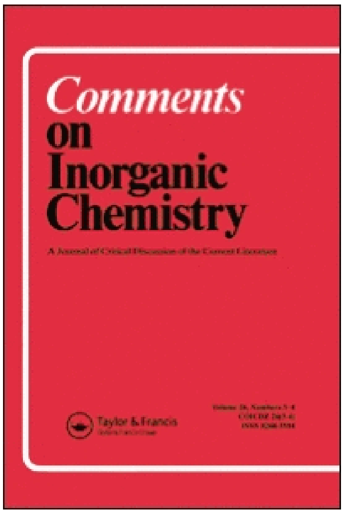

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GILDED ORGANOMETALLICS

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GILDED ORGANOMETALLICS

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The (phosphine)- and (*N*-heterocyclic carbene)gold(I) fragments are isolobal with the proton; they can attach terminally to fluorescent organic molecules in place of hydrogen. A new synthetic protocol, base-promoted transmetallation, has been developed that binds gold(I) to the peripheries of aromatic molecules through direct C–Au σ-bonds. Photophysical investigations indicate that a single gold center induces triplet excited-state behavior. Gold-induced perturbations of an azadipyrromethene chromophore are also discussed; here gold binds through nitrogen. In all instances considered, gold(I) acts as a relativistic functional group that perturbs its ligands' excited state manifolds through spin-orbit coupling.

Keywords: emission spectroscopy, gold, photophysics, transmetallation

Abbreviations: 2-MeTHF, 2-methyltetrahydrofuran; bpy, 2,2′-bipyridyl; Cy, cyclohexyl; DFT, density-functional theory; HOMO, highest occupied Kohn-Sham orbital; *i*-Pr, *iso*-propyl; LUMO, lowest unoccupied Kohn-Sham orbital; Me, methyl; NMR, nuclear magnetic resonance; OTf, triflate; PCM, polarizable continuum model; Ph, phenyl; TDDFT, time-dependent density-functional theory; THF, tetrahydrofuran

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INTRODUCTION

Gold(I) chemistry has long been remarkable for its profusion of photoactive compounds.[1–9] Real and proposed applications of gold-bearing luminophores include molecular light-emitting devices,[10–13] cellular probes,[14,15] and sensors of ions,[16] volatile organics,[17] and elemental oxygen.[18] Gold(I), being d^{10}, admits of no ligand-field transitions, and the naïve expectation is of spectroscopic silence (although the element is Mössbauer active). The excited-state properties of gold(I) compounds are dominated by dispersive interactions,[19,20] between closed-shell centers. Such aurophilic attractions[21] are comparable to hydrogen bonds in strength, with dissociation energies ranging from 24–46 kJ mol^{-1}.[22] Compounds having aurophilic interactions often exhibit broad, featureless luminescence from triplet excited states. If the aurophilic interactions are entirely intermolecular, then emission is typically concentration dependent and sometimes vanishes entirely upon dissolution. Sterically imposing ancillary ligands can overcome aurophilic attraction and quench the accompanying luminescence. The excited-state consequences of aurophilicity[23] have been reviewed.[24]

Linear, two-coordination is the predominant binding geometry for gold(I).[25] This preference is held to be at least partly relativistic, although copper(I) and silver(I) also adopt two-coordinate linear structures.[26] In the absence of aurophilic interactions, two-coordinate gold(I) centers are not themselves luminophoric (although the ligands may be). Three-coordinate geometries are less common.[27] Certain three-coordinate gold(I) complexes luminesce, and emission originates from a metal-centered state. Substantial excited-state distortions, brought about by Jahn-Teller instabilities, produce large Stokes shifts.[28] In some instances, two-coordinate gold(I) cations form exciplexes with their counterions to produce a distorted T-shaped excited state where gold is three-coordinate. Such cases are recognized both for mononuclear and di-gold centers.[29–36]

Recent work by Nocera and collaborators has emphasized the photoproperties of heterobimetallics containing three-coordinate gold(I). A d^8–d^{10} $Rh^I \cdots Au^I$ binuclear complex was described that has three-coordinate gold in an approximately T-shaped geometry. This compound is luminescent at 77 K in butyronitrile glass. Emission bands appear at 565 nm (weak) and 707 nm (stronger), with lifetimes < 10 ns and 20 μs, respectively. The low-energy emission is assigned as phosphorescence from a $^3d\sigma^*$ state.[37] A related d^8–d^{10} $Pt^{II}\cdots Au^{I}$ heterobinuclear complex was investigated photochemically.[38] Emission from this complex was not reported, but oxidation with $PhI{\cdot}Cl_2$ yields a metal-metal bonded Pt^{III}—Au^{II} complex that reverts to the starting $Pt^{II}\cdots Au^{I}$ bimetallic upon irradiation with visible light (405 nm) in the presence of a halogen-atom trap. The excited-state properties of other gold-containing heterometallics have been reviewed.[4,39]

Gold modifies the emission properties of nominally ligand-centered excited states. Che and collaborators have prepared the bridged di-gold(I) complexes $Cy_3PAu{-}C{\equiv}C{-}AuPCy_3$ and $Cy_3PAu{-}C{\equiv}C{-}C{\equiv}C{-}AuPCy_3$ (Cy = cyclohexyl).[40–42] The dicarbon-bridged compound is nonemissive at room temperature in fluid solution, but emission from both compounds is observed in solid samples and in glasses at 77 K. Structured luminescence is realized in CH_2Cl_2 at 298 K for butadiyne-bridged $Cy_3PAu{-}C{\equiv}C{-}C{\equiv}C{-}AuPCy_3$. Solid-state emission persists on a microsecond timescale at 77 K and 298 K for both complexes. The solution-phase luminescence of $Cy_3PAu{-}C{\equiv}C{-}C{\equiv}C{-}AuPCy_3$ undergoes bimolecular quenching with pyridinium salts. Both observations indicate a triplet-state parentage for the emission of these compounds. A clearly resolved vibronic progression in the emission spectrum of either compound suggests ligand-based luminescence from the bridging alkynyl and di-alkynyl ligands. The spin-orbit coupling of gold promotes intersystem crossing to the ligands' triplet excited states, and accounts for the phosphorescence of the carbon bridges.

The foregoing results illustrate something of the breadth of photophysical properties brought about by gold(I). Luminescence results from dispersive $Au\cdots Au$ interactions, from a three-coordinate geometry (possibly with bond formation in the excited state), and from heavy-atom induced perturbations of ligand excited states. It is clear that the photophysics of gold(I) compounds continues to present opportunities for the chemical investigator.

SYNTHESIS OF ORGANOGOLD COMPLEXES BY TRANSMETALLATION

Gold(I) alkynyls have prompted extensive photophysical investigation,[43,44] but not so gold(I) *aryls*. This circumstance is surprising, in that the (phosphine)- or (*N*-heterocyclic carbene)gold(I) fragment is isolobal with the proton. Further, the Pauling electronegativity[45,46] of gold (2.54) is fortuitously near that of carbon (2.55); by this scale, the C–Au bond is virtually nonpolar. Gold(I) fragments can bind terminally to aromatic rings, much as do hydrogen and the halogens. The spin-orbit coupling of gold, which for a 5d-electron is 5100 cm^{-1}, is comparable to that of iodine at 5700 cm^{-1}.[47–49] The (phosphine)gold(I) or (*N*-heterocyclic carbene)gold(I) moieties act as relativistic spectators, injecting spin-orbit coupling into the excited-state manifolds of appended organic ligands.[50,51] Intersystem crossing is facilitated, and readier access to the ligands' triplet states results.

Figure 1 is a cartoon depiction of a general class of triplet-state luminophore. A chromophoric organic ligand is the site of photoexcitation. Gold provides spin-orbit coupling through an internal heavy-atom effect. The ancillary (non-photoactive) ligand at gold modulates solubility in organic solvents or in water, as needed. Given sufficient girth, this supporting ligand also suppresses intermolecular aggregation through aurophilic contacts.

Existing chemistry can realize the strategy schematized in Figure 1 for simple hydrocarbon fragments.[9,25] However, the great majority of organic chromophores are functionalized, often heavily so, with reactive entities such as carbonyl groups. Much organogold(I) chemistry is in fact organolithium or organomagnesium chemistry. Auration necessitates reaction conditions that are incompatible with reducible and polar functionalities. A more tolerant auration protocol was therefore sought.

The Suzuki coupling[52,53] is a palladium-catalyzed coupling of arylboronic acids or esters with aryl, vinyl, propargyl, or (less commonly)[54] alkyl halides. This reaction has wide applicability in the construction of carbon-carbon bonds. Mechanistic studies[55] of the Suzuki coupling indicate that the transmetallation event, highlighted with a red box in Scheme 1, is rate-limiting in many cases. Transmetallation, which need not be an elementary reaction, produces a palladium-carbon bond. Suzuki couplings require a supporting base. Various functions for this base have been proposed. One is that the base quaternizes boron, either in the free state or coordinated to palladium. The organic substituents on boron become more anionic and hence more migratory.

A similar strategy suggests itself for transmetallation to gold. Indeed, Fackler and co-workers[56] had documented phenyl-group transfer from tetraphenylborate anion to gold(I), eqs (1)–(2) (Scheme 2). These reactions have the attractive feature of proceeding in water.[57] At roughly

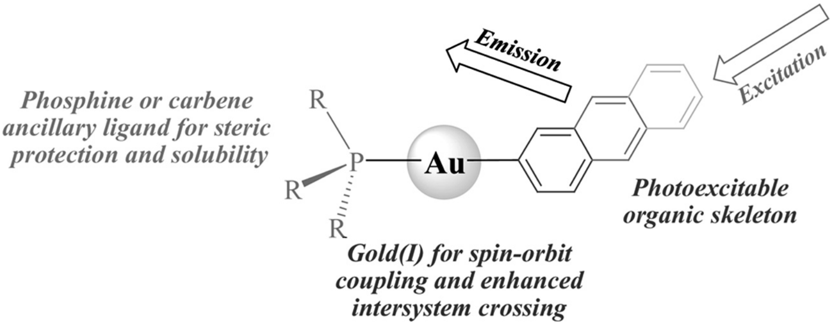
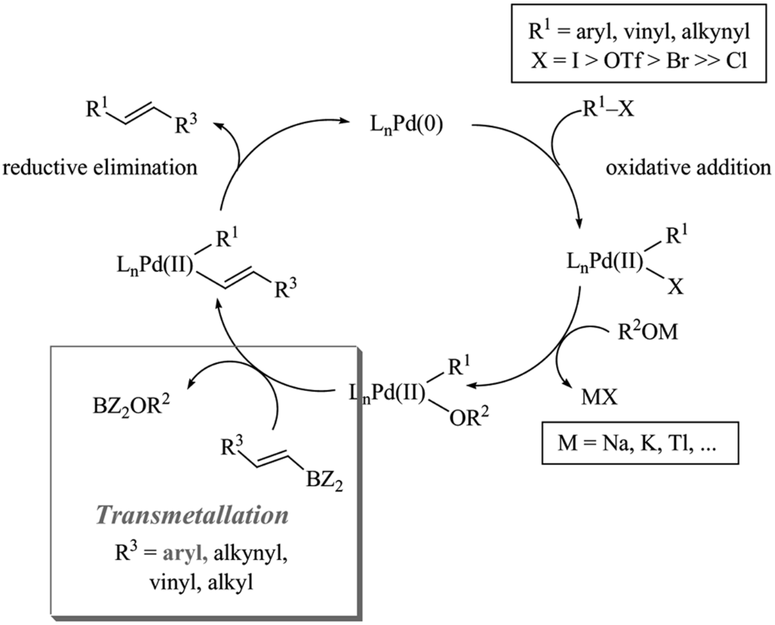
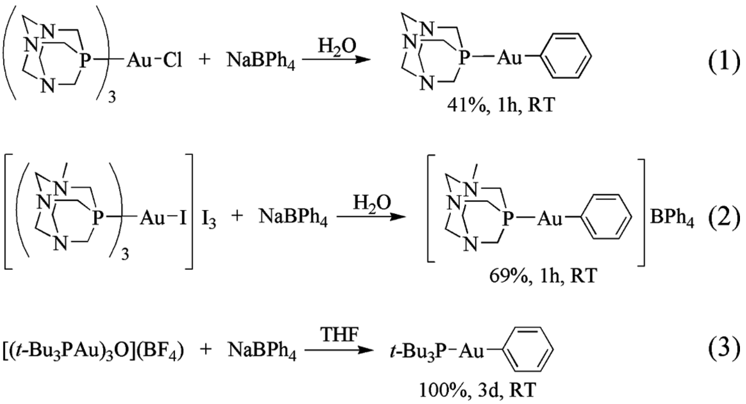


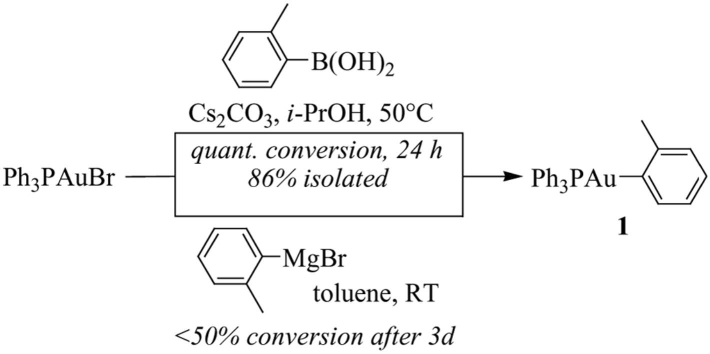
Figure 1. Gross structure of gold-functionalized aromatic organic skeletons.



Scheme 1. Proposed mechanism of Suzuki coupling. Adapted from Refs. 52–55.



Scheme 2. Early observations of transmetallation from boron to gold.



Scheme 3. Adapted from Ref. 59.

the same time, Schmidbaur and co-workers[58] disclosed reaction (3), a phenyl group transfer from BPh_4^- to a tri-gold(I) oxonium cation, with formation of uncharacterized boron-containing products. These precedents suggested the viability of transmetallation for binding gold generally to arylboronic acid (or ester) substrates.

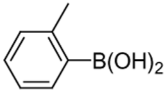
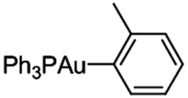
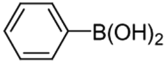
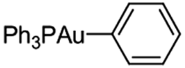
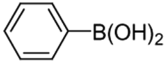
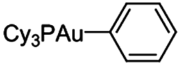
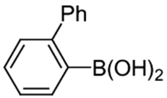
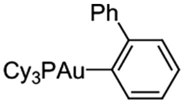
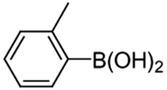
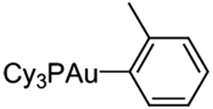
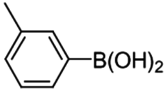
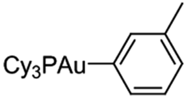
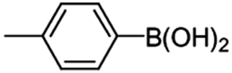
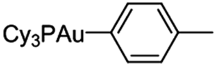
In 2006, Gray and co-workers[59] reported that the reaction of (triphenylphosphine)gold(I) bromide with *o*-tolylboronic acid in the presence of cesium carbonate in isopropyl alcohol at 55°C yields (triphenylphosphine)gold(I) *o*-tolyl, **1**. The reaction is quantitative by ^1H and ^{31}P NMR; complex **1** was isolated in 86% yield (Scheme 3). For comparison, reaction of Ph_3PAuBr with *o*-tolylmagnesium bromide at room temperature over three days did not proceed to completion, and **1** was recovered in 55% yield. Some 21 (phosphine)- and (*N*-heterocyclic carbene)gold(I) aryls have been isolated by this method. Table 1 collects these. All new compounds therein have been crystallographically characterized; in no case are aurophilic interactions observed. Figure 2 depicts crystal structures of two representatives.

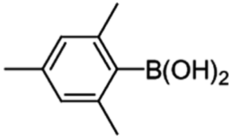
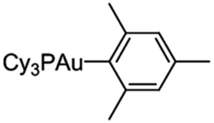
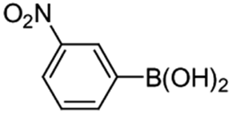
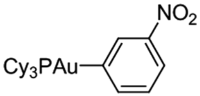
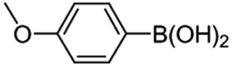
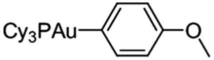
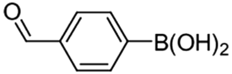
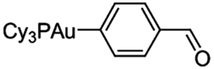
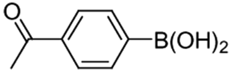
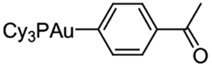
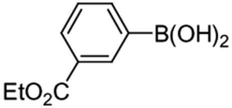
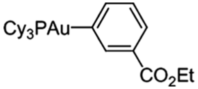
The new protocol, a base-promoted transmetallation, is general and functionally tolerant. Nitro, aldehyde, ketone, and ester groups are all accommodated. Heterocyclic boronic acids transmetallate, as illustrated by the syntheses of 2-thienyl and 4-pyridyl gold(I) complexes **16** and **17**. Ferrocenylboronic acid likewise transmetallates to yield **15**. Sterically hindered arylboronic acids transmetallate without apparent difficulty; (phosphine)gold(I) complexes bearing *o*-tolyl, mesityl, and *o*-biphenyl ligands are recovered in yields ranging from 61–86% (for **1**, **4**, **5**, and **8**). Transmetallations also proceed despite sterically demanding ancillary ligands. Gold(I) bromides bearing dialkylbiarylphosphine ligands are competent transmetallation partners, as are gold(I) complexes of bulky *N*-heterocyclic carbenes.[60] Compounds **19**, **20**, and **21** are isolated in 75%, 84% and 74% yields, respectively.

PHOTOPHYSICAL AND COMPUTATIONAL INVESTIGATIONS OF ARYLGOLD(I) SPECIES

Initial investigations of aromatic skeletons bearing terminal gold(I) functional groups find them to possess observable triplet-state photophysics that the parent hydrocarbon lacks. Substitution of a single terminal

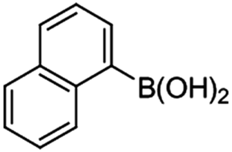
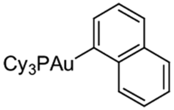
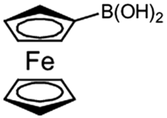
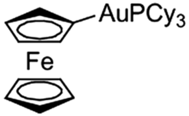
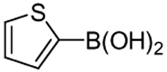
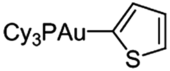
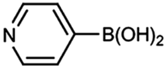
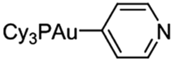
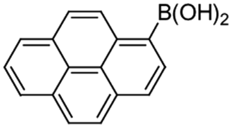
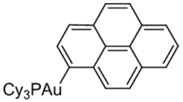
Table 1. Arylgold(I) products and isolated yields

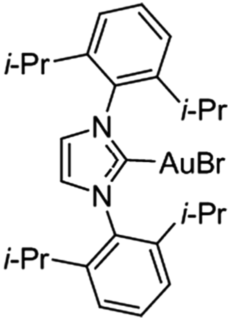
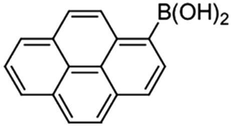
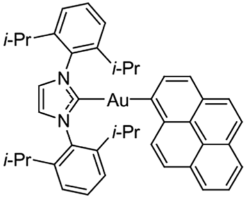
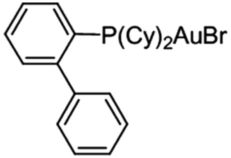
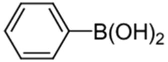
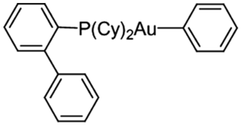
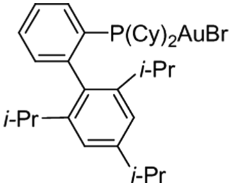
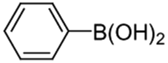
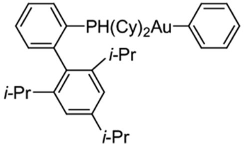
Gold(l) precursor	Arylboronic acid	Product	Isolated yield (%)
Ph_3PAuBr		 **1**	86
Ph_3PAuBr		 **2**	59
Cy_3PAuBr		 **3**	89
Cy_3PAuBr		 **4**	61
Cy_3PAuBr		 **5**	79
Cy_3PAuBr		 **6**	57
Cy_3PAuBr		 **7**	73

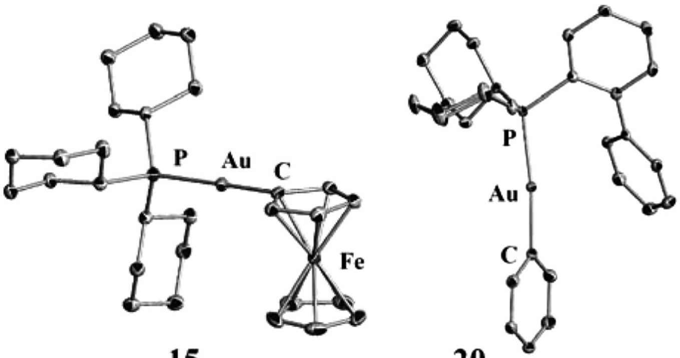
Cy_3PAuBr		 **8**	65
Cy_3PAuBr		 **9**	94
Cy_3PAuBr		 **10**	85
Cy_3PAuBr		 **11**	90
Cy_3PAuBr		 **12**	85
Cy_3PAuBr		 **13**	80

(Continued)

Table 1. Continued

Gold(l) precursor	Arylboronic acid	Product	Isolated yield (%)
Cy_3PAuBr		 **14**	86
Cy_3PAuBr		 **15**	85
Cy_3PAuBr		 **16**	86
Cy_3PAuBr		 **17**	88
Cy_3PAuBr		 **18**	80

			**19**	75
			**20**	84
			**21**	74



15 **20**

Figure 2. Crystal structures of **15** and **20** (50% probability ellipsoids; 100 K). Reproduced from Ref. 59.

hydrogen with gold elicits triplet-state luminescence that is both concentration and temperature dependent.

Compounds in Table 1 are colorless except for **15** (orange-red), **14**, **18**, and **19** (all pale yellow). Figure 3 depicts a conflated absorption and emission spectrum of 1-naphthyl complex **14** in THF solvent at 298 K. The emission spectrum was collected with **14** at a concentration of 5×10^{-6} M. Vibronically structured absorption extends from the solvent limit of THF to *ca.* 340 nm. This absorption is assigned to optically allowed, naphthyl-localized intraligand transitions. Two distinct emissions appear: a broad, featureless luminescence maximizing near 360 nm, and structured features between 480–560 nm. Lifetime experiments find the higher-energy emission to be singlet in nature, and the structured features to be spin-triplet. The structured emission (480–560 nm) is without counterparts in the fluorescence spectrum of naphthalene.[61] These structured features are quenchable, both by O_2 and methyl viologen hexafluorophosphate, the latter with linear Stern-Volmer quenching kinetics. The structured emission, which is attributed to triplet-state phosphorescence, is observable at smaller concentrations upon lowering the temperature.

Luminescence behavior of gold(I) pyrenyl complexes **18** and **19** is qualitatively similar. Figure 4 depicts the emission spectra of (*N*-heterocyclic carbene)gold(I) 1-pyrenyl compound **19** at 5×10^{-6} M concentration in deoxygenated 2-methyltetrahydrofuran (2-MeTHF). Emission spectra of the same complex at 5×10^{-8} M concentration are inset; spectra recorded at 298 K and 77 K are shown. Emission appears at both concentrations between *ca.* 400–500 nm; lifetime measurements and a smaller Stokes shift indicate this to be singlet-state fluorescence. At 5×10^{-6} M concentration, structured luminescence appears between 600 and 850 nm at 77 K. In still higher concentrations, the structured luminescence appears at room temperature. The lifetime of the structured features is 1.08 ± 0.01 ms at 77 K. For the tricyclohexylphosphine complex (**18**), the corresponding lifetime is 1.09 ± 0.01 ms, also at 77 K.

For all these complexes, the concentration-dependence of the vibronically structured emission suggests oligomer formation in solution. It is unclear if these oligomers unite through aurophilic gold-gold interactions, through gold-arene ligand π-interactions, or through arene-arene π-stacking. Emissions from excimers and aurophilically bound species are typically unstructured. One plausible excited-state hypothesis

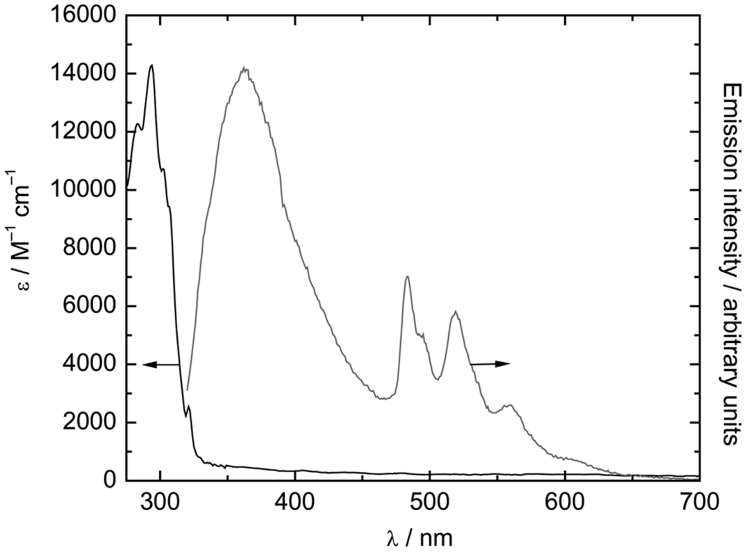


Figure 3. Room-temperature absorption (black) and emission (red) spectra of 1-naphthyl complex **14** in THF (10^{-6} M, $\lambda_{ex} = 310$ nm). Adapted from Ref. 59.

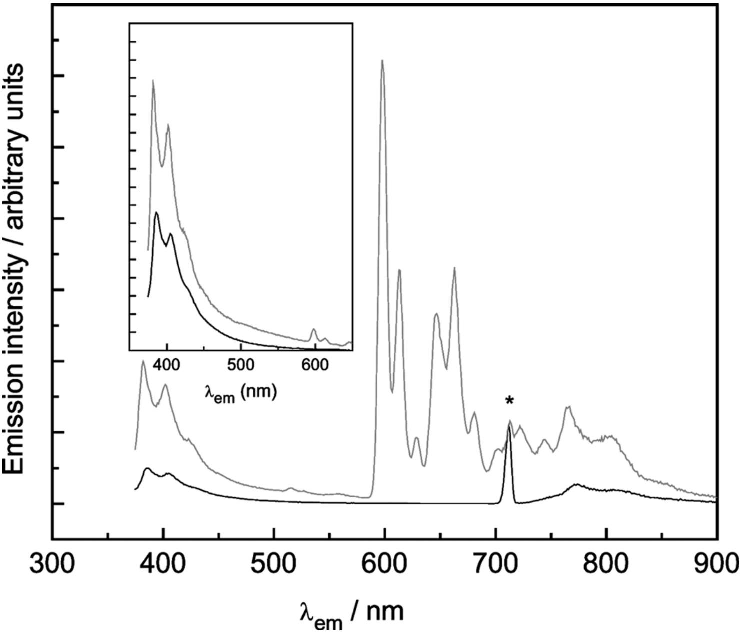
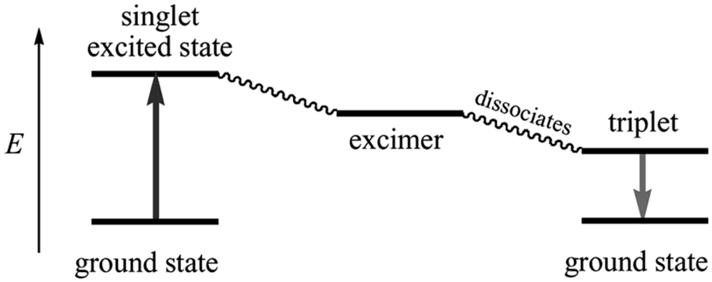


Figure 4. Emission spectra (77 K, red; 298 K, black; 305-nm excitation) of **19**, 5×10^{-6} M in degassed 2-MeTHF. Inset: emission of **2** at 5×10^{-8} M under otherwise identical conditions. No luminescence is observed past 650 nm at this concentration. Note that *y*-axes of the two spectra have different scales. An asterisk indicates the excitation pulse second harmonic. Reproduced from Ref. 60.

appears in Scheme 4. Photoexcitation of **14**, **18**, or **19** promptly yields a singlet excited state that decays to an excimer. The excimer has higher energy than the lowest-lying triplet state, to which it decays. Higher temperatures inhibit excimer buildup. Alternatively, nonradiative relaxation at higher temperatures may quench triplet-state emission. The structured emissions of the gold(I) 1-pyrenyl species are not observed for pyrene under identical experimental conditions. Substitution of a single terminal hydrogen with gold(I) begets photophysical behavior characteristic of triplet states. Further experimental studies of aromatic fragments functionalized with gold(I) are ongoing.

Density-functional theory (DFT) and time-dependent density-functional theory (TDDFT) calculations have been performed on luminescent gold(I) aryls.[59,60] Results for Me_3PAu(1-naphthyl) (**14′**), a truncated analogue of **14**, are representative. Implicit THF solvation was included in all calculations with the polarizable continuum model (PCM) of Tomasi and collaborators.[62–64] Figure 5 depicts a partial Kohn-Sham orbital energy level diagram of **14′**; selected orbitals are plotted at right. The highest occupied and lowest unoccupied Kohn-Sham orbitals (HOMO and LUMO, respectively) are separated by 3.290 eV. The LUMO ← HOMO transition is electric-dipole allowed (as are all transitions in C_s symmetry).[65] The LUMO is 87.5% naphthyl in character; the apportioning scheme is Mulliken's.[66] The HOMO has 93.2% of its density localized on the naphthyl ligand; it derives from the naphthyl HOMO–1. The HOMO–1 of **14′** is the primary C–Au σ-bonding orbital; 42.4% of its density derives from the a_1 LUMO of free Me_3PAu^+.

Time-dependent density-functional computations of the lowest-energy singlet excited states of **14′** indicate a transition at 324 nm of mixed origin, that derives from LUMO ← HOMO and LUMO + 1 ← HOMO excitations undergoing configuration interaction. Both one-electron promotions correspond to $\pi^* \leftarrow \pi$ transitions. Weaker absorptions (oscillator strengths ~10–20% that of the lowest singlet-singlet excitation) are calculated at 258 and 254 nm. No other optically allowed transitions of significant oscillator strength are predicted within the spectral transparency window of THF. The Franck-Condon triplet state is computed at 425.1 nm. Computational results for (phosphine)- and (*N*-heterocyclic carbene)gold(I) 1-pyrenyls (truncated analogues of **18** and **19**) are qualitatively similar.[60]



Scheme 4. Adapted from Ref. 60.

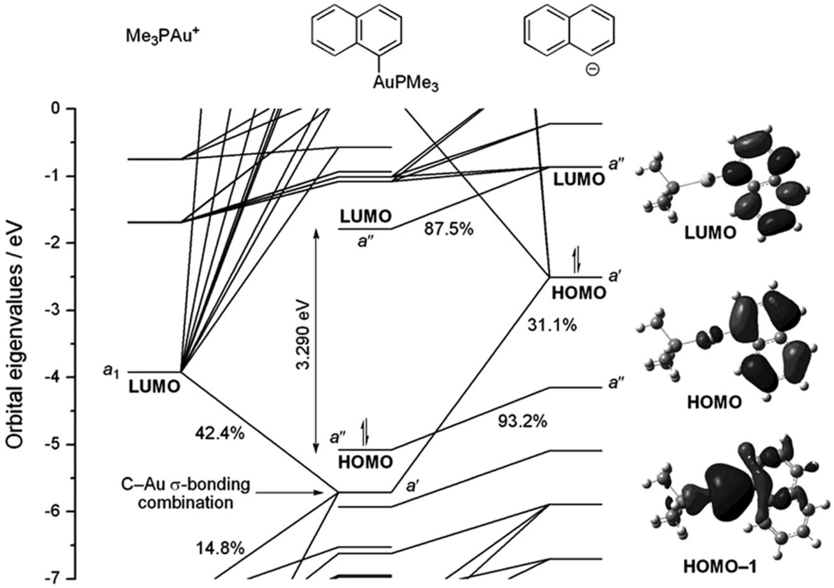


Figure 5. Kohn-Sham orbital energy level diagram of **14′** calculated with implicit THF solvation. Plots of selected orbitals (contour level 0.03) are inset. Adapted from Ref. 59.

A CHELATED GOLD(I) AZADIPYRROMETHENE. GOLD-NITROGEN BOND FORMATION

Boron azadipyrromethenes have gained much attention for their absorption of red light.[67,68] Recent investigations have suggested potential utility in sensing[69–71] and in human photodynamic therapy.[72,73] Figure 6 depicts the structure of an ordinary boron azadipyrromethene. The chelated BF_2^+ fragment is saturated and photoinactive. It is inserted in a complexation reaction of the pre-synthesized azadipyrromethene ligand with boron trifluoride etherate. Reaction of azadipyrromethenes with Lewis acids other than boron is an obvious entrée into these ligands' coordination chemistry. The photophysics of boron azadipyrromethenes is ligand-centered; that of simple chelates, such as for gold(I), is expected to be likewise.

Reaction (Scheme 5) of azadipyrromethene ligand **22** with triflate complexes Ph_3PMOTf (M=Cu^I, Ag^I) affords the corresponding azadipyrromethene complexes in 88% (M=Cu, **23**) and 62% (M=Ag, **24**) isolated yields, respectively.[74] More compelling conditions are needed to achieve a gold(I) azadipyrromethene complex. Reaction of **22** with Ph_3PAuCl in the presence of sodium *t*-butoxide affords gold complex **25** in 54% isolated yield. Figure 7 depicts a thermal ellipsoid plot of **25**. Gold adopts trigonal planar coordination; the gold-nitrogen bond distances are 2.2349(12) and 2.2448(12) Å. The near-C_{2v} local symmetry of gold(I) contrasts with the structure of $[(Ph_3P)Au(bpy)](PF_6)$ (bpy = 2,2′-bipyridyl). The bipyridyl complex adopts a distorted two-coordinate geometry about gold; Au–N distances are 2.166 and 2.406 Å; standard deviations are claimed to range from 0.001 to 0.003 Å.[75] Recently Roesky and co-workers[76] have disclosed structures of several (triphenylphosphine)gold(I) bis(iminotroponato) complexes also having trigonal-planar PNP coordination.

Gold(I) azadipyrromethene complex **25** absorbs intensely in the visible region, $\lambda_{max} = 600$ nm, $\varepsilon = 45\,000\ M^{-1}\,cm^{-1}$. This low-energy absorption is the signature optical feature of azadipyrromethenes, recurring in the free ligand, in boron chelates, and d^{10} mono- and bis(azadipyrromethene) complexes.[77] Gold complex **25** is weakly luminescent at 298 and 77 K. Figure 8 depicts room-temperature emission and absorption spectra of **25** in deoxygenated $CHCl_3$. A near mirror-image relationship pertains to the emission spectrum and the absorption feature near 600 nm; the Stokes shift is 1116 cm^{-1}. The emission quantum yield of **25** is 0.24%; that

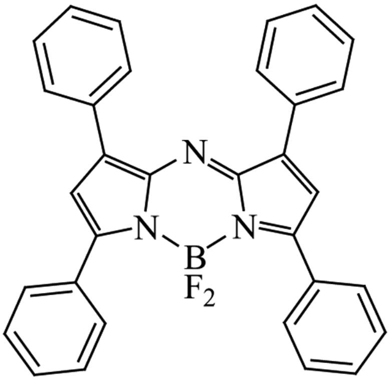
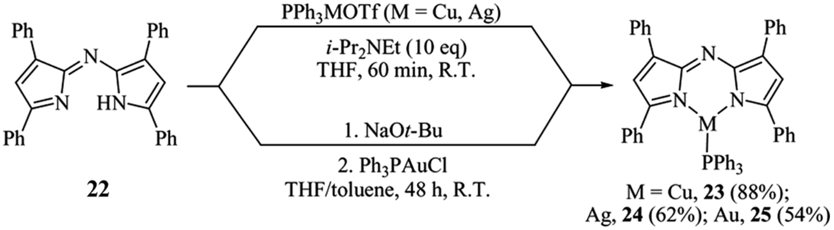


Figure 6. A typical boron azadipyrromethene.



Scheme 5. Adapted from Ref. 74.

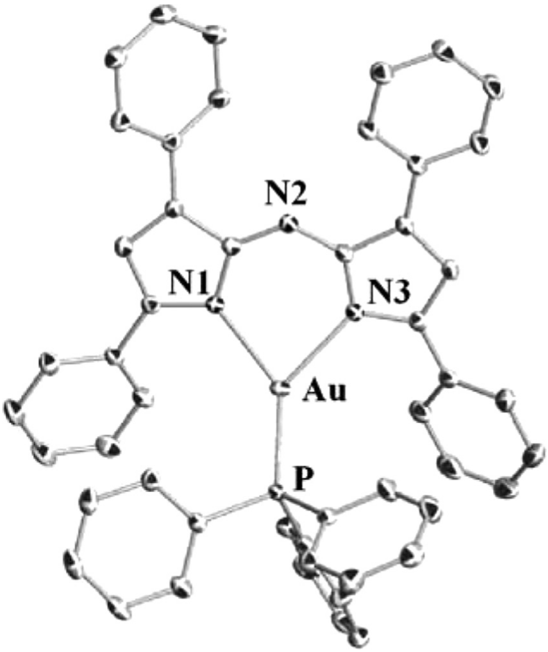


Figure 7. Thermal ellipsoid projection of **25** (50% probability, 100 K). Reproduced from Ref. 74.

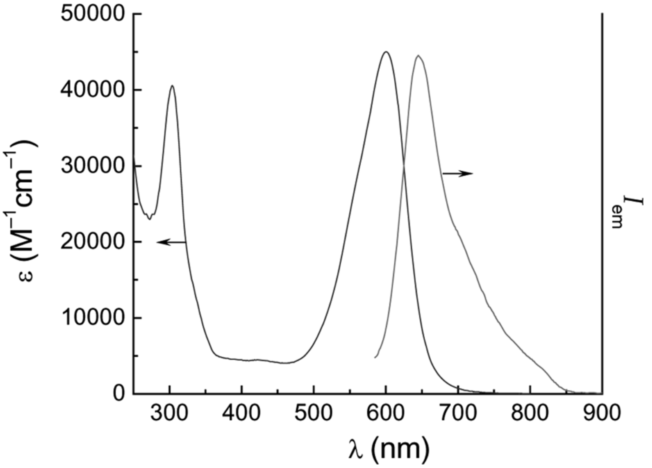


Figure 8. Absorption (blue) and emission spectrum (550-nm excitation, red) of gold complex **25** in deoxygenated $CHCl_3$ (298 ± 2 K). Reproduced from Ref. 74.

of the free ligand is 0.14%. A vibronic progression with an average peak-to-peak separation of 651 cm^{-1} emerges in the 77-K emission spectrum in 2-MeTHF glass. This frequency is consistent with vibronic activation of the azadipyrromethene skeletal modes.

SUMMARY

Complexes of gold(I) have rich and varied photophysical properties. The heavy-atom effect of gold ($Z = 79$) endows organogold(I) species with triplet-state photoproperties by enhancing intersystem crossing between singlet and triplet excited states. Notwithstanding, the photophysics of gold(I) aryls—that is, of nominally fluorescent aromatic species perturbed by terminal σ-bonds to gold—is only recently emerging.

Base-promoted transmetallation of arylboronic acids or their esters has been demonstrated to be a new and general means of aurating aromatic fragments having sensitive functionalities. Attachment of a single gold(I) center suffices for triplet-state properties to be observable. In the examples considered to date, triplet-state emission has been temperature and concentration dependent; involvement of excimers is probable.

Gold need not be carbon-bound to perturb a luminescent scaffold. Azadipyrromethene complex **25** is a three-coordinate gold(I) compound where gold attaches through nitrogen. Emission from this compound is comparable to that of the free azadipyrromethene ligand, but the quantum yield is much lower than those of boron azadipyrromethenes.

The controlled auration of aromatic molecules affords access to broad classes of triplet-state luminophores and provides opportunities in materials design and organometallic photochemistry.

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