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Gold Aryl Complexes

Geminally Diaurated Gold(I) Aryls from Boronic Acids**

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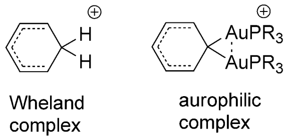
Gold catalysts and catalyst precursors have commanded attention for more than a decade. Several reviews[1–8] highlight the utility of gold in organic transformations. Recent efforts have succeeded in isolating putative intermediates of alkene and alkyne transformations. In 2008, Hammond and co-workers generated aurated γ-lactone complexes from allenes.[9] Later, Bertrand, Hashmi, and their respective co-workers independently reported vinylgold(I) species derived from alkynes.[10] Gagné and co-workers first implicated geminally diaurated species as resting states in catalytic cycles of gold by reacting vinylgold(I) species with one equivalent of gold(I) cation.[11] Fürstner and co-workers later showed that transmetalation from boron using the Gagosz complex[12] ($[Ph_3PAu]NTf_2$, Tf = trifluoromethanesulfonyl) gave only geminally diaurated species regardless of the number of equivalents used.[13]

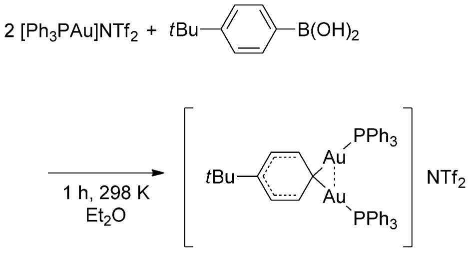
Such species are not recent discoveries. Work by Nesmeyanov and co-workers in the 1970s produced the first geminally diaurated aromatic ring systems, bis(triphenylphosphine)gold(I) complexes of ferrocene.[14] The work was soon expanded to include adducts of heteroarenes.[15] Schmidbaur and co-workers have reported geminally diaurated diketones and disulfones,[16] as well as arenes, although with lithiated reagents.[17] Most recently, Hashizume et al. generated a *gem*-diaurated 2-naphthyl species by protonation with perchloric acid of mono-gold complexes, with subsequent capture of the released cationic gold fragment.[18] In contrast to the recent development of diaurated vinyl complexes, the frontier of arene *gem*-diauration remains relatively quiet. A very recent report by Gagné and co-workers disclosed a preparation of several diaurated species from parent monoaurated arenes.[19] Such species deserve further investigation.

Due to the isolobality of the proton and the LAu^+ fragment (L = phosphine, carbene, and others),[20,21] diaurated arenes are analogues of Wheland intermediates in electrophilic aromatic substitutions (Scheme 1). However, future studies would benefit from mild methods of generating these complexes. All established routes require hazardous reagents, or they entail the loss of one half equivalent of aryl ligand—a costly issue in the case of value-added organic ligands. Here, we disclose syntheses of geminally diaurated arenes from arylboronic acids[22] without the need for activating silver salts, Brønsted acids, or Grignard reagents. The reactions are mild, quick, and high-yielding. In most cases the isolated solids are pure. No air- or moisture-free techniques were employed. All products are fully characterized by ^1H and ^{31}P NMR spectroscopy and elemental analysis, unless otherwise noted; ^{13}C NMR data are not reported because attempts to detect the bridging, *ipso*-carbon were unsuccessful.[23] For several of the products, crystals suitable for X-ray diffraction analysis were grown.



Scheme 1.

Reaction of one-half equivalent of arylboronic acid with $[Ph_3PAu]NTf_2$ in diethyl ether led to the precipitation of the expected diaurated complex $[(\mu\text{-aryl})(Ph_3PAu)_2]NTf_2$ (Scheme 2). Washing the solid with diethyl ether removed the boronimidate side product and small amounts of unreacted boronic acid. The as-isolated solids persist at room temperature, but decompose in solution within days. Monitoring the reaction by $^{31}P\{^1H\}$ NMR spectroscopy in tetrahydrofuran at room temperature showed the concomitant disappearance of starting material ($\delta = 26.0$ ppm) and appearance of two resonances: one major peak ($\geq 98\%$, approximately $\delta = 37.0$ ppm) and one minor ($\delta = 45.3$ ppm). The latter, minor peak corresponds to an in-solution decomposition product $[(Ph_3P)_2Au]^+$, in agreement with previous reports.[11,13] This peak gradually becomes dominant over a course of days in both THF and chlorinated solvents. Table 1 collects new gold compounds and yields of isolated products.



Scheme 2.

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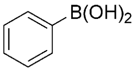
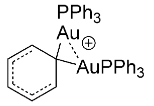
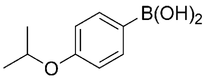
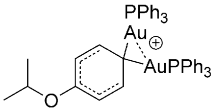
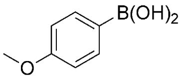
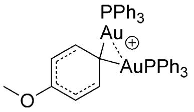
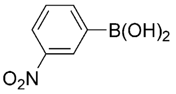
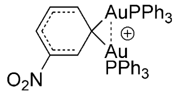
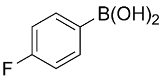
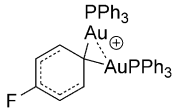
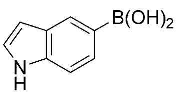
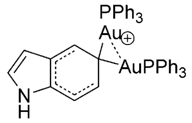
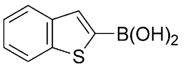
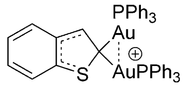
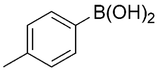
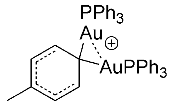
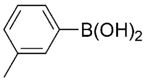
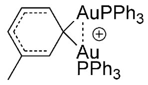
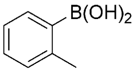
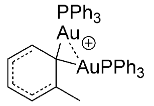
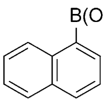
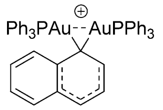
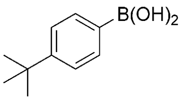
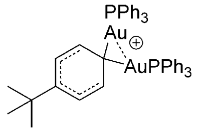
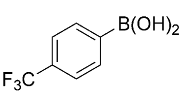
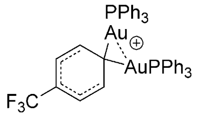
Table 1: Geminally diaurated arenes and yields of isolated products.

Arylboronic acid	[Product]NTf$_2$		Yield [%]
		**1**	95
		**2**	45
		**3**	94
		**4**	61
		**5**	99
		**6**	83
		**7**	96
		**8**	98
		**9**	89
		**10**	91
		**11**	90
		**12**	98
		**13**	79

X-ray crystallographic studies confirmed the geminal nature of the dinuclear complexes. Compounds **1**, **6**, **7**, **8**, and **12** grew suitable crystals by diffusion of diethyl ether into either saturated chloroform or THF solutions. Figure 1 shows the solid-state structure of **6**. Both gold atoms bind to C1 of the indole scaffold in a distorted tetrahedral geometry; the Au1-C1-Au2 angle is 81.3(2)° and lies perpendicular to the C2-C1-C6 angle, which is 117.8(6)°. Both gold atoms maintain

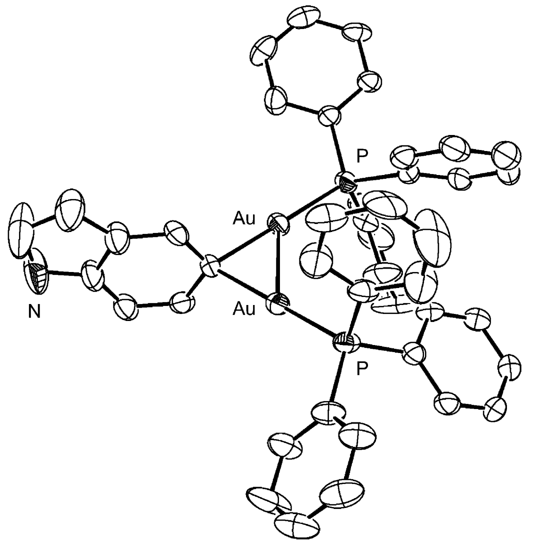


Figure 1. Thermal ellipsoid projection of indolyl derivative **6** (50%, 100 K). Hydrogen atoms are omitted for clarity. Unlabeled atoms are carbon.

an approximately linear geometry about the P-Au-C bonds; the bond angles are 176.46(19)° and 173.2(2)°. The molecule features a tight intramolecular aurophilic interaction; the Au···Au distance is 2.7699(7) Å. Examination of key bond lengths shows diminished aromaticity that is presumably compensated for by the stabilizing aurophilic interaction. The bond lengths C1–C2 and C6–C1 are 1.401(10) and 1.455(9) Å, respectively; those of the parent indole are 1.399 and 1.414 Å.[24] The longer bonds suggest that positive charge delocalizes across the benzopyrrole skeleton and diminishes the aromaticity.

The photophysical properties of **11** are representative. Optical spectra of this compound were collected in CH_2Cl_2. Absorption of **11** obeys Beer's law, and extends to 330 nm (see Supporting Information). Room-temperature emission (294 nm excitation) extends from 350–700 nm with a Stokes shift of 6700 cm^{-1}. Emission spectra of **11** and of its mono-gold analogue [Ph$_3$PAu(1-naphthyl)][22] appear in Figure 2. The emission profile of a solution of di-gold **11** is red-shifted

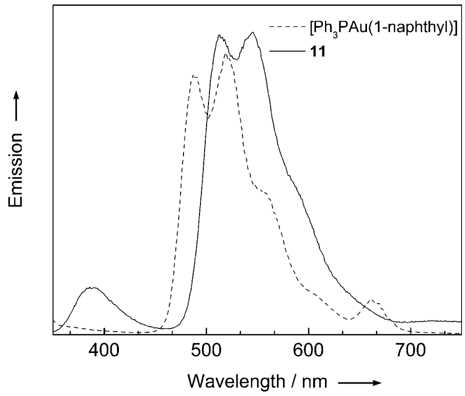


Figure 2. Room-temperature emission spectra of mono-gold and geminal di-gold 1-naphthyl complexes in methylene chloride.

from that of the mono-gold compound. Luminescence spectra of both compounds show vibronic structure, with peak-to-peak spacings near 1200 cm^{-1}. Structured emission is typical for gold(I) aryls; the peak separations suggest that ring deformation modes are activated in the emitting state. The vibronic emission and the large Stokes shift suggest phosphorescence from a triplet excited state, as observed in other gold(I) organometallics.[25–29]

Density functional theory calculations have been applied to models of **1**, **6**, and **11**, where PMe_3 ligands replace PPh_3 for computational simplicity. These model complexes are **1′**, **6′** and **11′**, respectively. Geometries were optimized with gold–gold distances constrained to those in the crystal structures. These constraints are imposed because of the dispersive nature of aurophilic interactions,[30] which DFT does not entirely capture. Converged geometries of **1′** and **6′** agree well with the crystal structures. Harmonic vibrational frequency calculations find all three to be energy minima. Full computational details appear in the Supporting Information.

For the three model compounds, the highest-occupied Kohn–Sham orbital (HOMO) resides on the aryl ligand. The lowest unoccupied Kohn–Sham orbital (LUMO) has mixed aryl–gold(I) character. Figure 3 depicts a frontier orbital energy diagram of **6′**; that for **11′** appears in the Supporting Information. Plots of selected orbitals appear at right. Methylene chloride solvation is included using a polarizable continuum model. In these compounds, the HOMO lies mainly on the aryl ligand, whereas the LUMO, the HOMO−1, and other near-frontier orbitals have sizable (> 10%) contributions from the (phosphine)gold(I) fragments. Percentages are of electron density, from Mulliken population analysis. A de facto separability of gold- and aryl-based orbitals in normal gold(I) aryls does not extend to geminally diaurated species. These results suggest some gold participation in the excited states of geminally diaurated aryls, whereas phosphorescence of normal gold(I) aryls and alkynyls is ligand-centered.[25–29,31–33]

The available crystal structures suggest disrupted aromaticity, as do the optimized geometries. Perturbations of carbon–carbon bond lengths decrease with distance from the dimetallation site. The same trend prevails for natural bond orders calculated for aromatic C−C bonds. The mean bond length between the metalated and adjacent carbons is 1.413 Å for **1′**, **6′**, and **11′** (range: 1.391–1.437 Å); the corresponding value calculated for $[Me_3PAuPh]$ (C_s symmetry) is 1.403 Å. For the three model compounds, the mean gold–carbon bond length is 2.169 Å (range: 2.162–2.174 Å); that computed for $[Me_3PAuPh]$ is 2.065 Å. The average, calculated C-$C_{metalated}$-C bond angle is 118.0°; for mono-gold $[Me_3PAuPh]$, it is 116.4°. A single metalation at carbon does not much perturb sp^2 hybridization, and the aurated carbon does not approach a tetrahedral geometry. The mean calculated Au-C-Au angle of **1′**, **6′** and **11′** is 78.0°; the aurophilic interaction precludes sp^3 hybridization at C. Wiberg bond orders in the Lowdin basis[34] also suggest diminished aromaticity. Table 2 collects bond orders calculated for **1′**, **6′**, and **11′**; for their mono-gold analogues, and for the corresponding Wheland complexes. Both calculated geometries and bond orders suggest that geminal diauration degrades aromaticity, but less so than outright protonation (Wheland complex formation). In agreement with Reed and co-workers,[35] we find that positive charge does not collect at carbon. Natural atomic charges are positive and roughly equal (ca. 0.25) for gold and hydrogen, and largest (> 0.95) for phosphorus. Carbon atoms have negative charges, be they protonated, geminally diaurated, or aromatic. The mean natural charge of dimetalated carbons across **1′**, **6′**, and **11′** is −0.50. In diaurated compounds, positive charge buildup at *ortho* and *para* sites is muted compared to that in Wheland complexes.

Time-dependent DFT calculations indicate that the aryl ligand dominates the emission and low-energy absorption features. Naphthyl **11′** is typical. The lowest excited singlet and triplet states are mainly LUMO←HOMO transitions; the triplet has small contributions from other triplet states with which it undergoes configuration interaction. The frontier orbitals of geminally diaurated aryls have greater gold character than in mono-gold analogues. Hence, emission from **11′** is not cleanly ligand-centered, but the naphthyl moiety dominates. Calculations on **1′**, **6′**, and other digold aryls herein suggest that their excited states are similar.

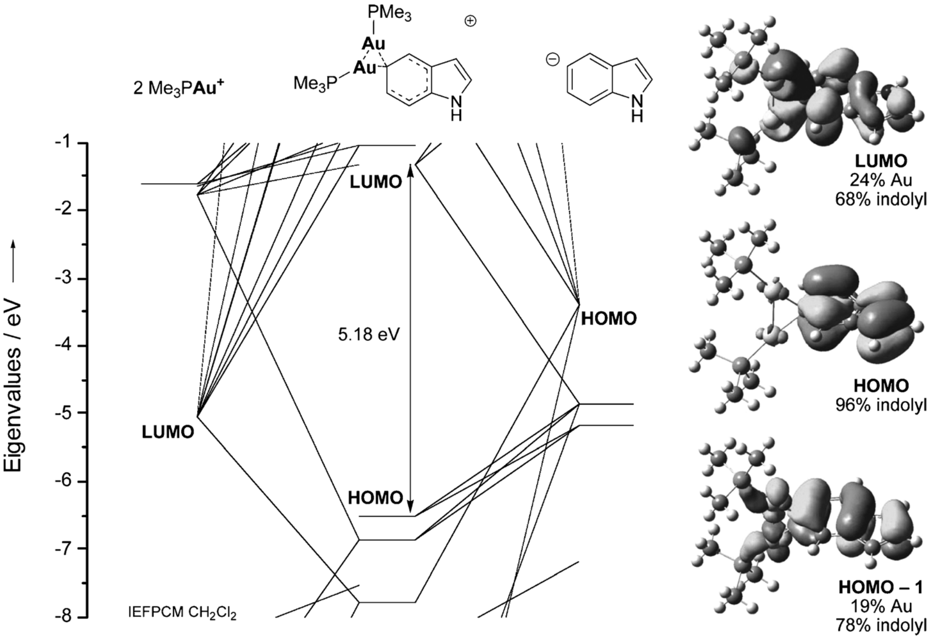


Figure 3. Partial Kohn–Sham orbital energy diagram of **6′**. Plots of selected orbitals and percentage compositions in terms of fragments appear at right. Implicit methylene chloride solvation is included; see Supporting Information for details.

Table 2: Bond lengths and calculated bond orders.

	Experimental bond length [Å] (**1**)	Calculated bond length [Å] (**1′**)	Bond order (**1′**)
Au–C1	2.153(4)	2.170, 2.172	0.384
C1–C2	1.396(6)	1.409	1.413
C2–C3	1.382(6)	1.387	1.396
C3–C4	1.371(7)	1.390	1.361
	Experimental bond length [Å] (**6**)	Calculated bond length [Å] (**6′**)	Bond order (**6′**)
Au–C5	2.126(6)	2.162, 2.163	0.426, 0.425
C4–C5	1.401(10)	1.406	1.337
C5–C6	1.455(9)	1.426	1.337
C6–C7	1.366(9)	1.379	1.455
C2–C3	1.352(14)	1.363	1.615
		Calculated bond length [Å] (**11′**)	Bond order (**11′**)
Au–C1		2.174, 2.174	0.448, 0.448
C1–C2		1.393	1.592
C2–C3		1.406	1.277
C3–C4		1.369	1.423
C5–C6		1.369	1.474
C6–C7		1.408	1.236
C7–C8		1.370	1.490

In summary, a method of generating geminally diaurated arenes is disclosed. Arylboronic acids were reacted with an electrophilic (phosphine)gold(I) cation source in ether, producing a series of air- and moisture-stable solids. The reaction tolerates a range of boronated substrates. Isolation of these species demonstrates the *gem*-diaurated arene to be stable, and a plausible resting state in gold-catalyzed transformations of olefins and alkynes. Because of the isolobality of the gold(I) cation with the proton, these species also represent analogues of Wheland intermediates of electrophilic aromatic substitution. It is hoped that the addition of these organometallics to the menagerie of gold-based (pre)-catalysts will stimulate future investigations.

Experimental Section

11: A suspension of [Ph_3PAu]NTf_2 (0.026 mmol) in diethyl ether (2 mL) was added to a solution of 1-naphthylboronic acid (0.015 mmol) in diethyl ether (2 mL). The white mixture was stirred in the dark for 6 h. The mixture was filtered, washed with 3 × 2 mL diethyl ether and pentane, and dried in vacuo to yield a light gray powder. Crystals suitable for X-ray diffraction were obtained by diffusion of diethyl ether into a saturated chloroform solution. Yield: 16 mg (90 %). ^{1}H NMR ($CDCl_3$): $\delta = 8.46$–8.42 (td, 2H, Ar$H^{4,7}$, $J = 6.9$ Hz), 8.21–8.19 (d, 1H, ArH^{2}, $J = 8.3$ Hz), 8.04–8.02 (d, 1H, ArH^{8}, $J = 7.6$ Hz), 7.79–7.66 ppm (m, 3H, Ar$H^{3,5,6}$). ^{31}P{^{1}H} NMR ($CDCl_3$): $\delta = 37.4$ ppm (s). Elemental analysis calcd for $C_{48}H_{37}Au_2F_6NO_4P_2S_2$ [%]: C 43.48, H 2.81, N 1.065; found: C 43.25, H 2.76, N 0.93.

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Keywords: aurophilicity · boronic acids · gold · luminescence · Wheland cations

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