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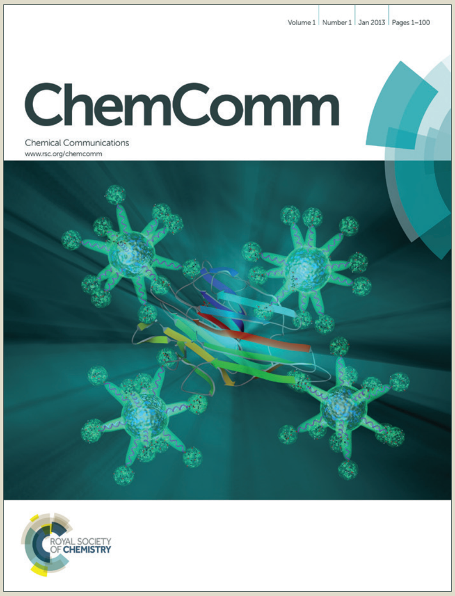

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# Cyclometalated (boroxinato)gold(III) complexes from arrested transmetalation

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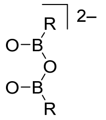
**Organic boroxines are ubiquitous, but metallaboroxine analogues remain rare. The first (boroxinato)gold species are demonstrated here, as are the first observations of phosphorescence from boroxinato complexes. Four new compounds are crystallographically characterized.**

Boroxines are non-aromatic, cyclic anhydrides of boronic acids.[1,2] Interest in boroxines has catapulted because of their utility in assembling porous network materials. Because boroxines form reversibly, the assembly process is self-correcting. Yaghi and co-workers have devised two-[3] and three-dimensional[4] covalent organic frameworks that condense by the formation of boroxine rings. These monolithic materials combine large void spaces with low densities and high thermal stability. Tour and co-workers[5] had previously shown that arylboroxines cross-link polymeric materials to impart flame-retardancy. Polymer-electrolytes have been realized in reactions of $B_2O_3$ with ethylene glycol and ethylene glycol monomethyl ether.[6,7] Telechelic polymers with $B(OH)_2$ termini form "star" species with central boroxine cores.[8,9] Many properties of boroxine-based materials derive in part from reversible assemblage of the $B_3O_3$ heterocycle.

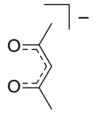
Surprisingly, *metalla*boroxine derivatives are rare. Aryl transfer (transmetalation) is the typical reaction of arylboronic acids with metal centers, especially in the presence of base. Boron transmetalation is the defining step of the Suzuki-Miyaura cross coupling reaction.[10–15] Transmetalation reactions of boron are gaining importance in the synthesis of metal σ-organometallics. We and others have applied boron transmetalation to the synthesis of (phosphine)- and (*N*-heterocyclic carbene)gold(I) aryls.[16–26] Reaction conditions can be selected to yield mono-gold(I) species or geminally diaurated aryls.[30,31] Analogous transmetalation reactions, mediated by boron, afford cyclometalated iridium(III) in room-temperature reactions.[32] Similar investigations have found stoichiometric transmetalation reactions for a variety of metals[27–29] and metalloids, and a comprehensive review is available.[33]

We have recently shown that chlorogold(III) complexes can react as electrophiles in Suzuki-Miyaura couplings to afford gold(III) aryls in the presence of base and catalytic quantities of palladium.[34] This reaction proceeds at room temperature. Nevado and co-workers[35] have published arylation reactions between gold(III) and arylboronic acids; these transformations require extended heating at 150 °C. Hansmann, Stephan, Hashmi, and co-workers[36] have described reactions of gold(I) alkynyl complexes with $B(C_6F_5)_3$ leading to π-coordinated gold(I) alkynylborates. With heating, these species transform into gold(I) pentafluorophenyls in an intramolecular transmetalation from boron. You and co-workers[37] examined the reactivity of arylboronic acids with cyclometalated gold(III) dihalides. Evidence was presented for arene carbon-hydrogen bond activation, transmetalation, and reductive elimination, but formation of (boroxinato)gold species was not described.

Here we describe trioxadiborrin complexes that result from *arrested* transmetalation reactions. Trioxadiborrin ligands are 2– chelators related structurally to β-diketonates. The first gold(III) trioxadiborrins are disclosed, along with crystallographic characterization of several. Reported also is the first systematic study of the photophysics of trioxadiborrin complexes.



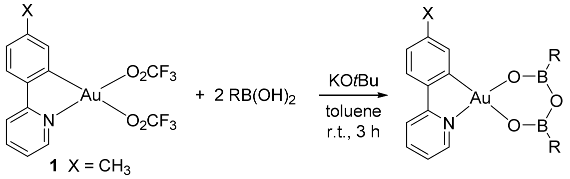
trioxadiborrin



acetylacetonate

Interaction of (4-tolylpyridyl)gold(III) chloride with boronic acids at room temperature gave no evidence of reaction. However, the trifluoroacetate species **1**, reported by Tilset and co-workers,[38] proved more reactive, Scheme 1. Room-temperature reactions of **1** with (4-isopropoxyphenyl)boronic acid in toluene with either $K_2CO_3$ or KO*t*-Bu gave full conversion to the (trioxadiborrin)gold(III) product in 4 h and 3 h, respectively. Trioxadiborrin complexes of

(4-tolylpyridyl)gold(III) are identified by the $^1$H chemical shift of the hydrogen *ortho* to pyridyl nitrogen. This proton resonates near δ 9.3 ppm for trioxadiborrins in $CDCl_3$ solution. The corresponding chemical shift for (4-tolylpyridyl)gold(III) aryls is 7.8 ppm, and 8.4 ppm for **1**. Scheme 1 summarizes optimized reaction conditions.

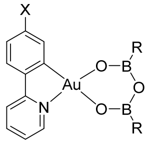


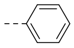
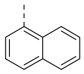
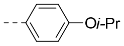
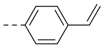
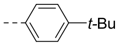
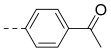
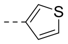
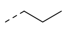
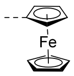
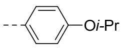
**1** X = $CH_3$
**2** X = H

**Scheme 1.** Optimized reaction conditions.

Table 1 collects new compounds and isolated yields. The reaction proceeds in high yield for boronic acids having electron-donating groups. For example, 4-isopropoxy and 4-*t*-butylphenyl boronic acids afford trioxadiborrins (**4**, **5**, and **12**) in good isolated yields. The heterocyclic 3-thienyl group is supported (**6**), as is ferrocenyl (**7**). Arylboronic acids with ring fusion (**8**) or modestly electron-withdrawing substituents (**9–10**) form boroxinato complexes in unimpaired yields, as does 4-acetylphenylboronic acid with a Lewis acidic carbonyl carbon in the *para* position. The isolation of **11** in 68% yield shows that alkylboronic acids are competent boroxinato ligand precursors. Isolated compounds are off-white powders (except **7**, which is orange) and sparingly soluble to soluble in methylene chloride.

**Table 1.**



| No. | X | R | Isolated Yield (%) | No. | X | R | Isolated Yield (%) |
|---|---|---|---|---|---|---|---|
| **3** | $CH_3$ |  | 76 | **8** | $CH_3$ |  | 76 |
| **4** | $CH_3$ |  | 68 | **9** | $CH_3$ |  | 92 |
| **5** | $CH_3$ |  | 74 | **10** | $CH_3$ |  | 69 |
| **6** | $CH_3$ |  | 77 | **11** | $CH_3$ |  | 68 |
| **7** | $CH_3$ |  | 72 | **12** | H |  | 84 |

Compounds **4**, **7**, **9**, and **10** were characterized by X-ray diffraction crystallography. The structure of **4** appears as Figure 1. The geometry of the 4-tolylpyridyl (tpy) ligand is unexceptional. Gold adopts the familiar planar geometry of low-spin d$^8$ metal centres. Gold-oxygen bond lengths reflect the relative *trans*-influences of carbon and nitrogen. The Au–O bond length opposite carbon is 2.041(4) Å; that *trans* to nitrogen is 1.972(4) Å.

The packing diagram of **4** shows that neighbouring molecules stack in a pairwise manner, Figure S2, ESI. Close approaches, within the sums of the van der Waals radii, occur between gold and C13 (3.310 Å), and B1 and O1 (3.276 Å), of adjoining complexes. A density-functional theory calculation, with heavy atoms in crystallographic positions and hydrogen atoms optimized, finds an interaction energy of 4.8 kcal mol$^{-1}$ in the gas-phase, after correction for basis set superposition error.[39] Pairwise stacking recurs in the structure of **7**, with the result that ferrocenyl substituents adopt a *syn*-configuration. A packing diagram appears as Figure S4, ESI. This stacking suggests that boron atoms within the ligands remain Lewis acidic, as does gold.

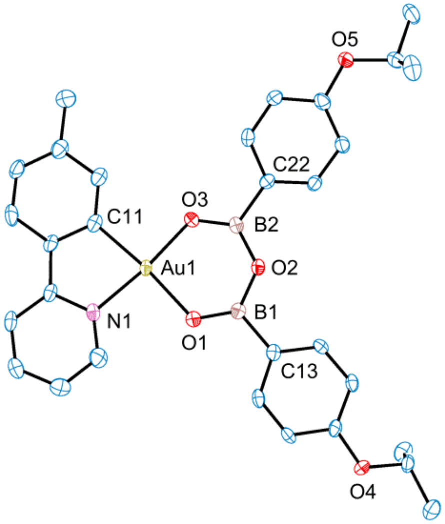


**Figure 1.** Crystal structure of **4** (50% probability). Hydrogen atoms are omitted for clarity; unlabeled atoms are carbon. Selected interatomic distances (Å): Au1–O3, 1.972(4); Au1–C11, 1.992(6); Au1–N1, 2.020(5); Au1–O1, 2.041(4); O1–B1, 1.324(8); O2–B2 1.394(7); O2–B1, 1.403(8); O3 B2–1.340(7). Selected angles (°): O3–Au1–C11, 91.5(2); O3–Au1–N1, 173.62(18); C11–Au1–N1, 82.1(2); O3–Au1–O1, 94.56(16); C11–Au1–O1, 173.9(2); N1–Au1–O1, 91.80(18); B1–O1–Au1, 122.7(4); B2–O2–B1, 128.2(5); B2–O3–Au1, 122.3(4).

Trioxadiborrin complexes of cyclometalated gold(III) are luminescent. Shown in Figure 2 is the emission spectrum of **4** in 2-methyltetrahydrofuran at room temperature; this compound is representative of the series. Excitation at anywhere within the absorption profile elicits vibronically structured emission that quenches on exposure to air. Table S2, ESI, compiles photophysical parameters. Emission lifetimes range from 1.44–2.53 μs at 298 K, suggesting a triplet excited state. Spectral shapes show little influence of the boroxine aryl substituents, implying that phosphorescence originates from the (tpy)Au$^{III}$ moiety.

Static and time-dependent density-functional theory calculations were performed on **4**. Figure 3 depicts a frontier Kohn-Sham orbital energy level diagram along with plots of selected orbitals. The two highest occupied Kohn-Sham orbitals (HOMOs) localize on the arylboroxinato fragment; they derive from an $E_{1g}$ HOMO of benzene. These orbitals are nearly degenerate, differing by only 0.05 eV. The lowest unoccupied Kohn-Sham orbital (LUMO) resides almost wholly on the cyclometalating tpy ligand. The $B_2O_3$ linkage is a spacer that isolates the boroxine aryls from the gold center and its cyclometalating ligand.

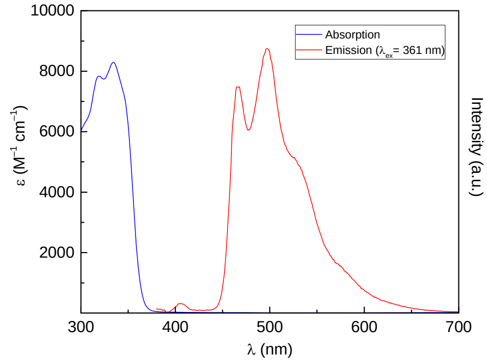


**Figure 2.** Absorption (blue) and emission (red) spectra of **4** in 2-methyltetrahydrofuran solution at 298 K.

Vertical excitation energies were estimated from time-dependent density-functional theory calculations. Compositions of excited states are collected in Tables S3, ESI. Absorptions in the visible and near-UV regions are assignable as ligand-centred and ligand-metal to ligand charge transfer transitions. The first Franck-Condon triplet state derives from the tolylpyridyl carbanion, and four triplets are calculated to lie below the first excited singlet. Configuration interaction singles (CIS) calculations lead to similar conclusions, except that six triplets lie below the first excited singlet. Results of these calculations appear in Table S4 ESI.

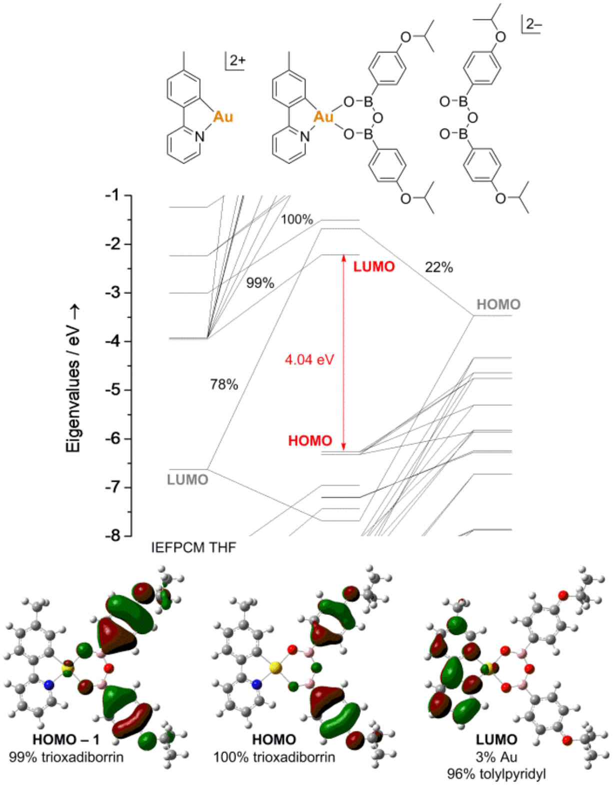


**Figure 3.** Frontier Kohn-Sham orbital energy level diagram of **3**. Orbital compositions appear as percentages of fragment electron density. Bottom: plots of selected orbitals (contour level 0.03 a.u.).

## Conclusions

We report a rational synthesis of heteroboroxines of gold(III). The reaction relies on labile (trifluoroacetato)gold(III) precursors and a desiccating base that forms insoluble potassium trifluoroacetate. Aryl- and alkylboronic acids deliver trioxadiborrin complexes in moderate to high isolated yields. Crystal structures of two complexes show intermolecular stacking of pairs of complexes. A DFT calculation finds the interaction energy to be 4.8 kcal mol$^{-1}$ for **4**. The new complexes (except for **7**) phosphoresce with microsecond lifetimes near 298 K. Luminescence spectra are nearly superimposable, suggesting a dominant role of the (tpy)Au(III) moiety. TDDFT and CIS calculations indicate that the lowest-lying Franck Condon triplet is ligand-centred, and that the first few Franck-Condon singlets have majority ligand character. The optical properties of gold(III) boroxinato complexes derive from Au and the organic moieties.

Investigations of boroxinato complexes have lagged for want of reliable syntheses. We show here that metallaboroxines support long-lived triplet excited states at room temperature. Further investigations of (boroxinato)gold(III) species are ongoing.

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## Notes and references

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Electronic Supplementary Information (ESI) available: Experimental, computational, and crystallographic details; table of photophysical data. CCDC 1408491-1408494. See DOI: 10.1039/c000000x/

(1) Korich, A. L.; Iovine, P. M. *Dalton Trans.* **2010**, *39* (6), 1423.
(2) Xiang, Z.; Cao, D. *J. Mater. Chem. A* **2013**, *1* (8), 2691.
(3) Côté, A. P.; Benin, A. I.; Ockwig, N. W.; O'Keeffe, M.; Matzger, A. J.; Yaghi, O. M. *Science* **2005**, *310* (5751), 1166.
(4) El-Kaderi, H. M.; Hunt, J. R.; Mendoza-Cortés, J. L.; Côté, A. P.; Taylor, R. E.; O'Keeffe, M.; Yaghi, O. M. *Science* **2007**, *316* (5822), 268.
(5) Morgan, A. B.; Jurs, J. L.; Tour, J. M. *J. Appl. Polym. Sci.* **2000**, *76* (8), 1257.
(6) Anne Mehta, M.; Fujinami, T.; Inoue, S.; Matsushita, K.; Miwa, T.; Inoue, T. *Electrochim. Acta* **2000**, *45* (8-9), 1175.
(7) Yang, Y.; Inoue, T.; Fujinami, T.; Mehta, M. A. *J. Appl. Polym. Sci.* **2002**, *84* (1), 17.
(8) De, P.; Gondi, S. R.; Roy, D.; Sumerlin, B. S. *Macromolecules* **2009**, *42* (15), 5614.
(9) Qin, Y.; Cui, C.; Jäkle, F. *Macromolecules* **2007**, *40* (5), 1413.
(10) Miyaura, N.; Yamada, K.; Suzuki, A. *Tetrahedron Lett.* **1979**, *20* (36), 3437.
(11) Lennox, A. J. J.; Lloyd-Jones, G. C. *Angew. Chem. Int. Ed. Engl.* **2013**, *52* (29), 7362.
(12) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95* (7), 2457.
(13) Miyaura, N. *J. Organomet. Chem.* **2002**, *653* (1-2), 54.
(14) Suzuki, A. *J. Organomet. Chem.* **1999**, *576* (1-2), 147.
(15) Miyaura, N.; Yamada, K.; Suginome, H.; Suzuki, A. *J. Am. Chem. Soc.* **1985**, *107* (4), 972.

(16) Partyka, D. V; Zeller, M.; Hunter, A. D.; Gray, T. G. *Inorg. Chem.* **2012**, *51* (15), 8394.
(17) Lenker, H. K.; Gray, T. G.; Stockland, R. A. *Dalton Trans.* **2012**, *41* (43), 13274.
(18) Gao, L.; Niedzwiecki, D. S.; Deligonul, N.; Zeller, M.; Hunter, A. D.; Gray, T. G. *Chemistry* **2012**, *18* (20), 6316.
(19) Partyka, D. V; Teets, T. S.; Zeller, M.; Updegraff, J. B.; Hunter, A. D.; Gray, T. G. *Chemistry* **2012**, *18* (7), 2100.
(20) Craig, S.; Gao, L.; Lee, I.; Gray, T.; Berdis, A. J. *J. Med. Chem.* **2012**, *55* (5), 2437.
(21) Peay, M. A.; Heckler, J. E.; Deligonul, N.; Gray, T. G. *Organometallics* **2011**, *30* (18), 5071.
(22) Gao, L.; Peay, M. A.; Partyka, D. V.; Updegraff, J. B.; Teets, T. S.; Esswein, A. J.; Zeller, M.; Hunter, A. D.; Gray, T. G. *Organometallics* **2009**, *28* (19), 5669.
(23) Partyka, D. V.; Updegraff, J. B.; Zeller, M.; Hunter, A. D.; Gray, T. G. *Organometallics* **2009**, *28* (6), 1666.
(24) Gray, T. G. *Comments Inorg. Chem.* **2007**, *28* (5-6), 181.
(25) Partyka, D. V.; Esswein, A. J.; Zeller, M.; Hunter, A. D.; Gray, T. G. *Organometallics* **2007**, *26* (14), 3279.
(26) Partyka, D. V.; Zeller, M.; Hunter, A. D.; Gray, T. G. *Angew. Chemie* **2006**, *118* (48), 8368.
(27) Suzaki, Y.; Osakada, K. *Organometallics* **2006**, *25* (13), 3251.
(28) Nishimura, T.; Yasuhara, Y.; Hayashi, T. *J. Am. Chem. Soc.* **2007**, *129* (24), 7506.
(29) Truscott, B. J.; Nelson, D. J.; Lujan, C.; Slawin, A. M. Z.; Nolan, S. P. *Chemistry* **2013**, *19* (24), 7904.
(30) Heckler, J. E.; Zeller, M.; Hunter, A. D.; Gray, T. G. *Angew. Chem. Int. Ed. Engl.* **2012**, *51* (24), 5924.
(31) Browne, A. R.; Deligonul, N.; Anderson, B. L.; Rheingold, A. L.; Gray, T. G. *Chemistry* **2014**.
(32) Maity, A.; Anderson, B. L.; Deligonul, N.; Gray, T. G. *Chem. Sci.* **2013**, *4* (3), 1175.
(33) Partyka, D. V. *Chem. Rev.* **2011**, *111* (3), 1529.
(34) Maity, A.; Sulicz, A. N.; Deligonul, N.; Zeller, M.; Hunter, A. D.; Gray, T. G. *Chem. Sci.* **2014**.
(35) Hofer, M.; Gomez-Bengoa, E.; Nevado, C. *Organometallics* **2014**, *33* (6), 1328.
(36) Hansmann, M. M.; Rominger, F.; Boone, M. P.; Stephan, D. W.; Hashmi, A. S. K. *Organometallics* **2014**, *33* (17), 4461.
(37) Wu, Q.; Du, C.; Huang, Y.; Liu, X.; Long, Z.; Song, F.; You, J. *Chem. Sci.* **2015**, *6* (1), 288.
(38) Shaw, A. P.; Tilset, M.; Heyn, R. H.; Jakobsen, S. *J. Coord. Chem.* **2011**, *64* (1), 38.
(39) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19* (4), 553.