

# Coinage metal complexes with N-heterocyclic carbene ligands as selective catalysts in diboration reaction

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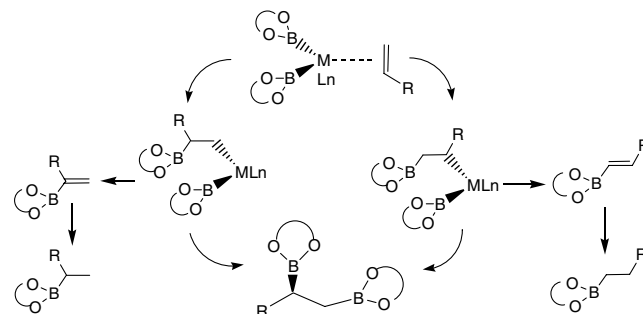
**Abstract**—We describe the improved catalytic reactivity of terminal alkenes with 1,2-diboranes in the presence of Au(I) and Ag(I) complexes when N-heterocyclic carbene ligands are used. The new catalytic systems are able to diminish the undesired  $\beta$ -H-elimination of the alkylboryl–metal intermediates, which leads to the formation of hydroborated byproducts. The electronic properties and the molecular structure of the precursors of the catalysts could explain the modest asymmetric induction provided.

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## 1. Introduction

A direct route to 1,2-bifunctional organic compounds can be carried out by diboration of alkenes through 1,2-bis(boronate)esters.<sup>1</sup> Some of the key advantages of the metal catalyzed diboration as opposed to noncatalyzed diboration include the ability to use less reactive but more stable diboranes, such as tetraalkoxydiboron compounds.<sup>2</sup> Thus low valent transition metal catalysts are required to cleave the B–B bond from the diboron reagent, generally via oxidative addition, to form the intermediate metal bis(boryl)complex.<sup>3</sup> Subsequent nonsymmetric alkene coordination and insertion into the M–B bond, eventually provides regioisomeric intermediates that can follow B–C reductive elimination generating the desired 1,2-bis(boronate)ester product (Scheme 1).

Depending on the catalyst precursor employed, various amounts of undesired vinylboronate esters can also be obtained by competitive  $\beta$ -hydride elimination processes (Scheme 1). In particular, when rhodium(I)–phosphine is involved, as the metal catalytic system, significant amounts of internal and terminal hydroborated products can be detected as by-products because of in situ formation of hydride–rhodium–boryl complexes. However, recent



Scheme 1.

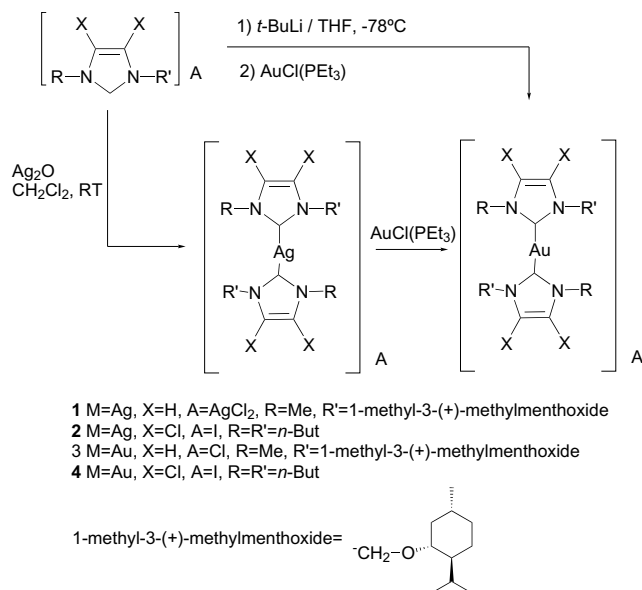
improvements in ligand design, have allowed this problem to be circumvented.<sup>4</sup> Clean alkene diboration can be achieved only if  $\beta$ -hydride elimination is inhibited. Progress was made when Baker, Marder and Wescott<sup>5</sup> decided to use the gold(I) catalytic system [Au(PEt<sub>3</sub>)Cl] + 1,2-bis(dicyclohexylphosphino)ethane on the basis of unknown mononuclear neutral gold-hydride complexes.<sup>6</sup> The desired 1,2-bis(boronate)ester was mainly attained from styrene and bis(catecholato)diboron, as a model reaction, although catalyst activity and stability were lower than desired. Alternatively, base-free Pt systems also contributed to clean diboration, but they are not appropriate for modification with chiral ligands.<sup>7</sup>

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## 2. Results and discussion

Inspired by these preliminary results and aimed to achieve clean alkene diboration, we focussed our efforts to find new catalytic systems that not only performed as clean diborating catalysts but also those that were able to induce asymmetry in the bifunctional products. Asymmetric diboration has only been achieved in a few recent examples in the literature through chiral Rh(I) catalytic systems,<sup>8</sup> despite the inherent competitive hydroborated by-product formation. In view of the promising catalytic activity of gold(I) complexes in the diboration reaction and because of the lack of any attempted synthesis of 1,2-bis(boronate)esters with catalytic chiral systems based on gold(I) complexes, we now report some results of N-heterocyclic carbene–Au(I)–X complexes, with an extension to the analogous silver complexes. NHCs are considered as better electron donors than phosphines, and hence provide enough electron richness to the metal centre to guarantee B–B cleavage of the diborane. Additionally, N-heterocyclic carbenes (NHC) have emerged as a promising family of ligands that can be used in the design of efficient homogeneous catalysts,<sup>9</sup> because of the great stability acquired by the metal complexes. Our first attempt to perform the catalytic diboration of alkenes with metal–N-heterocyclic carbene complexes was recently reported with the thermally and air-stable compound **1** (Scheme 2) which cleanly catalyzed the diboration of terminal alkenes with bis(catecholato)diboron at room temperature.<sup>10</sup> Despite its high activity, no asymmetric induction was observed, presumably because the chiral centre was far from the metal. Based on this previous result, we are now reporting the preparation of a series of new M–NHC (M = Ag, Au) complexes whose catalytic activities were explored. Scheme 2 summarizes the synthetic procedure to the new NHC complexes of Au but also of the analogous of Ag.

The silver complexes were obtained by the direct reaction of Ag<sub>2</sub>O with 1-methyl-3-(+)-methylmenthoxy imidazolium chloride or with 1,3-di-*n*-butyl-4,5-dichloroimidazolium iodide, to provide complexes **1** and **2**, respectively. The Au(I) complexes were obtained in high yield (ca. 90%) by in situ generation of the free carbenes from the corresponding imidazolium salts in THF at –78 °C with *t*-BuLi, and then addition of Au(PEt<sub>3</sub>)Cl. Alternatively, **3** and **4** were obtained from transmetalation of the corresponding carbenes from the silver complexes **1** and **2** to Au(PEt<sub>3</sub>)Cl, although yields were lower (ca. 50%) than those obtained by direct coordination of the free carbene to Au. The complexes were characterized by means of

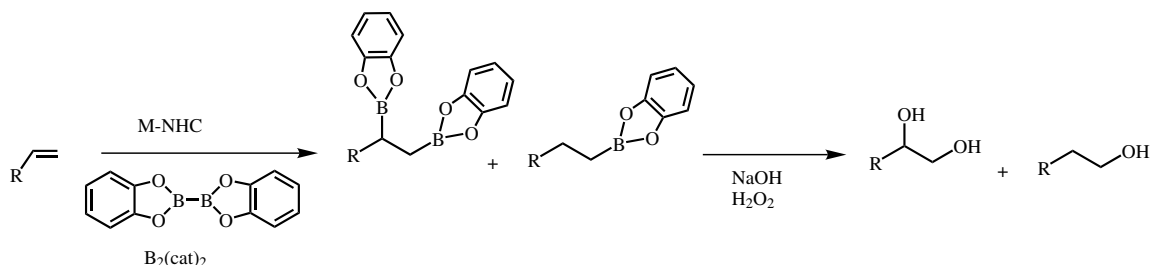


Scheme 2.

NMR, mass spectroscopy and elemental analysis (except for **3** that was obtained as an oily product and we failed to get accurate elemental analysis). The molecular structure of **1** was reported in a previous communication.<sup>10</sup> In principle, the idea of obtaining these complexes was to study the effect of introducing an N-heterocyclic carbene in the Au and Ag complexes in terms of catalytic activity compared to the related phosphine analogues.<sup>5</sup> The introduction of the chlorinated-NHC ligands would also allow us to examine the catalytic implications of the reduction of the electron donating character of the NHC ligand.

Initially, we examined the catalytic activity provided by compounds [NHC–Au(I)–NHC]X and [NHC–Ag(I)–NHC]X. The metal modification with an electron donating NHC ligand results in a clear enhancement of the catalytic performances,<sup>11</sup> thus supporting the previously reported work by Baker et al.<sup>5</sup> which suggests that arylphosphine Au complexes are not sufficiently electron rich to serve as competent alkene diboration catalysts. We were able to get 100% selectivity for the diborated product in the catalyzed diboration of styrene (Scheme 3), when using **2** and **4**, with 46% and 94% conversions, respectively (Table 1, entries 1 and 2).

The different activity of these catalysts may be due to the lability of the Ag–C<sub>carbene</sub> bond, which could favour an



Scheme 3.

**Table 1.** Catalytic diboration/oxidation reaction of alkenes with M–NHC complexes and bis(catecholato)diboron<sup>a</sup>

Entry	Catalytic system	Alkene	T (h)	Temperature (°C)	Conv. <sup>b</sup> (%)	Diol (%)
1	<b>2</b>	Styrene	60	25	46	100
2	<b>4</b>	Styrene	60	25	94	100
3	<b>1</b>	Styrene	60	25	76	100
4	<b>3</b>	Styrene	60	25	69	100
5	<b>3</b>	Styrene	20	70	86	100
6	<b>3</b>	Vinylcyclohexane	60	25	40	100
7	<b>5</b>	Styrene	60	25	40	100
8	<b>6</b>	Styrene	60	25	13	91 <sup>c,d</sup>
9	<b>6</b>	Styrene	24	70	42	100 <sup>c,e</sup>
10	<b>6</b>	Vinylcyclohexane	24	70	100	100
11	<b>6</b>	<i>p</i> -Fluorostyrene	24	70	51	100
12	<b>6</b>	<i>p</i> -Methoxystyrene	24	70	13	100
13	<b>7</b>	Styrene	60	25	10	93

<sup>a</sup> Standard conditions: alkene/diborane/M–carbene complex = 0.5/0.55/0.025. Solvent: THF.

<sup>b</sup> Determined by <sup>1</sup>H NMR before oxidation.

<sup>c</sup> Determined by GC with chiral column FS-Cyclodex B-IP, 50 m × 0.25 mm of the ketal derivatives.

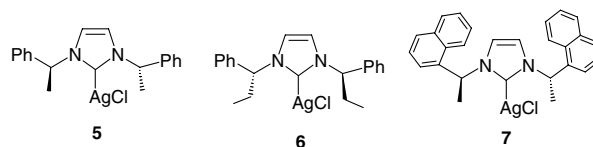
<sup>d</sup> ee = 9%.

<sup>e</sup> ee = 4%.

equilibrium between mono- and bis-carbene species, in solution.<sup>12</sup> In fact, while we have assigned a bis-NHC structure for both **1** and **2** (Scheme 2), we believe that the species present in solution have a mono-NHC structure, according to data reported in the literature for similar complexes.<sup>12b</sup> The NMR and crystallographic data do not permit unambiguous determination of electronic differences between the NHC–Ag moieties as a function of the NHC, although studies have been made in order to rationalize the nature of the species present in solution.<sup>13</sup> On the other hand Au–NHC complexes are known to have stronger Au–C<sub>carbene</sub> bonds,<sup>14</sup> thus allowing well defined molecular arrangements both in solid state and in solution. This may somehow justify the differences in the catalytic behaviour upon introduction of the chloro substituents in imidazolylidene rings of the silver and gold complexes. In the silver complex the introduction of the electron attracting atoms results in partial deactivation of the catalyst (compare entries 1 and 3) in the case of gold the effect is just the opposite (compare entries 2 and 4). We do not have a satisfactory explanation for this observation, but the structural versatility of the Ag–NHC complexes may also play a role, implying that the catalytic Ag(I) and Au(I) species have a different structural nature in solution. In any case, we would expect that diminishing the electron donating character of the ligand would imply a reduction of the catalytic performance, as in the trend that we have observed for our Ag–NHC complexes and in agreement to previously reported results.<sup>5</sup> For the chiral complexes **1** and **3**, again, total chemoselectivity for the diborated product was observed, with moderate to high conversions when the reaction was carried out at 70 °C (Table 1, compare entries 3–5). Lower conversions were obtained when the catalytic diboration was carried out with more sterically hindered substrates, such as vinylcyclohexane (Table 1, compare entries 4 and 6). However, no asymmetric induction was observed in the corresponding diols, after the oxidation procedure.

Aiming to study whether we could provide effective diboration catalysts that could also induce some asymmetry, we

decided to test a series of chiral NHC–Ag–Cl complexes (Fig. 1, complexes **5–7**) that have previously been described in the literature.<sup>15</sup>

**Figure 1.**

These compounds were tested in the catalytic diboration/oxidation of styrene (Table 1, entries 7–9 and 13) and **6** was tested in the diboration of a series of terminal olefins (entries 10–12). As shown for the catalysts described above (**1–4**) the diborated product remains the major product, although the conversion is lower, probably as a consequence of the more sterically hindered catalytic system involved. Interestingly, **6** was able to induce, modestly, some enantioselectivity, with ee values between 4% and 9%. We believe that this result may be due to the higher sterical crowding of the metal in **6** compared to the rest of the chiral catalysts. We are aware that these ee values are very low, but they must be compared to the maximum values (33%) achieved by the sophisticated *P,N*-Quinap–Rh(I) complex, so we believe chiral NHC–M(I)–X complexes may be a useful alternative for the clean asymmetric catalytic diboration of alkenes. Compound **6** was also tested in the diboration of vinylcyclohexane at 70 °C, showing quantitative conversion but negligible asymmetric induction (entry 10). The diboration of *p*-fluorostyrene and *p*-methoxystyrene (entries 11 and 12) allowed us to establish that the more electron attracting the substituents are, the higher the conversion to the diborated species.

### 3. Conclusion

We can conclude that we have described a series of NHC complexes of Au(I) and Ag(I) that have been tested in the

diboration of a series of terminal alkenes. This is the first example of Au–NHC catalytic systems applied in catalytic B addition. All catalysts showed clean conversions to the diboration products, not yielding any hydroborated products. The use of basic N-heterocyclic carbenes as ligands results in a clear enhancement of the catalytic performances. The introduction of chirality in the NHC ligands did not show any significant induction of asymmetry, except for the case of complex **6**, for which the higher sterical hindrance about the metal may justify its moderate induction.

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