡CC(=CH$_2$)Me}] (R = Ph **1**, *p*-Tol **2**) and [(μ-dppf)-Au$_2${C≡CC(=CH$_2$)Me}$_2$] **3**, with copper(I) or silver(I) ions led to the formation of a series of luminescent η^2-alkynyl mixed-metal complexes, [{η^2- (R$_3$P)Au{C≡CC(=CH$_2$)Me}}$_2$Cu]PF$_6$ (R = Ph **4**, *p*-Tol **5**) and [(μ-dppf)Au$_2${η^2-C≡CC-(=CH$_2$)Me}$_2$M]X (M = Cu, X = PF$_6$ **6**; M = Ag, X = OTf **7**). The X-ray crystal structures of **1** and **3** have been determined. The photophysical properties of the complexes have been investigated. Coordination of **1**–**3** as metalloligands to copper(I) and silver(I) ions to afford the respective complexes **4**–**7** has been demonstrated to be a versatile means to perturb the emission properties. The luminescence behaviour of **3** has been “turned on” upon copper(I) or silver(I) encapsulation in **6** and **7**.

Introduction

Since the first report on the X-ray crystal structural characterization of η^2-alkynyl-coordinated complexes by Abu Salah and Bruce in 1974,[1] in which dimeric complexes were formed from iron alkynyls that are π-bonded to copper *via* copper–halide bridges, the field has blossomed due to the potential application of such complexes in the deposition of thin copper films for electronic devices and extensive series of η^2-alkynyl-coordinated complexes have been reported.[2–5] In particular, the reports on [{η^2-(CO)$_5$ReC≡CRe(CO)$_5$-Cu(μ-Cl)}$_2$ by Beck and co-workers,[6] and a series of polyheteronuclear coinage metal alkynyl complexes by Abu-Salah and coworkers[7] have demonstrated the presence and importance of both σ- and π-bonding modes in the metal alkynyl systems. Recently, we reported the syntheses and photophysical properties of [{η^2-Re(bpy)(CO)$_3$(C≡CPh)}$_2$M]X, [Pt$_2$Cu$_4$(C≡CPh)$_8$]$_2$ and [Pt$_2$(dppm)$_2$(C≡CPh)$_4${M(MeCN)}$_2$]X$_2$ (M = Cu, Ag; X = PF$_6$, OTf), which demonstrated the possibility and feasibility of tuning the luminescence behaviour through the perturbation of the electron richness of the alkynyl ligands *via* π-coordination to different metal ions.[8–10] As an extension of our previous work on luminescent gold(I) alkynyls,[11] attempts have been made to probe the use of gold(I) alkynyl complexes as π-donor metalloligands to coordinate to metal centres. Here we report the syntheses and photophysical properties of a series of gold(I) enynyl complexes with ancillary tertiary phosphine ligands, [(R$_3$P)Au{C≡C-C(=CH$_2$)Me}] (R = Ph, **1**; *p*-Tol, **2**) and [(μ-dppf)Au$_2${C≡C-C(=CH$_2$)Me}$_2$] **3** (Scheme 1). These complexes have been shown to be capable of acting as metalloligands to coordinate to copper(I) and silver(I) to form the mixed-metal gold(I)–copper(I) and –silver(I) alkynyl complexes, [{η^2-(PPh$_3$)-Au{C≡CC(=CH$_2$)Me}}$_2$Cu]PF$_6$ **4**, [{η^2-(Ptol$_3$)Au{C≡C-C(=CH$_2$)Me}}$_2$Cu]PF$_6$ **5**, [(dppf)Au$_2${η^2-C≡CC(=CH$_2$)Me}$_2$-Cu]PF$_6$ **6** and [(dppf)Au$_2${η^2-C≡CC(=CH$_2$)Me}$_2$Ag]OTf **7**. The luminescence properties of these complexes have been found to be significantly perturbed through the coordination to copper(I) and silver(I) metal centres.

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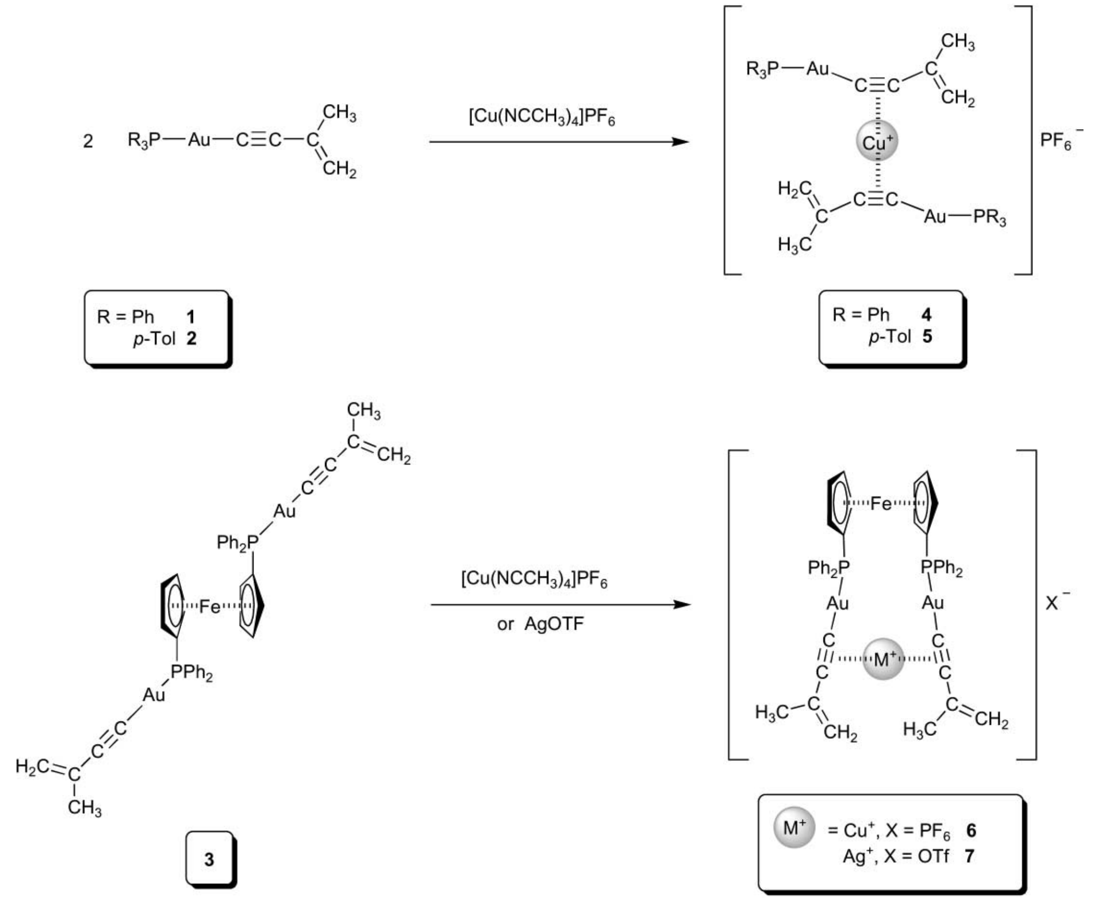
Experimental

Materials and reagents

Potassium tetrachloroaurate(III) (98+%, Strem), triphenylphosphine (Merck), tri(*p*-tolyl)phosphine (Strem), 2-methylbut-1-en-3-yne (Lancaster) and silver(I) trifluoromethanesulfonate (Aldrich) were used as received. [Cu(MeCN)$_4$]PF$_6$,[12] [(R$_3$P)AuCl][13,14] and [(μ-dppf)Au$_2$Cl$_2$][15] were prepared according to the published procedure. All solvents were purified and distilled using standard procedures before use.[16] All other reagents were of analytical grade and were used as received.

Physical measurements and instrumentation

UV-visible spectra were obtained on a Hewlett-Packard 8452A diode array spectrophotometer, IR spectra as KBr discs on a Bio-Rad FTS-7 Fourier-transform infrared spectrophotometer (4000–400 cm^{-1}), and steady state excitation and emission spectra on a Spex Fluorolog-2 Model F111 fluorescence spectrophotometer equipped with a Hamamatsu R-928 photomultiplier tube. Low-temperature (77 K) spectra were recorded by using a quartz sample tube in a quartz optical Dewar flask. ^{1}H NMR spectra were recorded on a Bruker DPX-300 (300 MHz) Fourier transform NMR spectrometer in CDCl$_3$ at 298 K, with chemical shift values (δ, ppm) recorded relative to tetramethylsilane (Me$_4$Si). Positive-ion FAB and positive ESI mass spectra were recorded on a Finnigan MAT95 mass spectrometer and a Finnigan LCQ mass spectrometer, respectively. Elemental analyses of the newly synthesized complexes were performed on a Carlo Erba 1106 or a Flash 1112 elemental analyser at the Institute of Chemistry, Chinese Academy of Sciences. Emission lifetime measurements were performed using a conventional laser system. The excitation source was the 355-nm output (third harmonic) of a Spectra-Physics Quanta-Ray Q-switched GCR-150-10 pulsed Nd-YAG laser. Luminescence decay signals detected by a Hamamatsu R928 photomultiplier tube were converted to voltage changes by connecting to a 50 Ω load resistor and were then recorded on a Tektronix model TDS 620A digital oscilloscope. The emission



Scheme 1

lifetime, τ, was determined by a single exponential fitting of the luminescence decay trace with the relationship $I = I_o\exp(-t/\tau)$, where I and I_o are the luminescence intensity at time = t and 0, respectively.

All solutions for photophysical studies were degassed on a high vacuum line in a two-compartment cell consisting of a 10 ml Pyrex bulb and a 1-cm path length quartz cuvette, and sealed from the atmosphere by a Bibby Rotaflo HP6 Teflon stopper. The solutions were subject to at least four freeze–pump–thaw cycles.

Synthesis of gold complexes

All reactions were performed under anaerobic and anhydrous conditions using standard Schlenk techniques under an inert atmosphere of nitrogen.

[(R$_3$P)Au{C≡CC(=CH$_2$)Me}] (R = Ph, 1; R = *p*-Tol, 2). **1** and **2** were synthesized in a similar manner, and a typical preparation of **1** is described as follows. An ethanolic solution of 2-methylbut-1-en-3-yne (14 mg, 0.21 mmol) and sodium ethoxide (prepared *in situ* by addition of Na (7 mg, 0.30 mmol) to EtOH (5 ml)) was added to a solution of [(Ph$_3$P)AuCl] (100 mg, 0.20 mmol) in EtOH/THF (10 ml; 1 : 1 v/v) at room temperature. The colourless solution turned to pale yellow upon stirring for 30 min. After stirring for 5 h, the solvent was evaporated to dryness and the residue was crystallized from dichloromethane–*n*-hexane to give **1** as pale yellow crystals (73 mg, 70%). **1**: ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.96 (s, 3H, –CH$_3$), 5.14 (d, 1H, J = 2.1 Hz, =CH$_2$), 5.31 (d, 1H, J = 2.1 Hz, =CH$_2$), 7.43–7.56 (m, 15H, PPh$_3$). IR (KBr, ν/cm^{-1}): 2112 (w) ν(C≡C). Positive-ion FAB-MS: *m*/*z* 525 {M + H}$^+$. Found: C, 52.59; H, 3.49%. C$_{23}$H$_{20}$AuP requires C, 52.68; H, 3.84%.

2: Yield: 78 mg, 69%. ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.95 (s, 3H, –CH$_3$), 2.43 (s, 9H, –C$_6$H$_4$CH_3), 5.12 (d, 1H, J = 2.1 Hz, =CH$_2$), 5.29 (d, 1H, J = 2.1 Hz, =CH$_2$), 7.29 (d, 6H, J = 7.8 Hz, –C$_6$H$_4$–), 7.45 (d, 6H, J = 7.8 Hz, –C$_6$H$_4$–). IR (KBr, ν/cm^{-1}): 2101 (w) ν(C≡C). Positive-ion FAB-MS: *m*/*z* 567 {M}$^+$. Found: C, 54.91; H, 4.82%. C$_{26}$H$_{26}$AuP requires C, 55.13; H, 4.63%.

[(μ-dppf)Au$_2${C≡CC(=CH$_2$)Me}$_2$] (3). An ethanolic solution of 2-methylbut-1-en-3-yne (14 mg, 0.21 mmol) and sodium ethoxide (prepared *in situ* by addition of Na (7 mg, 0.30 mmol) to EtOH (5 ml)) was added to a solution of [(μ-dppf)Au$_2$Cl$_2$] (100 mg, 0.10 mmol) in EtOH–THF (10 ml; 1 : 1 v/v), and the reaction mixture was stirred at room temperature. The solution turned to clear orange after 30 min. After stirring for 5 h, the solvent was evaporated to dryness and the resulting solid was crystallized from dichloromethane–*n*-hexane to give **3** as orange crystals (73 mg, 68%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.97 (s, 6H, –CH$_3$), 4.23 (m, 4H, –Cp), 4.69 (m, 4H, –Cp), 5.15 (d, 2H, J = 1.9 Hz, =CH$_2$), 5.31 (d, 2H, J = 1.9 Hz, =CH$_2$), 7.38–7.53 (m, 20H, –PPh$_2$). IR (KBr, ν/cm^{-1}), 2105 (w) ν(C≡C). Positive-ion FAB-MS: *m*/*z* 1078 {M}$^+$. Found: C, 48.28; H, 3.33%. C$_{44}$H$_{38}$Au$_2$FeP$_2$·¼CH$_2$Cl$_2$ requires C, 48.33; H, 3.53%.

[η^2-{(R$_3$P)Au{C≡CC(=CH$_2$)Me}}$_2$Cu]PF$_6$ (R = Ph, 4; R = *p*-Tol, 5). A typical preparation of **4** is described as follows: [(Ph$_3$P)Au{C≡CC(=CH$_2$)Me}] (105 mg, 0.20 mmol) was dissolved in THF (20 ml) and a solid sample of [Cu(MeCN)$_4$]PF$_6$ (40 mg, 0.11 mmol) was added. The resulting solution was stirred at room temperature for 30 min, and was then evacuated to dryness. The residue was recrystallized from CH$_2$Cl$_2$–*n*-hexane to give **4** as yellow crystals (43 mg, 34%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.59 (s, 6H, –CH$_3$), 5.31 (d, 2H, J = 2.0 Hz, =CH$_2$), 5.48 (d, 2H, J = 2.0 Hz, =CH$_2$), 7.46–7.65 (m, 30H, PPh$_3$). IR (KBr, ν/cm^{-1}): 1968 (w) ν(C≡C), 837 (s) ν(PF$_6^-$). Positive-ion FAB-MS: *m*/*z* 1112 {M − PF$_6$}$^+$. Positive ESI-MS: *m*/*z* 1112 {M − PF$_6$}$^+$. Found: C, 42.88; H, 3.32%. C$_{46}$H$_{40}$Au$_2$CuF$_6$P$_3$·½CH$_2$Cl$_2$ requires: C, 42.97; H, 3.18%.

5: Yield, 46 mg, 37%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.43 (s, 6H, $-CH_3$), 2.41 (s, 18H, $-C_6H_4CH_3$), 5.26 (d, 2H, J = 1.9 Hz, $=CH_2$), 5.75 (d, 2H, J = 1.9 Hz, $=CH_2$), 7.21–7.40 (m, 24H, $-C_6H_4-$). IR (KBr, ν/cm^{-1}): 1973 (w) ν(C≡C), 838 (s) $\nu(PF_6^-)$. Positive-ion FAB-MS: m/z 1196 {M − PF_6}$^+$. Positive ESI-MS: m/z 1196 {M − PF_6}$^+$. Found: C, 45.39; H, 3.97%. $C_{52}H_{52}Au_2CuF_6P_3$ requires: C, 45.57; H, 3.86%.

[(μ-dppf)Au_2{η^2-C≡CC(=CH_2)Me}$_2$Cu]PF_6 (6). [(μ-dppf)Au_2{C≡CC(=CH_2)Me}$_2$] (110 mg, 0.10 mmol) was dissolved in CH_2Cl_2 (20 ml) and a solid sample of [Cu(MeCN)$_4$]PF_6 (40 mg, 0.11 mmol) was added. The resulting solution was stirred at room temperature for 30 min, and was then evacuated to dryness. Orange crystals of **6** were obtained by recrystallization from CH_2Cl_2–n-hexane. Yield, 57 mg, 43%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.01 (s, 6H, $-CH_3$), 4.24 (m, 4H, –Cp), 4.72 (m, 4H, –Cp), 5.10 (d, 2H, J = 1.8 Hz, $=CH_2$), 5.25 (d, 2H, J = 1.8 Hz, $=CH_2$), 7.37–7.52 (m, 20H, $-PPh_2$). IR (KBr, ν/cm^{-1}): 2089 (w) ν(C≡C), 838 (s) $\nu(PF_6^-)$. Positive-ion FAB-MS: m/z 1142 {M − PF_6 + H}$^+$. Positive ESI-MS: m/z 1141 {M − PF_6}$^+$. Found: C, 40.20; H, 3.00%. $C_{44}H_{38}Au_2CuF_6FeP_3\cdot\frac{1}{2}CH_2Cl_2$ requires: C, 40.20; H, 2.96%.

[(μ-dppf)Au_2{η^2-C≡CC(=CH_2)Me}$_2$Ag]OTf (7). [(μ-dppf)Au_2{C≡CC(=CH_2)Me}$_2$] (110 mg, 0.10 mmol) was dissolved in CH_2Cl_2 (20 ml) and a solid sample of AgOTf (38 mg, 0.11 mmol) was added. The resulting solution was stirred at room temperature for 30 min, and was then evacuated to dryness. Orange crystals of **7** were obtained by recrystallization from CH_2Cl_2–n-hexane. Yield: 53 mg, 40%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.93 (s, 6H, $-CH_3$), 4.20 (m, 4H, –Cp), 4.65 (m, 4H, –Cp), 5.13 (d, 2H, J = 1.9 Hz, $=CH_2$), 5.23 (s, 2H, J = 1.9 Hz, $=CH_2$), 7.37–7.52 (m, 20H, $-PPh_2$). IR (KBr, ν/cm^{-1}): 2089 (w) ν(C≡C), 1436 (w) $\nu(OTf^-)$. Positive-ion FAB-MS: m/z 1185 {M − OTf}$^+$. Positive ESI-MS: m/z 1186 {M − OTf + H}$^+$. Found: C, 43.49; H, 3.23%. $C_{45}H_{38}AgAu_2F_3FeO_3P_2S\cdot\frac{2}{3}C_6H_{14}$ requires: C, 43.26; H, 3.51%.

Crystal structure determination

Crystals of **1** were obtained by slow diffusion of n-hexane into a concentrated dichloromethane solution of the complex. The X-ray diffraction data was collected on a MAR diffractometer with a 300 mm image plate detector using graphite-monochromatized Mo-Kα radiation (λ = 0.71073 Å). 43 images were collected. The images were interpreted and intensities integrated using the program DENZO.[17] The gold and most non-hydrogen atoms were located according to the direct method. The positions of the other non-hydrogen atoms were found after successful refinement by full-matrix least-squares using program SHELXL-97[18] on PC. The terminal methylene and methyl groups should not be distinguishable due to disorder but the C–C bond lengths provide a reference to locate them. The C(22) atom was temporarily assigned as the C atom of the methylene group and C(33) the methyl group, according to the C–C bond lengths of C(21)-C(22) 1.36(2) Å and C(21)–C(23) 1.44(2) Å. One crystallographic asymmetric unit consists of one formula unit. In the final stage of least-squares refinement, all non-hydrogen atoms were refined anisotropically. H atoms were generated by program SHELXL-97.[18] The positions of H atoms were calculated based on riding mode with thermal parameters equal to 1.2 times that of the associated C atoms, and participated in the calculation of final R-indices.

Crystals of **3** were obtained by slow diffusion of n-hexane into a concentrated dichloromethane solution of the complex. The X-ray diffraction data was collected on a MAR diffractometer with a 300 mm image plate detector using graphite-monochromatized Mo-Kα radiation (λ = 0.71073 Å). The space group was uniquely determined based on systematic absences and the structure was solved by direct method (SIR92)[19] and expanded by Fourier methods and refined by full-matrix least squares using the software package TeXsan[20] on a Silicon Graphics Indy computer. In the least-squares refinement, all 25 non-H atoms of the complex molecule were refined anisotropically, and 19 other H atoms at calculated positions with thermal parameters equal to 1.3 times that of the attached C atoms, were not refined. CCDC-198509.

The crystal and structure determination data for **1** and **3** are given in Table 1. Selected bond distances and angles are summarized in Table 2.

CCDC reference numbers 198508 (**1**) and 198509 (**3**).

See http://www.rsc.org/suppdata/dt/b2/b211909a/ for crystallographic data in CIF or other electronic format.

Results and discussion

All the gold(I) alkynyl complexes **1**–**3** were prepared by modification of literature procedures,[11,14,21] in which a mixed EtOH–THF (1 : 1 v/v) solvent system was employed to render the starting materials soluble in the reaction mixture. The use of a homogeneous solution medium may have the advantage of reducing the reaction time and leading to a more well-defined reaction product.

All the newly synthesized gold(I) complexes have been characterized by positive-ion FAB-MS, IR and ^{1}H NMR spectroscopy, and all of them gave satisfactory elemental analyses. Positive electrospray-ionization mass spectra were also obtained for all the charged gold(I) complexes **4**–**7**. The X-ray crystal structures of **1** and **3** have also been determined. Attempts to prepare the silver(I) analogues of **4** and **5** starting from **1** and **2**, respectively, have been made but only dark intractable materials have been obtained, indicative of the instability and rapid decomposition of the products.

From the IR spectral data, the relatively large perturbation and shift of the ν(C≡C) stretch from 2112, 2101 and 2105 cm^{-1} in **1**, **2** and **3**, respectively, to 1968, 1973, 2089 and 2089 cm^{-1} in **4**–**7** are consistent with the π-coordination of the alkynyl moieties to the copper(I) or silver(I) centre that resulted in a weakening of the C≡C bond.

Figs. 1 and 2 depict the perspective drawings of **1** and **3**, respectively, with atomic numbering scheme. The Fe atom was found to lie on an inversion centre in **3**. The observed Au–P bond distances of 2.2810(18) and 2.279(2) Å, Au–C bond distances of 2.029(82) and 2.005(10) Å and C≡C bond distances of 1.21(1) and 1.169(10) Å for **1** and **3**, respectively, are comparable to those observed in other alkynylgold(I) phosphine systems.[11c,22] The observation of the Au–P bond distances being longer than those in the chlorogold phosphine complexes[23] is in line with the higher *trans* influence of the alkynyl group. The

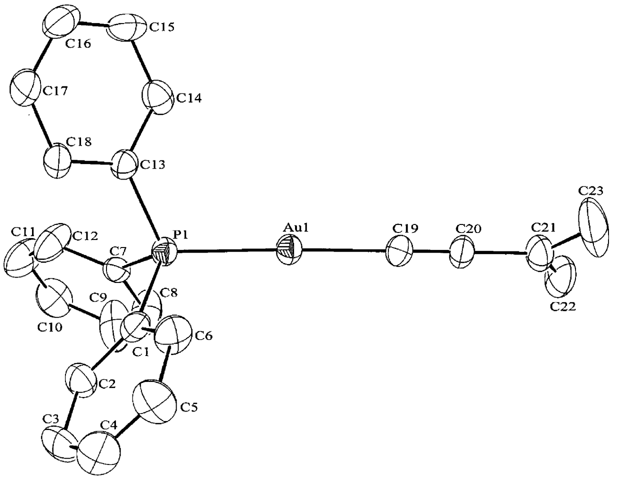


Fig. 1 Perspective drawing of **1** with atomic numbering. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids were shown at the 30% probability level.

Table 1 Crystal and structure determination data for **1** and **3**

Complex	**1**	**3**
Molecular formula	$C_{23}H_{20}AuP$	$C_{44}H_{38}Au_2FeP_2$
M_w	524.33	1078.51
Crystal colour	Pale yellow	Yellow
Crystal size/mm	0.30 × 0.25 × 0.20	0.35 × 0.15 × 0.10
Collection range	*h*: −16 to 12; *k*: −12 to 12; *l*: −15 to 15	*h*: 0 to 12; *k*: 0 to 10; *l*: −23 to 23
$2\theta_{max}/°$	51.0	50.9
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)
a/Å	14.100(3)	10.464(2)
b/Å	10.423(2)	9.378(2)
c/Å	13.900(3)	19.868(3)
α/°	90	90
β/°	97.41(3)	104.14(2)
γ/°	90	90
V/Å^3	2025.7(7)	1890.6(6)
Z	4	2
F(000)	1008	1032
μ/cm^{-1}	73.43	82.61
D_c/g cm^{-3}	1.719	1.894
T/K	301(2)	301(2)
R	0.0456 [a]	0.058 [b]
wR	0.1150 [a]	0.071 [b]
Max shift $(\Delta/\sigma)_{max}$	0.001	0.02
Goodness-of-fit	1.016	1.78
No. of data collected	9094	15800
No. of unique data	3509	3483
R_{int}	0.0464	0.066
No. of data used in refinement	2713 [c]	2782 [d]
No. of parameters refined	226	223
Residual extrema in final diff. map/eA^{-3}	+1.471, −2.103	+1.20, −2.45

[a] $w = 1/[\sigma^2(F_o^2) + (0.0721P)^2]$, where P is $[2(F_c^2) + \mathrm{Max}(F_o^2,0)]/3$. [b] $w = 4F_o^2/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2) = [\sigma^2(I) + (0.040F_o^2)^2]$ with $I > 3\sigma(I)$. [c] $I > 4\sigma(I)$. [d] $I > 3\sigma(I)$.

Table 2 Selected bond distances (Å) and bond angles (°) for **1** and **3**

1			
Au(1)–C(19)	2.029(8)	C(19)–Au(1)–P(1)	178.3(2)
Au(1)–P(1)	2.2810(18)	C(20)–C(19)–Au(1)	179.4(7)
C(19)–C(20)	1.169(10)	C(19)–C(20)–C(21)	179.6(11)
C(20)–C(21)	1.455(11)		
C(21)–C(22)	1.365(17)		
C(21)–C(23)	1.443(17)		
3			
Au(1)–C(1)	2.005(10)	P(1)–Au(1)–C(1)	172.3(3)
Au(1)–P(1)	2.279(2)	Au(1)–C(1)–C(2)	166.3(9)
C(1)–C(2)	1.21(1)	C(1)–C(2)–C(3)	174(1)
C(3)–C(4)	1.43(2)	Fe(1)–C(6)–C(7)	69.4(5)
C(3)–C(5)	1.37(2)		
C(21)–C(23)	1.443(17)		

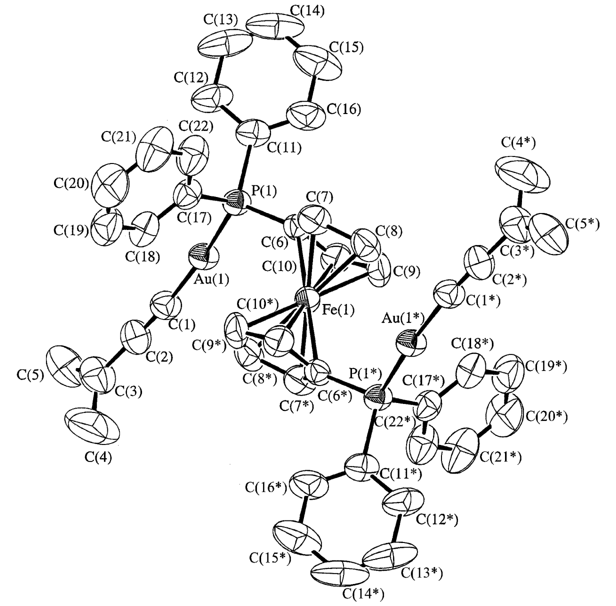


Fig. 2 Perspective drawing of **3** with atomic numbering. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids were shown at the 40% probability level. Starred atoms have coordinates at [−*x*, 1 − *y*, 1 − *z*].

P–Au–C angles of 178.3(2) and 172.3(3)° and Au–C–C angles of 179.4(7) and 166.3(9)° in **1** and **3**, respectively, are slightly deviated from the ideal 180° geometry. Such deviations are commonly observed in other gold(I) phosphine and alkynyl complexes.[11,21,22] All other bond lengths and angles are normal.

The electronic absorption spectra of **4** and **5** (Table 3) show absorption bands at *ca.* 282–328 nm, which are red-shifted with respect to their respective [(PR$_3$)Au{C≡CC(=CH$_2$)Me}] precursors, **1** and **2** (Fig. 3). In addition, a new band appears at *ca.* 440–450 nm. With reference to our previous studies on the d^{10} metal–alkynyl systems,[11] the high-energy bands at *ca.* 282–328 nm are assigned as metal-perturbed intraligand (IL) [π ⟶ π*(C≡C)] transitions with some metal-to-ligand charge transfer (MLCT) character. The red shift in absorption energy is in line with the lower π* orbital energy of the alkynyl unit upon π-coordination to copper(I). The low-energy band at *ca.* 440–450 nm, which is absent in the gold(I) precursors may originate from transitions characteristic of the copper(I)–π-alkynyl core. On the other hand, the electronic absorption spectra of **6** and **7** showed intense absorption bands at 268–306 nm and a weak shoulder at *ca.* 440–450 nm, with patterns very similar to that of their precursor complex **3**. The high-energy bands are similarly assigned to IL [π ⟶ π*(C≡C)] and [σ ⟶ π*(Ar)] transitions, while the band at *ca.* 440–450 nm, which is also present in

Table 3 Photophysical data for **1**–**7**

Complex	Absorption in CH_2Cl_2 λ_{abs}/nm (ε/dm^3 mol^{-1} cm^{-1})	Medium (T/K)	Emission λ_{em}/nm (τ_o/μs)
1	258 (14770), 270 (14150), 294 sh (1530)	Solid (298)	454 (1.5)
		Solid (77)	488, 522
		CH_2Cl_2 (298)	423 (0.7)
2	256 (13090), 270 (7230), 290 sh (1620)	Solid (298)	463 (2.4)
		Solid (77)	496, 522
		CH_2Cl_2 (298)	439 (<0.1)
3	262 (46920), 272 (43270), 284 (32490), 310 (2400), 440 (210)	Solid (298)	–[a]
		Solid (77)	–[a]
		CH_2Cl_2 (298)	–[a]
4	282 (14710), 328 sh (4850), 444 (960)	Solid (298)	653 (0.14)
		Solid (77)	606
		CH_2Cl_2 (298)	639 (0.22)
5	282 (15020), 328 sh (3020), 448 (870)	Solid (298)	664 (0.27)
		Solid (77)	613
		CH_2Cl_2 (298)	660 (0.39)
6	272 (26,800), 306 sh (8,210), 452 (360)	Solid (298)	583 (<0.1)
		Solid (77)	572
		CH_2Cl_2 (298)	585 (<0.1)
7	268 (32,540), 306 sh (6,470), 444 (180)	Solid (298)	565 (<0.1)
		Solid (77)	542
		CH_2Cl_2 (298)	553 (<0.1)

[a] Not emissive.

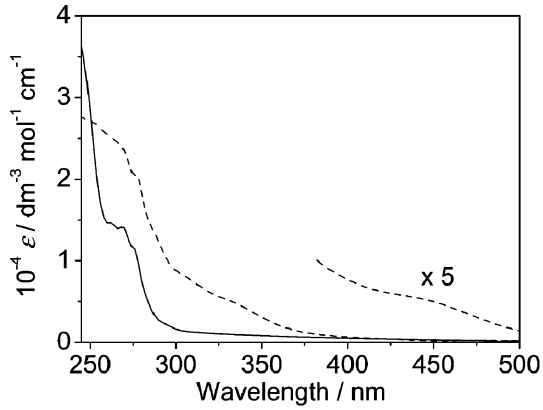


Fig. 3 Electronic absorption spectra of **1** (—) and **4** (- - -) in CH_2Cl_2 at 298 K.

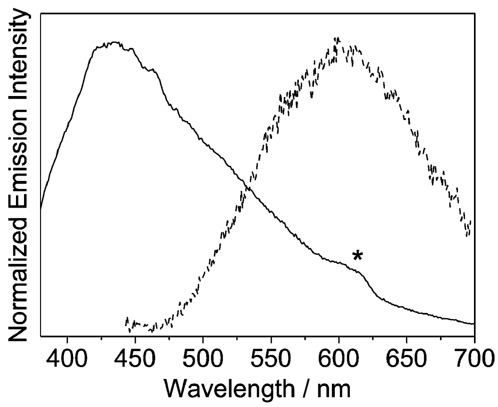


Fig. 4 Normalized solid-state emission spectra of **1** (—) and **4** (- - -) at 298 K; *denotes an artifact from the spectrofluorometer.

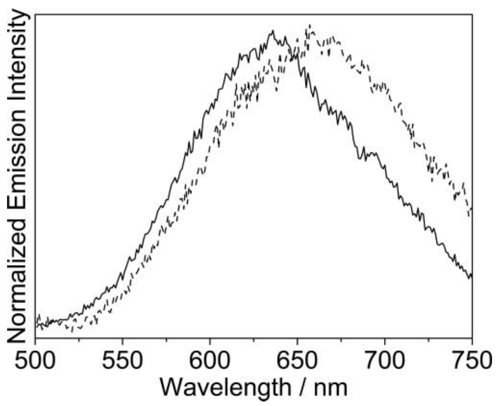


Fig. 5 Normalized emission spectra of **4** (—) and **5** (- - -) in CH_2Cl_2 at 298 K.

[Au_2(dppf)Cl_2] and **3**, is characteristic of ferrocene-containing compounds.

Photo-excitation of **1** and **2** in the solid state at λ = 350 nm gave rise to an intense long-lived blue luminescence at 454 and 463 nm, respectively. With reference to the findings for [(Ph_3P)Au(C≡CPh)], [24] it is possible to assign the emission origin of **1** and **2** as derived from an admixture of metal-perturbed $^3[\pi \longrightarrow \pi^*(C\equiv C)]$ IL and $^3[\sigma(Au–P) \longrightarrow \pi^*(C\equiv C)]$ MLCT states. The slight red shift in emission energy on going from **1** to **2** is in line with the fact that $PTol_3$, being a better electron donor than PPh_3, would render the gold(I) centre more electron rich and the σ(Au–P) orbital higher-lying in energy, giving rise to a slightly lower $^3[\sigma(Au–P) \longrightarrow \pi^*(C\equiv C)]$ emission energy. On the other hand, excitation of the mixed-metal η^2-alkynyl coordinated complexes **4** and **5** at λ = 350 nm gave rise to an intense long-lived orange–red luminescence at *ca.* 606–664 nm, which is red-shifted relative to the respective precursor complexes **1** and **2** (Fig. 4). Such emission is likely assigned to originate from a metal-perturbed $^3[\pi \longrightarrow \pi^*(C\equiv C)]$ IL or a $^3[\sigma(Au–P) \longrightarrow \pi^*(C\equiv C)]$ MLCT origin. Upon π-coordination to the copper(I) metal centre, the π*(C≡C) orbital energy is lowered, giving rise to a lower energy emission. The lower emission energy of **5** than **4** is again in line with the better electron-donating ability of $PTol_3$ over PPh_3 (Fig. 5). However, one cannot exclude the possible assignment of the emission as derived from states associated with the copper(I)–π-alkynyl core. For the dppf-containing complex **3**, no emission was observed in the solid state, probably due to the efficient quenching effect of the ferrocenyl moiety. By contrast, the solid-state emission spectra of **6** and **7** at room temperature showed emission maxima at *ca.* 565–583 nm. This band, which is absent in the gold(I) precursor **3**, may originate from emissive states characteristic of the copper(I)/silver(I) π-alkynyl core. With reference to our previous investigation on copper(I) and silver(I) alkynyl systems and the fact that **6** has a lower emission energy than **7**, such an emission is tentatively ascribed to be derived from states of a

LMCT parentage mixed with a metal-centred $nd^9(n + 1)s^1$ state, with some [π ⟶ π*(C≡C)] IL character. Similar assignments have been reported previously.[25]

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