Gold–Boron Interactions

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A Trimetallic Gold Boride Complex with a Fluxional Gold–Boron Bond**

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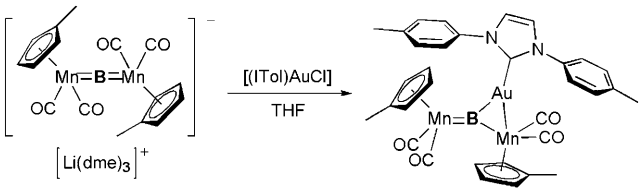
Stable compounds featuring gold–boron bonds are rare, and until 2006, were limited to those containing hypercoordinate boron ligands, for example, polymetallic monoboron clusters[1] and complexes in which a {LAu^+} fragment formally bridges an apical boron atom of a carborane cluster and another metal atom.[2] Linking low-coordinate boron to gold has proved a challenging task, but this has recently been shown to reflect little more than a synthetic roadblock. Traditional methods for constructing transition-metal–boron bonds (based on B^+/M^- polarity)[3] were found to be unsuitable: Au^I appears to lack sufficient reducing strength or nucleophilicity to perturb boron–halide bonds or to donate to an nonbridging Lewis acidic borane. Synthetic strategies based on the opposite polarity (B^-/M^+) were unthinkable until very recently, because of the absence of boron-based nucleophiles.[4] In the last three years, success has been found with both of these strategies, and two new boron–gold coordination modes have been discovered, namely the borane gold complexes (Au→B), and the boryl gold complexes (Au←B), by the groups of Bourissou,[5] and Yamashita and Nozaki,[4b] respectively. Unlike the earlier complexes, these two new bonding patterns are considered to be classical two-center-two-electron interactions, adding to their novelty.[6]

The borane gold complexes feature one or more tethered phosphine groups binding orthogonally to the boron–gold axis (B-Au-L: 79–84°, L = chelating phosphino group), while in the boryl gold complexes, the B-Au-L (L = phosphine, N-heterocyclic carbene) axis is effectively linear.[4b,5] There is a correspondingly large difference between the Au–B distances of borane gold complexes (2.32–2.66 Å) and those of boryl gold complexes (2.08–2.09 Å). These structural patterns correlate well with the generally accepted understanding of the boryl ligand as a pure σ-donor, and the borane ligand as a pure σ-acceptor. Herein we experimentally and theoretically examine the structure of an unusual dimanganese boryl gold complex with a bonding situation that is not described correctly by either of the abovementioned patterns.

The anionic complex $[Li(dme)_3][\{(\eta^5\text{-}C_5H_4Me)(OC)_2Mn\}_2B]$ (**1**, dme = 1,2-dimethoxyethane; Scheme 1), and its nucleophilic reactivity with methyl iodide, were reported recently.[7] The tendency for low-valent late-transition-metal fragments (such as {$M(PCy_3)$}, M = Pd, Pt) to undergo addition to metal–borylene bonds is now well-documented,[8] and accordingly we were interested in the reactivity of **1** towards late-transition-metal halide complexes.



1 **2**

Scheme 1. Synthesis of **2**.

Stirring of gold carbene complex [(ITol)AuCl] (ITol = *N*,*N*′-bis(4-methylphenyl)imidazol-2-ylidene) with **1** in toluene at room temperature resulted in a color change from pale-yellow to orange, and a moderate downfield shift of the broad ^{11}B NMR signal to $\delta_B = 209$ ppm (Scheme 1).[9] The position of this signal is in stark contrast to those of the trimetallic boron systems containing M→B dative bonds $[(\eta^5\text{-}C_5Me_5)(OC)Fe(\mu\text{-}CO)M(PCy_3)(\mu\text{-}Br)Pt(PCy_3)Br(\mu_3\text{-}B)]$ (M = Pd, $\delta_B = 144$ ppm; M = Pt, $\delta_B = 130$ ppm),[8e] but is closer to the recently reported "trimetalloborane" complex $[(OC)_3Mn(\mu\text{-}CO)_2Co(CO)_3(\mu_3\text{-}B)Mn(CO)_5]$ (δ_B = 195 ppm).[10a] The signal also correlates well with the family of anionic, neutral, and cationic dimetalloborylene complexes **1** ($\delta_B = 195$ ppm),[7] $[\{(\eta^5\text{-}C_5Me_5)Fe(CO)_2\}(\mu\text{-}B)\{Cr(CO)_5\}]$ ($\delta_B = 205$ ppm),[10b] $[\{(\eta^5\text{-}C_5Me_5)Fe(CO)_2\}(\mu\text{-}B)\{Fe(CO)_4\}]$ ($\delta_B = 191$ ppm),[10b] $[\{(OC)_5Mn\}_2(\mu\text{-}B)][BAr^F_4]$ (δ_B = 225 ppm; $[BAr^F_4] = [B\{C_6H_3(CF_3)_2\}_4]^-$)[10c], and $[\{(\eta^5\text{-}C_5H_4R)(OC)_2Fe\}_2(\mu\text{-}B)][BAr^F_4]$ (R = H, $\delta_B = 191$; R = Me, $\delta_B = 194$ ppm).[10c] In addition, this shift downfield in the new species **2** contrasts to the moderate shifts upfield of ^{11}B NMR signals noted upon M→B bond formation in borane gold complexes of Bourissou and co-workers,[5] and the relative stasis of the signal upon B→M bond formation in the boryl gold complexes of the Yamashita and Nozaki group.[4b]

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After filtration, **2** was crystallized from the solution providing a moderate yield (30%) of orange crystals suitable for X-ray crystallographic analysis (Figure 1).[11] The most

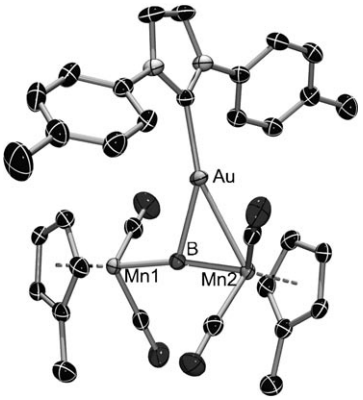

Figure 1. Molecular structure of **2**; thermal ellipsoids are set at 50% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: B–Au 2.187(3), B–Mn1 1.871(3), B–Mn2 1.964(3), Au–Mn2 2.651(4); B-Au-C1 153.0(1), Mn2-Au-C1 160.29(7), Mn1-B1-Mn2 168.9(2), Au-B-Mn2 79.17(9).

apparent features of the structure are the inequivalent Mn–B bonds (1.871(3) and 1.964(3) Å), the longer one being that spanned by the {(ITol)Au} fragment. The other Mn–B bond is short and can be considered a terminal borylene bond, being comparable to those of $[(\eta^5\text{-}C_5H_5)Mn(CO)_2(B\textit{t}Bu)]$ (1.809(9) Å),[8f] anionic **1** (1.881(1) Å),[7] and cationic $[\{(OC)_5Mn\}_2(\mu\text{-}B)][BAr^F{}_4]$ (1.9096(5) Å).[10c] The longer Mn–B bond lies within the range of other bridged manganese borylene complexes,[12] yet is still shorter than the corresponding bonds of structurally characterized manganese boryl complexes.[13] Despite the addition of the gold fragment to the Mn–B bond, the Mn-B-Mn angle (168.9(2)°) does not remarkably deviate from linearity.

The Au–B distance of **2** (2.187(3) Å) is markedly different from the corresponding distances of both boryl gold[4b] and borane gold[5] complexes, however it correlates well with Au–B distances of bimetallic systems bridged by carborane boron atoms (2.20–2.29 Å).[2a,b,d] The $C_{carbene}$-Au-B angle in **2** (153.0(1)°) similarly lies in the wide gap between the ranges of L-Au-B angle seen in boryl gold and borane gold complexes. It should be noted, however, that the crystallographic inequivalency of the two manganese fragments does not persist in solution. The signals for the η^5-C_5H_4Me ligands were found to be equivalent in the ^{1}H NMR spectrum at both 25 and −90 °C, suggesting that the Au–Mn interaction is readily broken.

The infrared spectrum of **2** shows four bands between 1842 to 1938 cm^{-1}. This range is moderately shifted to higher frequency when compared to that of the precursor **1** (three bands, 1831–1911 cm^{-1}), which is perhaps an indication of draining of electron density from the complex upon coordination of the cationic $\{Au(ITol)\}^+$

The overall impression gained from the structure of **2** is that the parameters related to the gold–boron moiety bisect those of known boryl gold and borane gold systems. To gain an understanding of the bonding in **2**, we applied methods of density functional theory (DFT).[14] The analyses of bonding used the electron localization function (ELF),[15] natural bond orbital analysis (NBO),[16] natural population analysis (NPA),[17] and topological analyses of the electron density within quantum theory of atoms in molecules (QTAIM).[18]

The direction of charge transfer within the B–Au donor–acceptor interaction has been traced by comparison of the NPA atomic and fragment charges of **2** with the corresponding charges of the anionic fragment of **1** (Scheme 1) and the cationic fragment $\{(ITol)Au\}^+$ (**3**), which **2** may be thought to include (Table 1). As has been shown for related anionic

Table 1: Selected atomic and fragment NPA charges computed at the B3LYP/TZVPP//RI-BP86/TZVP level of theory.

Compound	Atom/fragment	NPA charge
1	B	0.44
	Mn[a]	−0.59
	$\{MnCp(CO)_2\}$	−0.72
3	Au	0.47
	ITol	0.53
2	B	0.09
	Mn1	−0.55
	Mn2	−0.52
	$\{Mn1Cp(CO)_2\}$	−0.51
	$\{Mn2Cp(CO)_2\}$	−0.33
	Au	0.52
	ITol	0.23
	fragment **1**[b]	−0.75
	fragment **3**[b]	0.75

[a] Averaged value over both manganese atoms. [b] Sum over all atomic NPA charges of the corresponding fragments in **2**.

systems,[19] the overall negative charge of **1** is located on the manganese complex fragments (particularly on the metal atoms), leaving a positive NPA charge on boron. About half of the cationic charge in **3** is located on the gold atom. Upon formation of **2**, a noticeable charge redistribution takes place between and within the fragments. While the atomic charges on boron and gold would suggest charge transfer from the gold fragment, our examination of the fragment charges suggested a different situation. The fragment charges indicate an overall charge transfer of 0.25 a.u. from the anion of **1** to the cationic **3**. This result defines a zeroth-order picture of a side-on coordination of an anionic dimetallaboraallene-type system **1** to the gold-based cation **3**.

However, no reasonable NBO-type Lewis structures could be found (even if we replace the notoriously delocalized cyclopentadienyl (Cp) ligands by chloride). The NBO results point clearly towards a delocalized situation within the B-Au-Mn2 triangle, a picture that is confirmed by the QTAIM analyses: Figure 2 exhibits appreciable inward curvature of the B–Au and B–Mn2 bond paths near boron, consistent with delocalized bonding.[18] Furthermore, the ELF (Figure S1a in

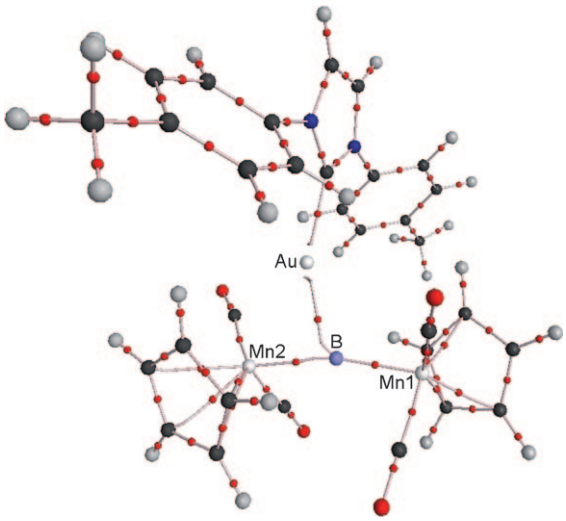

Figure 2. QTAIM molecular graph of **2**. Bond critical points are indicated as red dots.

the Supporting Information) exhibits a B–Mn2 valence basin that is distorted towards the B–Au connection line. (The B–Mn1 basin is more symmetric.) Similar patterns are found, for instance, in bi- or trimetallic complexes with bridging boron ligands.[8e,20] QTAIM provides no bond critical point between Au and Mn2 (Figure 2). Together with the low Wiberg bond index[21] of 0.16 this suggests relatively weak direct Au–Mn interactions. Indeed, moving the $\{(ITol)Au\}^+$ fragment towards a symmetrical position above the Mn1-B-Mn2 moiety in a relaxed potential-energy surface scan gives an inversion barrier of only about 5 kJ mol^{-1} for a change of coordination from the B–Mn2 side to the B–Mn1 side. This situation is again consistent with relatively weak Au–Mn bonding. Moreover, the result demonstrates a facile intramolecular rearrangement process which provides a straightforward explanation for the experimentally observed equivalency of the η^5-C_5H_4Me resonance signals in the ^{1}H NMR spectrum down to −90 °C. In contrast, moving the {(ITol)Au} fragment exclusively to the side of one Mn center to create a direct Mn–Au interaction (Au-Mn2-B angle near 90°) costs about 66 kJ mol^{-1}, indicating strong Au–B interactions.

With the exception of a handful of carborane-based systems featuring hypervalent boron atoms,[2a,b,d] boron–gold interactions have thus far fitted tidily into one of two schemes: pure boron acceptor (borane) and pure boron donor (boryl). By exploiting the nucleophilicity of anionic metallaborylene **1**, we have obtained an unusual trimetallic complex which does not fit either of these descriptions. While side-on coordination of an anionic heteroallene to a cationic $\{(ITol)Au\}^+$ fragment provides a rough first approximation to bonding in this complex, closer analysis clearly indicates an unprecedented delocalized Mn-B-Au bonding. Moreover, the complex features an interesting facile rearrangement process that renders the two manganese complex fragments equivalent on the NMR time scale down to −90 °C.

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