Synthesis, Characterization and Photophysics of Luminescent Organogold(I) Phosphines†

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Reaction of $[Au_2(dmpm)Cl_2]$ or $[Au_3(dmmp)Cl_3]$ with an excess of organolithium reagent LiR in diethyl ether gave $[Au_2(dmpm)R_2]$ or $[Au_3(dmmp)R_3]$ in high yield [dmpm = $Me_2PCH_2PMe_2$; dmmp = $Me_2PCH_2P(Me)CH_2PMe_2$; R = Me or C_6H_4OMe-*p*]. These compounds were found to be emissive both in the solid state and in fluid solutions. An excited-state redox potential of −2.0(1) V *vs.* sodium chloride saturated calomel electrode has been estimated for $[Au_3(dmmp)(C_6H_4OMe\text{-}p)_3]$.

Polynuclear d^{10} metal complexes have been shown to exhibit rich photophysical and photochemical properties.[1,2] However, most studies have focused on simple Werner-type co-ordination complexes, there being relatively few on organometallic complexes.[1b,c,3] Our recent emphasis on the design and development of novel luminescent materials for photochemically induced homogeneous organic transformation reactions has prompted us to search for organometallic systems which are co-ordinatively unsaturated and are soluble in common organic solvents. Here we report on the synthesis, characterization and photophysical properties of a new class of organometallic polynuclear gold(I) phosphine complex.

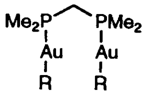
Experimental

Bis(dimethylphosphinomethyl)methylphosphine (dmmp) and bis(dimethylphosphino)methane (dmpm) were obtained from Strem Chemicals, potassium tetrachloroaurate, 2,2′-thiodiethanol, and methyllithium (1.4 mol dm^{-3} in diethyl ether) from Aldrich. Diethyl ether (Ajax, AR) was distilled over sodium–benzophenone before use. Dichloromethane (Ajax, AR) was successively treated with concentrated sulfuric acid, water and aqueous sodium carbonate before distillation over calcium hydride. The aryllithium reagents were prepared from *n*-butyllithium and the respective aryl bromide.[4] The pyridinium salts for quenching studies were prepared by refluxing the corresponding alkylating reagent such as methyl iodide in acetone–ethanol (1:1, v/v) for 4 h, followed by metathesis in water using ammonium hexafluorophosphate and recrystallization from acetonitrile–diethyl ether.

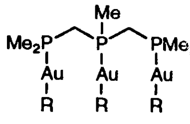
Synthesis of Gold Complexes.—All reactions were performed under strictly anhydrous and anaerobic conditions using standard Schlenk techniques under an atmosphere of nitrogen.

$[Au_2(dmpm)Cl_2]$. This was prepared according to a modified procedure.[5] Gold(I) was generated *in situ* by treatment of a methanolic solution of $K[AuCl_4]$ (0.5 g, 1.29 mmol in 20 cm^3) with an excess of 2,2′-thiodiethanol (0.6 cm^3). A methanolic solution of dmpm (0.088 g, 0.65 mmol) was added dropwise to the colourless gold(I) solution to give an immediate white precipitate. The mixture was stirred for 1 h and then the white precipitate was filtered off and washed successively with distilled water, methanol and diethyl ether to give $[Au_2(dmpm)Cl_2]$ as a white solid. Yield: 0.35 g, 90%.

$[Au_3(dmmp)Cl_3]$. This was similarly prepared. Gold(I) was generated *in situ* as above and a methanolic solution of dmmp (0.084 g, 0.43 mmol) was added dropwise to give an immediate white precipitate. The mixture was stirred for 1 h and then the white precipitate was filtered off and washed successively with distilled water, methanol and diethyl ether to give $[Au_3(dmmp)Cl_3]$ as a white solid. Yield: 0.33 g, 85%.



$[Au_2(dmpm)R_2]$



$[Au_3(dmmp)R_3]$

$[Au_2(dmpm)Me_2]$. A solution of 1.4 mol dm^{-3} methyllithium (0.72 cm^3, 1.01 mmol) was added to a suspension of $[Au_2(dmpm)Cl_2]$ (0.1 g, 0.17 mmol) in freshly distilled diethyl ether (20 cm^3) at −78 °C. The mixture was allowed slowly to rise to room temperature. After stirring for 12 h, it was reduced in volume to *ca.* 5 cm^3 and CH_2Cl_2 (20 cm^3) added. Filtration followed by removal of solvent and subsequent recrystallization from dichloromethane–diethyl ether gave $[Au_2(dmpm)Me_2]$ as a white solid. Yield: 0.05 g, 54% (Found: C, 15.05; H, 3.60. Calc.: C, 15.00; H, 3.55%). NMR(CD_2Cl_2): ^{1}H, δ 0.25 ['dd', $(A_3X)_2$, 6 H, *J* = 7.0, AuMe], 1.62 (m, 12 H, Me_2P) and 2.14 [t, 2 H, *J*(P–H) = 10.5 Hz, CH_2); ^{31}P, δ 19.3. UV/VIS (CH_2Cl_2): λ/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}) 230 (14 200), 245 (sh) (11 900) and 269 (10 200).

$[Au_2(dmpm)(C_6H_4OMe\text{-}p)_2]$. A solution of 0.78 mol dm^{-3} *p*-methoxyphenyllithium (1.3 cm^3, 1.01 mmol) was added to a suspension of $[Au_2(dmpm)Cl_2]$ (0.1 g, 0.17 mmol) in freshly distilled diethyl ether (20 cm^3) at −78 °C. The mixture was allowed slowly to rise to room temperature. After stirring for 12 h it was reduced in volume to *ca.* 5 cm^3 and CH_2Cl_2 (20 cm^3) added. Filtration followed by removal of solvent and subsequent recrystallization from dichloromethane–diethyl ether gave $[Au_2(dmpm)(C_6H_4OMe\text{-}p)_2]$ as a yellow solid. Yield: 0.08 g, 65%. Positive FAB MS: *m/z* 744, M^+. NMR(CD_2Cl_2): ^{1}H, δ 1.85 (m, 12 H, Me_2P), 2.18 [t, 2 H, *J*(P–H) = 10.5 Hz, CH_2], 3.71 (s, 6 H, OMe) and 6.7–7.3 (m, 8 H, Ph); ^{31}P, δ 11.4. UV/VIS (CH_2Cl_2): λ/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}) 230 (25 000), 249 (18 200) and 285 (11 000).

$[Au_3(dmmp)Me_3]$. A solution of 1.4 mol dm^{-3} methyllithium (0.72 cm^3, 1.01 mmol) was added to a suspension of $[Au_3(dmmp)Cl_3]$ (0.1 g, 0.11 mmol) in freshly distilled diethyl ether (20 cm^3) at −78 °C. The mixture was allowed slowly to rise to room temperature. After stirring for 12 h it was reduced in volume to *ca.* 5 cm^3 and CH_2Cl_2 (20 cm^3) added. Filtration followed by removal of solvent and subsequent recrystallization from dichloromethane–diethyl ether gave $[Au_3(dmmp)Me_3]$ as

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

a white solid. Yield: 0.06 g, 65% (Found: C, 14.8; H, 3.15. Calc.: C, 14.4; H, 3.35%). NMR(CD_2Cl_2): ^1H, δ 0.35 [‘dd’ $(A_3X)_3$, 9 H, J = 8.3, AuMe], 1.63–1.80 [m, 15 H, J(P–H) = 8.6 Hz, Me_2P and MeP) and 2.21–2.79 (m, 4 H, CH_2); ^{31}P NMR, δ 17.0 and 20.5. UV/VIS (CH_2Cl_2): λ/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}) 230 (19 800), 265 (sh) (14 000) and 275 (13 500).

[Au_3(dmmp)(C_6H_4OMe-*p*)$_3$]. A solution of 0.78 mol dm^{-3} *p*-methoxyphenyllithium (1.3 cm^3, 1.01 mmol) was added to a suspension of [Au_3(dmmp)Cl_3] (0.1 g, 0.11 mmol) in freshly distilled diethyl ether (20 cm^3) at −78 °C. The mixture was allowed slowly to rise to room temperature. After stirring for 12 h it was reduced in volume to *ca.* 5 cm^3 and CH_2Cl_2 (20 cm^3) added. Filtration followed by removal of solvent and subsequent recrystallization from dichloromethane–diethyl ether gave [Au_3(dmmp)(C_6H_4OMe-*p*)$_3$] as a yellow solid. Yield: 0.08 g, 65% {Found: C, 31.35; H, 3.60. Calc. for [Au_3(dmmp)(C_6H_4OMe-*p*)$_3$]·0.5Et_2O: C, 31.45; H, 3.95%}. NMR(CD_2Cl_2): ^1H, δ 1.78–2.10 (m, 15 H, Me_2P and MeP), 2.28–3.36 (m, 4 H, CH_2), 3.70 (s, 9 H, OMe) and 6.6–7.6 (m, 12 H, Ph); ^{31}P, δ 12.1 and 15.0. UV/VIS (CH_2Cl_2): λ/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}) 230 (33 700), 250 (23 500) and 288 (17 200).

Physical Measurements and Instrumentation.—The UV/VIS spectra were obtained on a Milton Roy Spectronic 3000 diode-array spectrophotometer, and steady-state emission spectra on a Spex Fluorolog 111 spectrofluorometer. 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 DCR-3 pulsed Nd-YAG laser (10 Hz, G resonator). Luminescence decay signals were recorded on a Tektronix model 2430 digital oscilloscope, and analysed using a program for exponential fits. All solutions for photophysical studies were prepared under vacuum in a round-bottom flask (10 cm^3) equipped with a 1 cm sidearm 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. Luminescence quenching experiments were monitored by time-resolved (lifetime) emission measurements, and data were treated by a Stern–Volmer fit as described by $\tau_0/\tau = 1 + k_q\tau_0[Q]$, where τ_0 and τ are the respective excited-state lifetimes in the absence and in the presence of quencher Q, k_q is the bimolecular quenching rate constant, and [Q] is the concentration of the quencher.

Results and Discussion

Reaction of [Au_2(dmpm)Cl_2] or [Au_3(dmmp)Cl_3] with an excess of organolithium reagent (LiR, R = Me or C_6H_4OMe-*p*) in diethyl ether under strictly anhydrous and anaerobic conditions resulted in [Au_2(dmpm)R_2] or [Au_3(dmmp)R_3] in high yield. The identity of the newly synthesised compounds has been confirmed by satisfactory elemental analyses and NMR spectroscopy. The electronic absorption spectra of [Au_2(dmpm)R_2] and [Au_3(dmmp)R_3] in CH_2Cl_2 exhibit similar absorption patterns. With reference to our previous spectroscopic work on d^{10}–d^{10} systems,[1] the intense absorption at *ca.* 269 nm of dimeric [Au_2(dmpm)Me_2] and at *ca.* 275 nm of trimeric [Au_3(dmmp)Me_3] are attributed to the spin-allowed $d_{\sigma^*}\rightarrow p_\sigma$ transition. The intense absorption of [Au_2(dmpm)Me_2] is similar to that observed for [$Au_2(dmpm)_2]^{2+}$.[1a,d] The red shift of the transition energy from the bi- to the tri-nuclear species (0.1 eV) is in accord with the assignment to the $d_{\sigma^*}\rightarrow p_\sigma$ transition, since increasing the number of gold units causes a rise in the energy of the d_{σ^*} orbital, and hence a narrowing of the d_{σ^*} −p_σ gap. Similar red shifts have also been observed for other polynuclear d^{10} systems.[1a,d] The smaller red shift observed for the organogold(I) complexes probably arises as a result of the larger Au···Au distance and hence a smaller Au···Au interaction.

Excitation of solid samples or fluid solutions of [Au_2(dmpm)R_2] and [Au_3(dmmp)R_3] at λ > 350 nm at room temperature resulted in long-lived intense luminescence. The photophysical data are collected in Table 1. The long lifetime of the excited state suggests that the emission is likely to be of triplet parentage. The relatively indiscernible difference in emission energies upon changing the number of gold units, and the very large Stokes shift between the $d_{\sigma^*}\rightarrow p_\sigma$ transition energies and the emission energies suggest that the lowest emitting electronic states are unlikely to be derived from the pure $(d_{\sigma^*})^1(p_\sigma)^1$ triplet, but rather from the $(d_{\delta^*})^1(p_\sigma)^1$ triplet or mixtures of both. This is in accord with our previous assignments for related gold(I) systems where the $d_{\delta^*}\rightarrow p_\sigma$ transition energy has been shown to be relatively insensitive to the number of gold units present.[1a,d] However, the possibility of the third Au atom being non-interacting with an *anti* configuration to the other two Au atoms in the trimer could not be excluded. Such a configuration could also account for the similarity of the emission energies for both the dimer and trimer. The excitation spectra of the organogold(I) complexes in degassed dichloromethane exhibit excitation maxima at 330–400 nm, probably of triplet parentage.

The phosphorescence of [Au_2(dmpm)R_2] and [Au_3(dmmp)R_3] was found to be quenched by a number of electron acceptors. In order to investigate the redox activity of the excited triplet state, a study of the electron-transfer quenching by a series of pyridinium acceptors of variable reduction potential was undertaken. The quenching rate constants for [Au_3(dmmp)(C_6H_4OPh-*p*)$_3$] are collected in Table 2. The excited-state redox potential E°[Au_3(dmmp)(C_6H_4OMe-*p*)$_3{}^{+/0*}$] was estimated to be −2.0(1) V *vs.* sodium chloride saturated calomel electrode (SSCE) (λ = 0.90 eV) by

Table 1 Photophysical data for organogold(I) complexes in degassed dichloromethane at room temperature

Complex	λ_{abs}/nm (ε/dm^3 mol^{-1} cm^{-1})	λ_{em}/nm (τ_0/μs)
[Au_2(dmpm)Me_2]	230 (14 200), 245 (sh) (11 900), 269 (10 200)	426, 506[a] 486, 575 (sh)[b] 424, 485 (sh) (0.5)[c]
[Au_2(dmpm)(C_6H_4OMe-*p*)$_2$]	230 (25 000), 249 (18 200), 285 (11 000)	512[a] 502[b] 432, 500 (7.5), 585 (sh) (5.0)[c]
[Au_3(dmmp)Me_3]	230 (19 800), 256 (sh) (14 000), 275 (13 500)	422, 511[a] 485, 576[b] 420, 448 (sh) (0.7)[c]
[Au_3(dmmp)(C_6H_4OMe-*p*)$_3$]	230 (33 700), 250 (23 500), 288 (17 200)	497[a] 484[b] 421, 499 (55), 577 (sh) (1.8)[c]

[a] Solid state at 298 K. [b] Solid state at 77 K. [c] In degassed dichloromethane at 298 K.

Table 2 Rate constants for the quenching of $[Au_3(dmmp)(C_6H_4OMe\text{-}p)_3]$ by pyridinium acceptors in dichloromethane at room temperature

Quencher[a]	$E(A^{+/0})$[b]/ V *vs.* SSCE	$k_q{}'$[c]/dm^3 mol^{-1} s^{-1}	ln $k_q{}'$
4-Cyano-*N*-methylpyridinium	−0.67	1.2×10^9	20.86
4-Aminoformyl-*N*-ethylpyridinium	−0.93	1.0×10^9	20.74
3-Aminoformyl-*N*-methylpyridinium	−1.14	9.1×10^8	20.63
N-Ethylpyridinium	−1.36	6.0×10^8	20.21
2,6,*N*-Trimethylpyridinium	−1.52	2.3×10^8	19.25
2,4,6,*N*-Tetramethylpyridinium	−1.67	3.0×10^7	17.20

[a] All the compounds are hexafluorophosphate salts. [b] From ref. 7. [c] See ref. 6; k_d is taken to be 1.5×10^{10} dm^3 mol^{-1} s^{-1}.

three-parameter, non-linear least-squares fits using equation (1),[6] where $k_q{}'$ is the rate constant corrected for diffusional

$$(RT/F)\ln k_p{}' = (RT/F)\ln K\kappa\nu - (\lambda/4)[1 + (\Delta G/\lambda)]^2 \quad (1)$$

effects, $K = k_d/k_{-d}$ which is approximately 1–2 dm^3 mol^{-1}, k_d is the diffusion-limited rate constant in dichloromethane which is taken to be 1.5×10^{10} dm^3 mol^{-1} s^{-1}, κ is the transmission coefficient, ν is the nuclear frequency, and λ is the reorganization energy for electron transfer, and ΔG, the standard free-energy change of the reaction which is given by equation (2) for oxidative quenching, where w_r and w_p are work

$$\Delta G = E^\circ[Au^{ox/red*}] - E^\circ[Q^{ox/red}] + w_p - w_r \quad (2)$$

terms for bringing reactants or products to the mean separation for reaction. The work term associated with the neutral organogold(I) and a pyridinium acceptor is extremely small and is neglected in the analysis of the electron-transfer rate data. 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 $E^\circ[Au_3(dmmp)(C_6H_4OMe\text{-}p)_3{}^{+/0*}]$ is indicative of the strong reductive nature of the organogold(I) excited state. The stronger reducing power of $[Au_3(dmmp)(C_6H_4OMe\text{-}p)_3]^*$ relative to the analogous tricationic $[Au_3(dmmp)_2]^{3+*}$ and $[Au_3(dmmp)_3]^{3+*}$ is consistent with the electron richness of the uncharged organogold(I) species.

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