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Gold(I) Pyrenyls: Excited-State Consequences of Carbon−Gold Bond Formation

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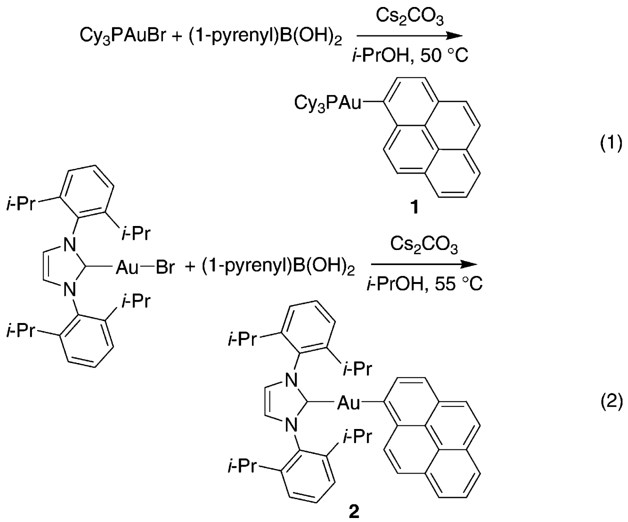
Summary: Two 1-pyrenyl derivatives of gold(I) have been prepared by base-promoted transmetalation of 1-pyreneboronic acid. Triplet-state luminescence observed from the new complexes at 77 K is assigned to a pyrene $\pi-\pi^*$ state.

The design of photoactive compounds having both predefined optical absorption and triplet-state luminescence is an imperative in organic materials chemistry. Applications are varied and include light-emitting diode fabrication, sensor technology, in vivo photochemistry, and photodynamic therapy.[1−6] A staple of phosphorescence emitter design is the spin−orbit coupling brought about by heavy-atom substituents.[7] A recent report[8] describes a general protocol for aromatic carbon−gold bond formation from arylboronic acid precursors. The reaction tolerates polar and reducible functionalities that recur in organic fluorophores. Steric encumbrance, heterocyclic substrates, and ring fusion are all accommodated. The carbon−gold bond is minimally polar and nonchromophoric in the visible region. Here, gold is intended as a relativistic spectator.[9−13] Spin−orbit coupling associated with the heavy-atom nucleus intermingles singlet and triplet excited states. Optical access to the triplet manifold of organic chromophores can thereby result. Benchmark properties associated with triplet excited states include microsecond-scale or longer excited-state lifetimes and triplet-state photosensitization. Presented here are syntheses and optical characterization of gold-substituted 1-pyrenyls prepared by the new method. Photophysical consequences of auration are directly interrogated.

Scheme 1



Commercially available 1-pyreneboronic acid was reacted with Cy_3PAuBr[14] (Cy = cyclohexyl) in isopropyl alcohol in the presence of Cs_2CO_3 to afford Cy_3PAu(1-pyrenyl) (**1**) as an air-stable, yellow-brown solid in 80% isolated yield after crystallization (eq 1 of Scheme 1).[15] An analogous reaction with the N-heterocyclic carbene complex IPrAuBr[16] afforded the corresponding 1-pyrenyl derivative **2** in 75% isolated yield (eq 2 of Scheme 1). Full experimental details appear in the

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(15) Synthesis of **1**: isopropyl alcohol (5 mL) was added to a flask charged with Cs_2CO_3 (113 mg, 0.35 mmol) and 1-pyreneboronic acid (84 mg, 0.34 mmol). To this suspension was added [$(PCy_3)AuBr$] (95 mg, 0.17 mmol), and the mixture was stirred at 50 °C for 24 h. After it was cooled, the mixture was stripped of solvent in vacuo and extracted into benzene, and the extract was filtered through Celite and taken to dryness by rotary evaporation. The solid was triturated with pentane (to remove traces of isopropyl alcohol), the residual of which was removed by rotary evaporation. The solid was again extracted into benzene, and the extract was filtered through Celite and concentrated to saturation. Vapor diffusion of pentane caused separation of yellow-brown crystals. The supernatant was decanted, and the recrystallization was repeated. The light yellow crystals were collected and dried. Yield: 92 mg (80%). ^{1}H NMR (100 MHz; C_6D_6): δ 9.32 (d, 1H, 1-pyrenyl), 8.78 (q, 1H, 1-pyrenyl), 8.25 (d, 1H, 1-pyrenyl), 8.16 (d, 1H, 1-pyrenyl), 7.97−8.01 (m, 3H, 1-pyrenyl), 7.77−7.86 (m, 2H, 1-pyrenyl), 0.97−1.98 (m, 33H, C_6H_{11}). ^{31}P NMR (162 MHz; C_6D_6): δ 58.0 ppm. UV−vis (THF, 10^{-6} M): λ, nm (ϵ, M^{-1} cm^{-1}) 281 (48 900), 310 (sh, 8490), 324 (18 100), 338 (38 800), 354 (53 100), 378 (5200). Anal. Calcd for $C_{34}H_{42}AuP$: C, 60.17; H, 6.24. Found: C, 60.14; H, 6.42.

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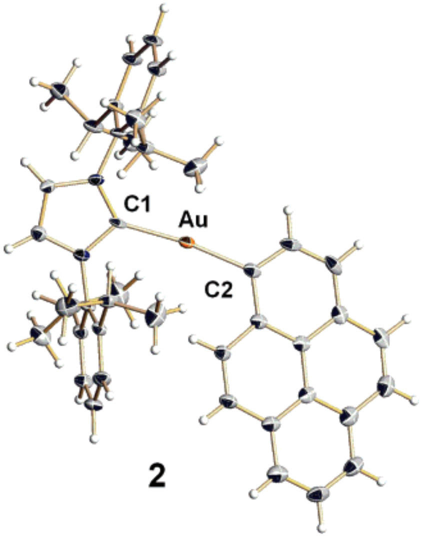

Figure 1. Crystal structure of **2** (50% probability, 100 K). Selected bond lengths (Å) and angle (deg): Au−C1, 2.000(6); Au−C2, 2.005(7); C1−Au−C2, 172.7(2).

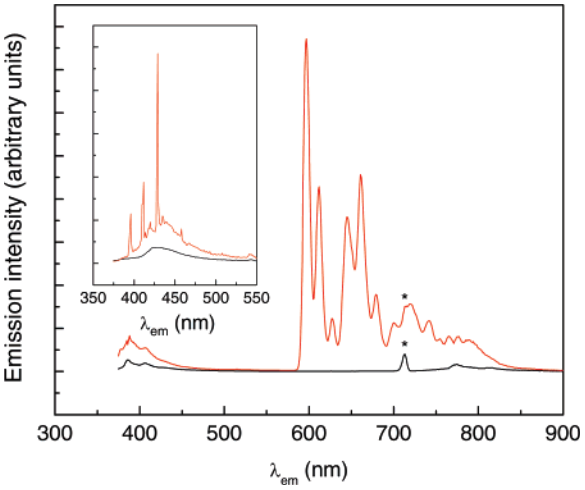

Figure 2. Emission spectra (77 K, red; 298 K, black; 355 nm excitation) of (Cy$_3$P)Au(1-pyrenyl) (**1**; 5 × 10^{-6} M) in degassed 2-MeTHF. Inset: emission of **1** at 5 × 10^{-8} M under otherwise identical conditions. No luminescence is observed past 550 nm at this concentration. Note that *y* axes of the two spectra have different scales. An asterisk indicates the excitation pulse second harmonic.

Supporting Information. The new compounds have been characterized by elemental analysis, optical absorption and emission, multinuclear NMR, X-ray diffraction crystallography,[17] and combustion analysis.

Diffraction-quality crystals of **1** and **2** were grown by vapor diffusion of pentane into concentrated benzene solutions at room temperature. A thermal ellipsoid projection of **2** appears in Figure 1. The crystal structure of **1** is provided as Supporting Information, along with full crystallographic data for both compounds. Metric parameters in the new structures are unexceptional. In both, gold adopts a nearly linear two-coordinate geometry. In neither structure are aurophilic interactions evident: the closest approach of neighboring gold atoms in **2** is 7.01 Å; that of **1** is 8.16 Å. Neither structure exhibits pyrene π-stacking.

Compounds **1** and **2** absorb light of wavelengths below 400 nm. Their absorption spectra are similar to that of pyrene and are included as Supporting Information. Room-temperature excitation at 355 nm in 2-methyltetrahydrofuran (2-MeTHF) elicits weak luminescence between 400 and 500 nm (Figure 2). Cooling to 77 K leads to concentration-dependent emission. At 5 × 10^{-8} M concentration (Figure 2, inset), the emission from 400 to 500 nm is the more intense of the two observed luminescence profiles. Structured emission is evident at low temperatures, with a mean peak-to-peak separation of 971 cm^{-1}. No higher wavelength emission is apparent at this concentration. At increased concentration (5 × 10^{-6} M), the same luminescence occurs between 400 and 500 nm. However, structured emission appears at 77 K, beginning near 600 nm and extending to 800 nm. A vibronic progression is clearly resolved between 600 and 700 nm, with an average peak spacing of 404 cm^{-1}. Structured luminescence at 77 K extends to at least 800 nm, albeit with lesser resolution. This structured luminescence is quenched at room temperature. The 77 K emission lifetime of the structured emission collected at 603 nm is 1.09 ± 0.01 ms. Luminescence behavior of the N-heterocyclic carbene variant **2** is closely analogous. Here also, concentration-dependent structured emission occurs at 77 K with a 1.08 ± 0.01 ms lifetime. Emission spectra of **2** appear as Supporting Information. Under identical conditions, pyrene is nonemissive at wavelengths exceeding 600 nm.

Static and time-resolved density-functional theory calculations have been performed[18,19] on Me$_3$PAu(1-pyrenyl) (**1′**), a truncated analogue of **1**. The geometry was optimized in the gas phase with the TZVP basis set of Godbout and co-workers.[20] A harmonic frequency calculation confirmed the resulting structure to be an energy minimum. Calculated (observed for **1**) metrics are as follows: Au−C = 2.071 Å (2.073(8) Å), Au−P = 2.351 Å (2.3115(19) Å), and ∠C−Au−P = 179.13° (174.0(2)°). Implicit THF solvation was included in single-point calculations

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(17) (a) Crystallographic data for **1**:_ colorless rods, crystal dimensions 0.40 × 0.13 × 0.12 mm^3, space group $I\bar{4}$, a = 24.9180(15) Å, b = 24.9180(15) Å, c = 9.2140(11) Å, V = 5721.0(8) Å^3, Z = 8, ρ_{calcd} = 1.576 Mg/m^3, μ(Mo Kα) = 5.220 mm^{-1}, data measured on a Bruker AXS SMART APEX CCD-based diffractometer (Mo Kα, λ = 0.710 73 Å) at 100(2) K, structure solved by direct methods, 29 261 reflections collected, 7109 unique reflections (R_{int} = 0.0472), 7109/127/375 data/restraints/parameters, final R indices ($I > 2\sigma(I)$) R1 = 0.0468 and wR2 = 0.1204, R indices (all data) R1 = 0.0500 and wR2 = 0.1240, largest difference peak and hole +6.089 and −1.243 e Å^{-3}. (b) Crystallographic data for **2**: colorless block, crystal dimensions 0.39 × 0.32 × 0.20 mm^3, space group $P2_1/c$, a = 12.2122(13) Å, b = 12.1108(13) Å, c = 23.060(3) Å, β = 90.024(2)°, V = 3410.6(6) Å^3, Z = 4, ρ_{calcd} = 1.532 Mg/m^3, μ(Mo Kα) = 4.347 mm^{-1}, data measured on a Bruker AXS SMART APEX CCD-based diffractometer (Mo Kα, λ = 0.710 73 Å) at 100(2) K, structure solved by direct methods, 28 480 reflections collected, 8437 unique reflections (R_{int} = 0.0398), 8437/0/423 data/restraints/parameters, final R indices ($I > 2\sigma(I)$) R1 = 0.0522 and wR2 = 0.1273, R indices (all data) R1 = 0.0595 and wR2 = 0.1310, largest difference peak and hole +7.679 and −3.385 e Å^{-3}.

(18) Full details appear in the Supporting Information.

(19) Calculations employed the Gaussian03 suite of programs: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision D.01; Gaussian, Inc.: Wallingford, CT, 2004.

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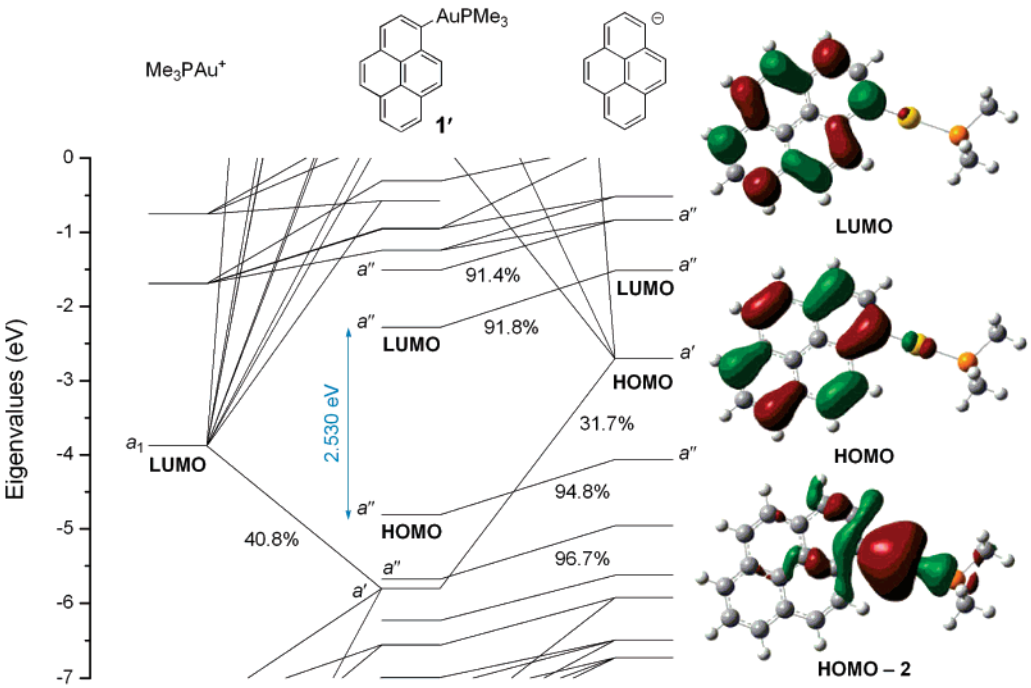
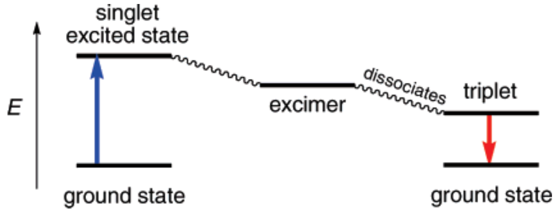


Figure 3. (left) Kohn−Sham orbital energy-level diagram of (Me$_3$P)Au(1-pyrenyl) (**1′**) (mpwpw91/Stuttgart ECP and basis on Au). Implicit THF solvation is included through a polarizable continuum model. Percentage contributions of (phosphine)gold(I) cation and pyrenyl anion fragments are indicated. (right) Plots of selected orbitals (contour level 0.03 au).

through the polarizable continuum model of Tomasi and coworkers.[21,22] Figure 3 depicts a partial Kohn−Sham orbital energy level diagram; plots of selected orbitals are given on the right-hand side of the figure. The highest occupied Kohn−Sham orbital and the lowest unoccupied Kohn−Sham orbital (HOMO and LUMO, respectively) are pyrene π-orbitals, as are the HOMO−1 and LUMO+1 (not shown). The HOMO−2 primarily accounts for the carbon−gold σ-bond. This orbital has 51.9% gold, 9.0% phosphorus, and 32.0% pyrenyl character, as apportioned by Mulliken analysis.[23] Energetically this σ-orbital lies 1.01 eV below the HOMO of **1′**. Time-dependent density functional calculations of **1′** (in the singlet geometry) indicate that the lowest four triplet states have pyrene $\pi-\pi^*$ character; all transform as A′ in C_s symmetry. The two lowest lying singlet excited states are also $\pi-\pi^*$ in nature. The calculations suggest that the intense absorption ($\epsilon = 52\,000$ M^{-1} cm^{-1}) at 336 nm is attributable to an optically allowed transition that is a combination of LUMO ← HOMO and LUMO+1 ← HOMO−1 one-electron excitations.

The structured luminescence encountered at low temperature indicates triplet-state parentage, as does its millisecond-length lifetime. The concentration dependence of the structured emission indicates oligomer formation. However, aurophilic[24−27] and excimer[28,29] emissions are typically structureless. Scheme 2 depicts a plausible excited-state hypothesis. Excitation of **1** (or **2**) leads promptly to a singlet excited state that decays to an excimer. The excimer lies at higher energy than the triplet, to which it decays. The excimer effectively pumps the triplet. Higher temperatures suppress excimer formation. Alternatively, nonradiative decay processes at higher temperature may subvert triplet-state emission. This hypothesis qualitatively reconciles the observed temperature- and concentration-dependent emission of aurated hydrocarbons.[8]

Scheme 2



Excited-state consequences of metalation with gold have been evaluated for two 1-pyrenyl complexes. The absorption profile of pyrene is substantially retained. Triplet-state photophysical properties emerge at low temperature upon replacement of a single terminal hydrogen with (phosphine)- or (carbene)gold(I) fragments. A structured luminescence of millisecond duration occurs in a 2-MeTHF glass at 77 K; no comparable emission is observed for pyrene under identical conditions. Density functional calculations indicate an emitting triplet state of pyrenyl $\pi-\pi^*$ parentage. Ongoing efforts seek to enhance intersystem crossing by attaching multiple gold(I) fragments to the pyrene core and to alter the luminescence temperature dependence by varying the ancillary phosphine or N-heterocyclic carbene ligand.

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Supporting Information Available: Text, figures, and tables giving experimental and computational protocols, details of the emission spectrum of **1** at 5 × 10^{-6} M and 5 × 10^{-8} M in 2-MeTHF, crystallographic data, and optimized Cartesian coordinates of **1′** and CIF files giving crystal data for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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