COMMUNICATION

Synthesis and Reactivity of [Au(NHC)(Bpin)] Complexes

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A new class of [Au(NHC)(Bpin)] complexes has been synthesized and their unusual reactivity was investigated using computational and experimental methods. The gold-boryl complexes exhibit unexpected high stability and reactivity.

Metal-boron complexes are important intermediates in catalytic hydroboration, diboration and selective C-H bond activation.[1] Three different coordination modes can be found in metal-boron complexes, metal-borylene (**A** and **B**), metal-borane (**C**) and metal-boryl (**D**) (Figure 1).[2]
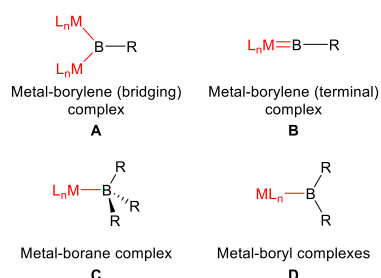

Figure 1. Examples of metal-boron coordination mode.

In this report, we are only focusing on M-boryl bond formation which can be accessed through four main synthetic approaches; 1) salt elimination of an anionic metal carbonyl complex followed by reaction with a haloborane;[1] 2) oxidative addition of a boron-heteroatom bond to a transition metal;[3] 3) σ-bond metathesis reaction either between an alkyl metal complex and a hydroborane[4] or an oxygen-bound metal complex (M-OR) and

a diborane;[5-7] and 4) nucleophilic substitution of metal chloride complexes using boryl lithium compounds.[8a]

The electronics of the boryl ligand can be tuned by varying the substituents on the boron atom, which can then translate into the boryl moiety having an electrophilic or nucleophilic character that then adopts one of the coordination mode represented above.[9] Transition-metal-boryl complexes have been investigated as intermediates in important organic/organometallic reactions.[10,11] Their isolation and study, has shed light on reaction mechanism and on the nature of true catalytic species. For example, Thomas and Denmark have reported three different species containing palladium-oxygen-boron linkages as possible intermediates in the ubiquitous Suzuki-Miyaura reaction.[12] Sadighi, in a seminal contribution, has reported on the synthesis of copper(I) β-boroalkyl complexes from alkene insertion into [Cu(IPr)(Bpin)] (IPr = N, N'-bis(2,6-diisopropyl)imidazol-2-ylidene).[13] Miyaura and co-workers have reported on the synthesis of nucleophilic β-boryl copper species starting from B_2pin_2 where α-β-unsaturated carbonyl compounds and terminal alkynes are added to the boryl copper species affording β-boryl carbonyl compounds and alkenylboronates.[5a]

Examples of gold bonding to boron as in **D** are however rare.[8] With our experience in stabilizing reactive transition metal complexes, in general, with the aid of N-heterocyclic carbene (NHC) ligands,[14] we sought to isolate a stable gold-boron complex using this ligand family. A series of gold synthons (Figure 2) were deployed to this end. Initially, these complexes were mixed with B_2pin_2 at room temperature and reaction outcome was assessed by ^{1}H NMR spectroscopy.

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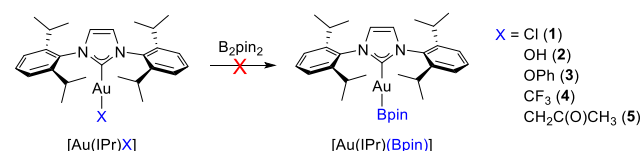
Figure 2. Au(I)-NHC synthons used in this study.

Disappointingly, all starting gold complexes were recovered unreacted after this reaction time under these conditions. Harsher conditions were applied (heating to 60 °C for 1 h or 16

h) but the lack of reactivity of these precursors persisted. This ineffective or non-existent reactivity, especially for **2**, **3** and **5** was somewhat surprising as Sadighi[15a] had successfully isolated [Cu(IPr)(Bpin)] from B_2pin_2 and [Cu(SIPr)(O^{t}Bu)], as a copper synthon. More recently, Kleeberg and co-workers have extended this same methodology to other boryl moieties.[15b] From these initial studies, a more nucleophilic Au-X bond was thought necessary to enable the Au-B bond formation. To test this hypothesis, the reactive [Au(IPr)(OMe)][16] was formed *in-situ* by dissolving [Au(IPr)(OH)] (**2a**)[17] in dry methanol and left stirring for 10 min. The solvent was then removed under reduced pressure with gentle heating. The resulting [Au(IPr)(OMe)] (**6a**) complex was not isolated but immediately dissolved in benzene under inert atmosphere, followed by addition of excess B_2pin_2. The reaction was left stirring at r.t. for 16 h and resulted in the formation of the desired [Au(IPr)(Bpin)] (**7a**) in high yield (Scheme 1).
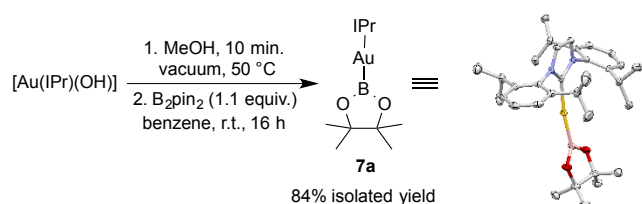

Scheme 1. Synthesis of [Au(IPr)(Bpin)] (**7a**) and its molecular structure. Hydrogens are omitted for clarity.

Complex **7a** was fully characterized by ^{1}H, ^{11}B{^{1}H} and ^{13}C {^{1}H} NMR and elemental analysis. Interestingly, the chemical shift of the $C_{carbene}$ in the ^{13}C{^{1}H} NMR spectrum appears at 216.7 ppm. This is shifted quite downfield for a transition metal-NHC complex and resembled more the shift of a free NHC.[18] This peculiarity was also observed by Yamashita and Nozaki who have reported on other types of gold-boryl complexes.[8] Single crystals of **7a** were grown by slow diffusion of pentane into a dichloromethane solution of the complex under inert atmosphere. The X-ray analysis showed a distorted linear structure ($C_{carbene}$-Au-B angle of 170.96(18)°) with a Au-B bond length of 2.063(5) Å and an Au-$C_{carbene}$ bond length of 2.084(4) Å.[19]

This synthetic procedure was then extended to other NHC ligands. Gratifyingly, [Au(IPr*)(Bpin)] (**7b**) (75%), [Au(SIPr)(Bpin)] (**7c**) (65%) and [Au(IPr^{Cl})(Bpin)] (**7d**) (56%) were successfully synthesised using the methoxide intermediate protocol and crystal structures were obtained for **7b** and **7d** (Scheme 2). Both structures show a linear distortion with C-Au-B angles of 172.1(6)° and 166.9(7)° for **7b** and **7d**, respectively. The Au-C(carbene) distances show similar elongation (2.048(10) Å (**7b**); 2.109(16) Å (**7d**)) while the Au-B distances are all within normal range (2.085(17) Å (**7b**); 2.05(2) Å (**7d**)). Of note and quite surprisingly, all four complexes **7a-d** are bench-stable in the solid state and do not require storage under inert atmosphere.

Having these complexes on hand, we explored their reactivity. We targeted the reduction of CO_2 to CO with **7**. Surprisingly, no reaction occurred. This is somewhat unexpected and in direct contrast with the reactivity of copper congeners that have been reported efficient in this transformation.[15a]
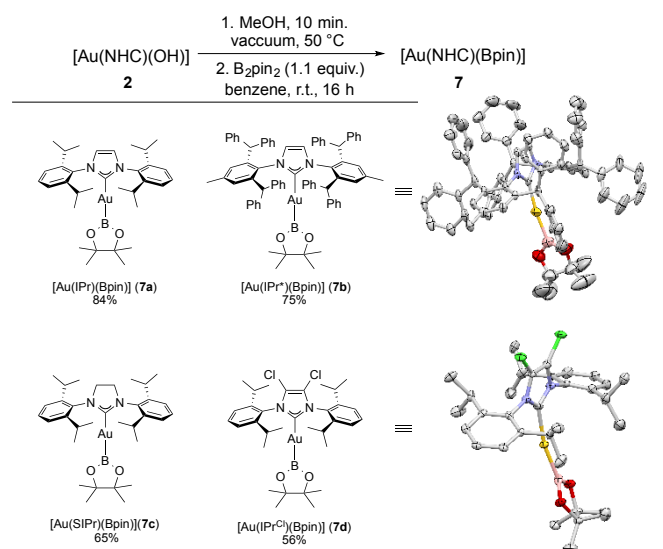
Scheme 2. Synthesized [Au(NHC)(Bpin)] complexes.

Reactions with electron-poor organic molecules such as alkenes, alkynes and aldehydes were next examined. Styrene, benzaldehyde, diphenylacetylene and phenylacetylene were separately mixed with **7a** in a NMR tube in benzene-d_6 in a 1:1 ratio. Surprisingly, no reactivity was observed, resulting in recovery of all starting materials and no decomposition of the starting gold reagents even after 24 h at r.t. or at elevated temperatures (60 °C, overnight). The contrast in reactivity is flagrant when compared with the copper analogues where alkene insertion into [Cu(IPr)(Bpin)][20] as well as the catalytic diboration of aldehydes using the same copper complex as catalyst are feasible.[13] The copper-boron bond in [Cu(IPr)(Bpin)] reacts with electron-rich organic molecules; a similar reactivity might have been expected for **7a** but is not an operating reaction avenue for gold.

The electronic structure of **7a** was investigated computationally. Complex **7a** was compared with two Au(I)-NHC complexes, namely [Au(IPr)(OH)] (**2**) and [Au(IPr)F] (**8**). The dissociation free energy of the anionic ligand X (X = Bpin$^-$, F$^-$ and OH$^-$) is calculated to be much higher for the IPr-Au-Bpin system respect to the other two Au-X bonds considered (see ESI). To this extent, we performed an energy decomposition analysis (EDA) to rationalize the difference between Au-Bpin and Au-F, Au-OH bonds and to investigate the impact of the Bpin, F and OH on the IPr-Au bond (see again ESI for details). The overall bond strength of the bonds was determined to be almost 50:50 shared between the steric and orbital terms. The calculations conducted (Table S-5 in ESI) indicated that the weaker bond strengths for Au-F (696 kJ/mol) and Au-OH (756 kJ/mol) compared to Au-Bpin (838 kJ/mol) are ascribed to both a lower ΔE_{int} (due to a lower σ contribution) and ΔE_{elstat}. Both these features are related to the key differences in the orbitals involved in the Au-X bond (see Figure S-6 in the ESI). For instance, even though the LUMO is almost identical for all three systems, this is not the case for the HOMO. The Au contribution

is clearly higher in the BPin system (47.6% vs 31.5% and 19.4% in the F and OH systems, respectively). It should be noted that Fernández and co-workers reported the Au contribution in this exact complex to be 42.6%;[9] though, their calculations were based on a "virtual" complex (virtual = calculated and not yet synthesized at the time). In their report, they briefly elude to the large difference in contribution compared to the copper analog (31.5% Cu contribution in this case) and rightly conclude that the Bpin moiety in the gold analogs should exhibit much lower nucleophilicity. This quite nicely correlates to the observations made in this work.

The orbitals involved are the Au d_{x2-y2}, mainly, with a small contribution from the Au d_{z2} for the BPin system, and the HOMO results in a strong bonding interaction from the Au center to the O-B-O moiety, with the B atom mainly participating with the s and p_y orbitals. Differently, in the F and OH complexes the HOMO corresponds to an antibonding interaction between the Au d_{yz} and the p_z of F and OH. Moreover, the fact that for Au-Bpin system the orbitals of three atoms are involved in the bond leads to a higher delocalization of the charge resulting in a more polarized Au-X bond (see also charge analysis in the ESI).

The new information about **7a** clearly indicates that this complex, although a congener of [Cu(IPr)(Bpin)] should exhibit drastically different reactivity (Scheme 3). As a reminder, the [Cu(IPr)(Bpin)] complex acts as a nucleophile in reactions with electron-deficient systems. Lin and Marder have studied the borylation of α,β-unsaturated carbonyl compounds with a phosphine copper(I) boryl complex and the proposed mechanism occurs through a similar pathway.[21a] Their study clearly showed that the reaction initiated *via* the insertion of the C=C bond into the Cu-B bond to yield a β-boryl alkyl C-bound Cu(I) enolate intermediate. The Au-B bond in **7a** on the other hand, as revealed by computational studies, is very strong with a significant Au contribution to the bond and therefore the Au-B bond is less likely to initiate reactivity in a manner similar to copper. In fact, quite the opposite would be expected (**II**, Scheme 3). The lone pair of an oxygen-containing substrate would react with the empty orbital on boron, weakening the Au-B bond, resulting in the Au being bound to the β carbon and the boryl moiety bound to the oxygen. The computational studies clearly explain the lack of reactivity in our initial foray into the reaction chemistry of **7a**. It should be noted that Lin and Marder have shown similar reactivity with platinum complexes when investigating the mechanism of the diboration of acyclic α,β-unsaturated carbonyl compounds.[21b]
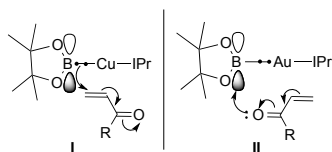
Scheme 3. Reactivity of Cu- vs Au-Bpin complexes.

The reactivity of **7a** with H₂ was next examined. Interestingly, when **7a** was exposed to one atmosphere of H₂, no reaction was observed. Keeping the bond polarity in mind, we reasoned that addition of triethylamine in the presence of H₂ might form a

Frustrated Lone Pair (FLP) system and enable H₂ activation.[22] Indeed, upon addition of triethylamine (3 equiv.), H₂ splitting occurred as evidenced by the formation of [Au(IPr)H] (**9**) (isolated in 97%) and HBpin (observed by ¹H NMR spectroscopy). In the absence of H₂, no interaction between **7a** and NEt₃ was observed as one would expect from a FLP system. The reactivity with various acids was investigated next (Scheme 4). We recently reported the synthesis of Au(I)-NHC complexes from different mineral acids such as HNO₃, H₂SO₄ and H₃PO₄.[23] When **7a** was reacted with 1.1 equiv. of HNO₃, the deprotonation of HNO₃ resulted in the formation of **10** and HBpin. Complex **10** was isolated in 98% yield after 5 min. This can be compared with the reactivity of **2** that requires one hour to reach completion. The exposure of HCl to **7a** afforded [Au(IPr)Cl] **1** in 95% isolated yield. The reactivity with Bronsted acids was further investigated, and **7a** was reacted with 1.1 equiv. of acetic acid at room temperature. The reaction proceeds much slower than with nitric acid, affording [Au(IPr)(OCOCH₃)] (**11**) in 90% yield.
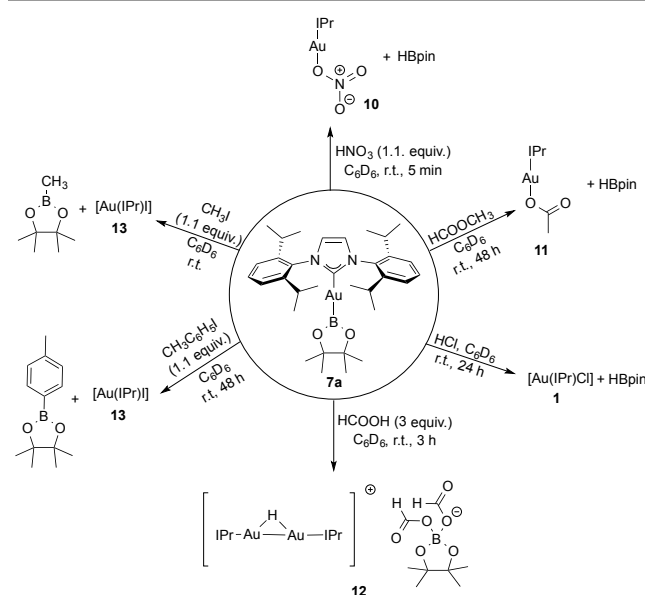
Scheme 4. Reactivity of **7a**.

Gold carboxylates have been proposed as intermediates in carboxylation/decarboxylation reactions.[24] Although reactions with these Bronsted acids have yielded the expected products, a typical acid-base reaction may not be in play here. Based on DFT calculations of the Au-Bpin bond polarisation, we cannot rule out a prior activation of the boryl moiety as in Scheme 3. This may have manifested most evidently in the reaction of **7a** with acetic acid (reaction complete after 48 h) and HCl (reaction complete after 24 h), since other Au(I)-NHC complexes such as **2**[25] and **5**[26] react almost instantaneously with acetic acid and HCl to yield the same desired complexes **11** and **1**, respectively. Complex **7a** was reacted with formic acid at room temperature and, after 3 h, a new species formed as detected by ¹H NMR spectroscopy. This species was spectroscopically characterised and a crystal structure was obtained. The X-ray diffraction data revealed the newly synthesised species not as the expected

[Au(IPr)(OCOH)], but as a cationic Au(I)-NHC dimer bearing a four-coordinated boron diformato species, **12**. This product represents a clean stepwise decomposition of formic acid by cooperative action of the gold and boron fragments in **7a**. Details (stoichiometric reactions, proposed mechanism and DFT calculations) describing the route by which this complex is formed are discussed in the ESI. The reactivity towards alkyl/aryl iodide was next investigated using methyl iodide and tolyl iodide. The Au-B bond in **7a** is more polarized than the previously reported Au-NHC complexes, therefore the reactivity towards methyl iodide was intriguing. Complex **7a** and methyl iodide were mixed in a 1:1 ratio in benzene-d_6 at room temperature. The reaction proceeds over 16 hours and results in the full conversion of **7a** to [Au(IPr)I)] (**13**). Both products were isolated and characterised by NMR spectroscopy. Next, **7a** was reacted with tolyl iodide to ascertain any difference between alkyl and aryl iodo substrates. Full conversion was reached after 48 hours and complex **13** and p-tolylpinacolboronate were isolated and characterized by ^{1}H and ^{13}C{^{1}H} NMR spectroscopies. As aryl boronates are widely used in organic chemistry, i.e. in the Suzuki-Miyaura reaction, their preparation from aryl halides is an appealing approach and has been previously investigated using a copper-phosphine catalyst.[27] Current investigations on the use of these gold-boryl complexes as catalysts to access aryl boronates from aryl halides are ongoing.

In summary, new [Au(NHC)(BPin)] complexes have been synthesised and fully characterized. Their reactivity was studied using experimental and computational approaches that shed light on the unique character of the Au-B bond. These complexes display high stability and can readily activate dihydrogen. Borylation of iodide substrates was also established in stoichiometric manner with an effective and well-defined gold-boryl complex but this reaction proves sluggish under the present conditions. This also attests to the quite unique and highly stable nature of the Au-B bond.

Conflicts of interest

There are no conflicts to declare.

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