DOI: 10.1002/anie.201206927

Frustrated Lewis Pair Induced Boroauration of Terminal Alkynes**

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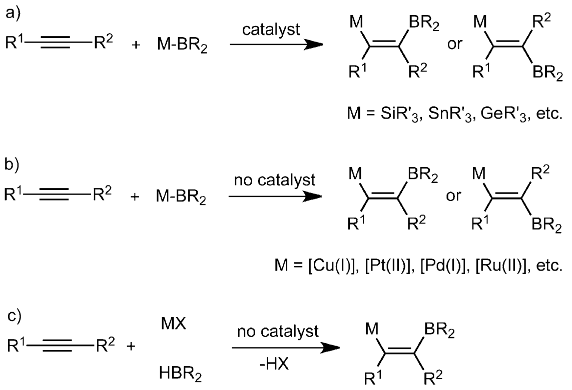
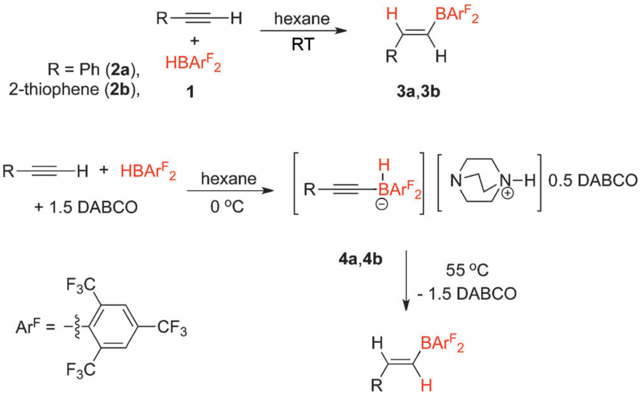
Organoborane compounds are versatile reagents for organic synthesis. Various methods have been developed to incorporate boryl groups into organic frameworks. Among others, borometallation of alkynes, such as silaboration and stannaboration, has received substantial attention in recent years.[1] These reactions can introduce multiple functionalities in one step, providing an efficient way for the stereoselective synthesis of highly substituted alkenes. Whereas silaboration and stannaboration of alkynes often require transition-metal complexes as catalysts (Scheme 1 a),[1] the alkynes were reported to be able to directly insert into the M−B bond of boryl transition-metal complexes, resulting in the formation of (2-borylalkenyl)metal complexes (Scheme 1 b).[2–6] One drawback of the abovementioned approaches is the requirement of boryl metal species, some of which are not easily accessible. Thus it will be highly interesting to develop a method through which the borometalation reaction can be directly achieved with hydroborane and metal complexes (Scheme 1 c).



Scheme 1. Different approaches to the borometalation of alkynes.

Recently, the chemistry of frustrated Lewis pairs (FLP) has provided a new avenue for small-molecule activation.[7,8] Particularly, Stephan[9] and Berke[10] et al. discovered that FLPs can activate terminal alkynes, which can lead to the formation of alkynylborates. Inspired by their work, we became interested in applying such a concept to the borometallation of alkynes. Herein, we describe the reaction of terminal alkynes with a FLP comprised of $HBAr^F_2$ (**1**, Ar^F = 2,4,6-tris(trifluoromethyl)phenyl)) and 1,4-diazabicyclo[2.2.2]octane (DABCO)[11] and its application in catalyst-free boroauration of terminal alkynes.

When **1** was mixed with phenylacetylene in hexane solution at room temperature, the hydroboration reaction took place in a very slow manner, and only 80% conversion was obtained after 5 h, which is possibly due to the large steric bulk around the boron center in **1**. When $DBAr^F_2$ was applied to phenylacetylene, the formation of E-PhC(D)=C(H)BAr^F_2 was observed, confirming that the resulting alkenylborane was obtained through 1,2-hydroboration (Scheme 2).



Scheme 2. Synthesis and reactivity of complexes **3** and **4**.

The slowness of this hydroboration reaction allowed us to investigate the FLP reactivity of **1** and DABCO against terminal alkynes. When **1** was added to the mixture of the alkyne **2a** or **2b** and DABCO in the hexane solution at 0 °C, a white precipitate was immediately observed. After 3 h, the precipitate was isolated in 75% (from **2a**) or 72% (from **2b**) yield, and subsequently identified as ammonium alkynylhydridoborate salts **4a** and **4b** resulting from the deprotonation of the corresponding alkynes (Scheme 2).[9,10] In the ^{11}B NMR spectra, a doublet (−21.6 ppm with 85 Hz for **4a** and −22.1 ppm with 82 Hz for **4b**) was observed, indicating the existence of the hydridoborate moiety. Both elemental analysis and ^{1}H NMR spectrum suggest that each ammonium alkynylhydridoborate salt molecule contains one half of a neutral DABCO molecule. The salt **4b** was further characterized by X-ray diffraction. In each unit cell, there are two ammonium alkynylhydridoborate salt molecules and

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[**] Financial support from Shanghai Science and Technology Committee (10ZR1404200), Shanghai Leading Academic Discipline Project (B108), the National Nature Science Foundation of China (21102018, 20973041) and National Basic Research Program of China (2011CB808505) is gratefully acknowledged.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201206927.

one neutral DABCO molecule, which was linked to an ammonium cation through N···H···N hydrogen bonds.

Heating the solution of **4a** or **4b** in C_6D_6 to 55 °C prompted the conversion of these ammonium alkynylhydridoborate salts into alkenylborane **3a** or **3b** and DABCO (Scheme 2). The thermolysis of the ammonium alkynyldeuterioborate salt, prepared from $DBAr^F_2$/DABCO and phenylacetylene, led to the formation of *E*-Ph(H)C=C(D)BAr^F_2, which suggests that the thermolysis process occurs through 1,2-hydride migration and proton transfer, thus resulting in a formal 1,1-hydroboration.[12] While Wrackmeyer et al. have shown that 1,1-hydroboration can take place for activated alkynes (EC≡CR′, E = SiR_3, SnR_3),[13,14] 1,1-hydroboration for terminal alkynes is extremely rare. The only other case we noticed is reported by Paetzold et al,[15] who claimed the observation of 1,1-hydroboration of terminal alkynes with 6-aza-*nido*-decarboranes.[16]

Kinetic studies of the thermolysis of **4a** in C_6D_6 by monitoring ^{19}F NMR revealed that this reaction is a first-order reaction. The activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are estimated to be 25(1) kcal mol^{-1} and 14(1) cal K^{-1} mol^{-1}. The positive value of $\Delta S^{\ddagger}$ is consistent with a dissociation process. To further characterize the reaction mechanism of this process, a kinetic isotope effect (KIE) was obtained by measuring the rate constants of the thermolysis of **4a** and [PhC≡CB(D)Ar^F_2][HDABCO][0.5 DABCO]. The KIE value at 55 °C is 1.49(7), which falls within the range for a secondary kinetic isotope effect,[17] and rules out the hydride migration as the rate limiting step.

The reaction mechanism was further investigated by DFT (M06-2X) calculations (Figure 1).[18,19] The calculation of the reaction between phenylacetylene and **1**/DABCO indicates that **1** first coordinates to phenylacetylene to form the intermediate **IM1** through weak unsymmetrical π interaction, which is then depronated by DABCO to yield **4a** via transition state **TS2**.[10] In the simulated structure of **IM1**, the distances between the boron atom and two alkynyl carbons are 1.80 Å (for terminal carbon) and 2.41 Å (for internal carbon). The corresponding bond orders are 0.55 and 0.16 as suggested by natural bond orbital analysis.[20] The bond order of C≡C bond decreases to 2.34. We also calculated the free-energy barrier for the direct 1,2-hydroboration reaction between **1** and phenylacetylene ($\Delta G^{\ddagger} = 18.2$ kcal mol^{-1}), which is 2.5 kcal mol^{-1} higher than that of the FLP-induced deprotonation process, which is consistent with the experimental observation that **4a** is the major product in the presence of DABCO. The transformation of **4a** to **3a** is via transition state **TS3**, and the calculated activation enthalpy ($\Delta H^{\ddagger} = 25.2$ kcal mol^{-1}) is very close to the experimental value. The large deviation of the calculated activation entropy ($\Delta S^{\ddagger} = -2.3$ cal K^{-1} mol^{-1}) from the experimental value is possibly due to the fact that the half neutral DABCO molecule in **4a** was omitted in the calculation process to simplify the calculation. Examining the transition state **TS3** reveals that the proton transfer and hydride migration take place in a concerted manner. The computed KIE value of 1.60 is in good agreement with the measured KIE value.

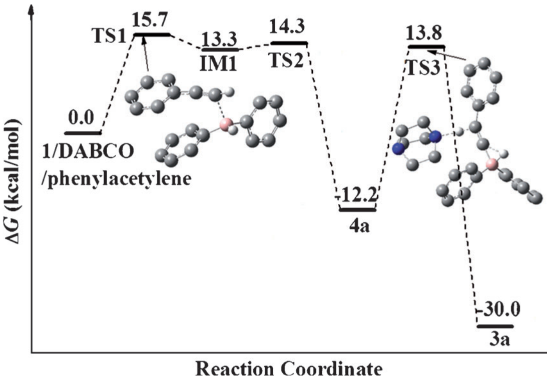
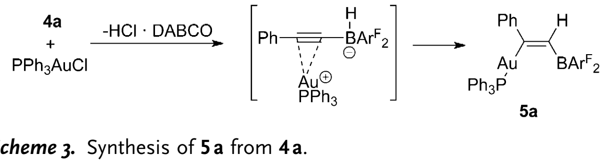


Figure 1. The Gibbs free energy profile at 328 K for the reaction between **1**/DABCO and phenylacetylene. The CF_3 groups and the hydrogen atoms except B–H and C≡C–H are omitted for clarity.

Noticing that Au^I species are often considered to be isolobal to a proton,[21] we wondered whether Au^I could be applied as an electrophile to attack the triple bond of **4a** or **4b**, which would lead to the formation of (2-borylalkenyl)gold complexes.[22,23] When one equivalent of PPh_3AuCl was added to **4a** in CD_2Cl_2 solution at room temperature, the reaction mixture turned to bright yellow instantly and both starting materials were consumed within 30 min, affording the (*Z*)-(2-borylalkenyl)gold complex **5a** as the only isomer in nearly quantitative yield, as indicated by NMR spectroscopy. Complex **5a** was fully characterized by NMR spectroscopy and elemental analysis. In the ^{1}H NMR spectrum of **5a**, the signals for Ar^F appeared as three broad singlets with an integral ratio of 1:2:1, indicating hindered rotation of Ar^F substituents at room temperature. The ^{11}B NMR resonance appeared at 60.4 ppm for **5a**, which is comparable to the alkenylborane species **3a** ($\delta = 65.1$ ppm), implying no significant Au–B interaction.[24] This was further confirmed by the X-ray diffraction analysis of **5a** (Figure 2). In the solid structure of **5a**, the distance between Au and B atoms is 3.55 Å, which is close to the sum of van der Waals radii of gold (1.66 Å) and boron atoms (1.92 Å). Owing to the considerable steric congestion, both C2-C1-Au (126.9(4)°) and C1-C2-B (127.3(5)°) angles are deviated from the ideal 120°. Our preliminary theoretical studies suggested that upon mixing **4a** with PPh_3AuCl, an intermediate gold–alkyne π adduct is formed,[25] which then undergoes concerted 1,2-hydride migration and Au–C σ bond formation to yield **5a** (Scheme 3). This concerted process could be responsible for the observation that only the *cis* addition product exists in the reaction mixture despite considerable steric repulsion between the gold and boryl moieties. The free-energy barrier of this auration process is 18.0 kcal mol^{-1} at 298 K, which is 7.9 kcal mol^{-1} lower than the thermolysis of **4a**, in agreement with our observation that the former process is much faster.



Scheme 3. Synthesis of **5a** from **4a**.

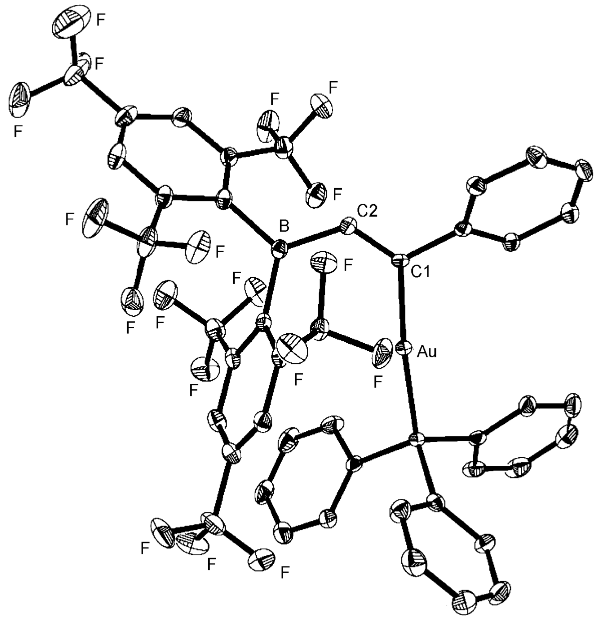
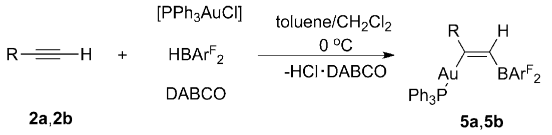


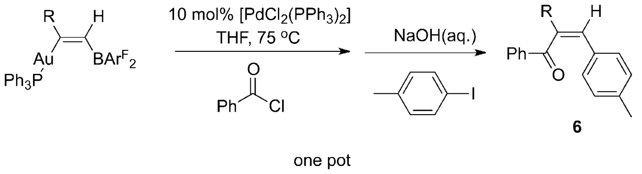
Figure 2. ORTEP of the molecular structure of **5a** (ellipsoids set at the 30% probability). Hydrogen atoms are omitted for clarity.

The swiftness of this reaction prompted us to design a tandem reaction through which boroauration of terminal alkynes can be achieved directly with a hydroborane and PPh_3AuCl in the presence of DABCO. Addition of **1** into the mixture of phenylacetylene, DABCO, and PPh_3AuCl in toluene/CH_2Cl_2 solution at 0 °C led to the formation of **5a**, which can be isolated with 74 % yield (Scheme 4). Complex **5b** can be prepared in an analogous fashion in 70 % yield. To the best of our knowledge, this is the first example of a borometalation of alkynes without employing catalysts and boryl metal complexes.



Scheme 4. Synthesis of complexes **5a** and **5b** directly from alkynes.

As both gold and boryl moieties can be utilized in palladium-catalyzed C−C formation,[26,27] the synthetic application of (*Z*)-(2-borylalkenyl)gold complexes was demonstrated by one-pot synthesis of a multisubstituted alkene through one-pot palladium-catalyzed coupling reactions.[28] owing to the different reactivity of gold and boryl moieties in coupling reactions, variant functional groups can be added into the alkene framework with high regio- and stereoselectivity. Treatment of **5a** with benzoyl chloride and 10 mol% $[PdCl_2(PPh_3)_2]$ in THF at 75 °C and subsequent addition of 4-iodotoluene with NaOH(aq) resulted in the formation of a benzoyl-substituted stilbene derivative **6**, which can be isolated with 41 % yield (Scheme 5).



Scheme 5. One-pot synthesis of the trisubstituted alkene **6**.

In conclusion, we have described the facile activation of terminal alkynes with **1**/DABCO pair as well as the subsequent auration reaction. As these two reactions can occur in a tandem fashion, (*Z*)-(2-borylalkenyl)gold complexes can be straightforwardly prepared from alkynes, hydroborane, PPh_3AuCl, and organic base, thus circumventing the necessity of transition-metal catalysts or boryl metal complexes. Our preliminary tests show that these (*Z*)-(2-borylalkenyl)gold complexes could be useful building blocks for the stereoselective synthesis of trisubstituted alkenes. Efforts to extend the scope of metal complexes applied in this new type of borylation reaction are currently underway.

Received: August 27, 2012

Keywords: alkynes · boron · gold · metalation

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