

Unprecedented use of silver(I) N-heterocyclic carbene complexes for the catalytic preparation of 1,2-bis(boronate) esters

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Catalytic diboration of internal and terminal alkenes with Ag(I) N-heterocyclic carbene complexes leads to 1,2-bis(boronate) esters as single intermediates, that can be oxidised towards the corresponding diols.

Transition metal complexes play an important role in the diboration reaction, allowing the introduction of two functional groups into an organic molecule at a time.^{1,2} According to the catalytic cycle proposed,³ insertion of the metal complex into the B–B σ bond of stable alkoxy diboranes^{4,5} occurs, yielding a metal-diboryl intermediate which determines the chemo- (diboration *versus* hydroboration) and enantioselectivity when reacting with alkenes (Scheme 1). Thus, the design of proper catalysts that selectively provide 1,2-bis(boronate) esters (**1**) is one of the main challenges in this catalytic reaction.⁶

While cationic rhodium(I) complexes with chiral P,N-bidentate ligands (Quinap) allow enantioselective addition of bis(catecholadiboron) to alkenes,⁶ chemoselectivity becomes very low due to the inherent competitive β -H-elimination that provides alkyl-, **2a**-, and alkenylboronate ester, **3**. Alternatively, gold(I)-diphosphine catalytic systems improve chemoselectivity towards the desired 1,2-bis(boronate) ester **1**, although catalyst activity and stability remain lower than desired.³ Finally, base-free Pt systems also

contribute to clean diboration, but the scope of the reaction is not general to internal and terminal alkenes and they are not appropriate for modification with chiral ligands.^{7,8}

With the aim of avoiding competitive β -hydride elimination we thought that cationic silver(I) complexes with N-heterocyclic carbenes could be good candidates. These complexes combine enough electron richness to guarantee B–B cleavage of the diborane, with low energy *d*-orbitals that minimize π -backbonding and thus β -elimination.

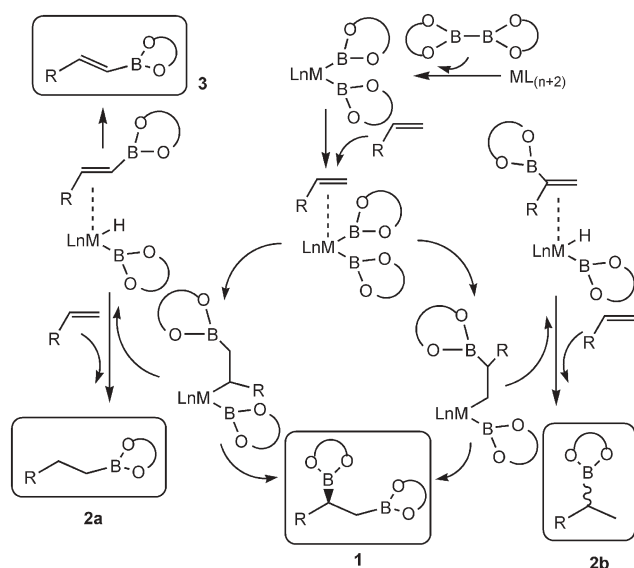
N-heterocyclic carbenes (NHC) have emerged as a promising family of ligands that can be used in the design of efficient homogeneous catalysts.⁹ The structural diversity of silver(I) N-heterocyclic carbenes has been studied in a number of papers,^{10–12} and their application as carbene transferring agents has widened their use as an easy access to various important metal NHC-complexes.^{11,13,14} However, despite the number of silver NHC complexes reported to date we have no knowledge of these being applied in catalytic processes.

Based on our previous experience, we now report the synthesis and catalytic properties of a new NHC-complex of Ag(I). With the aim of obtaining a sterically hindered complex that could help us to provide high stereoselectivity in the diboration reaction, we decided to use 1-methyl-3-(+)-methylmenthoxide imidazolium chloride as the precursor of the N-heterocyclic carbene.[†]

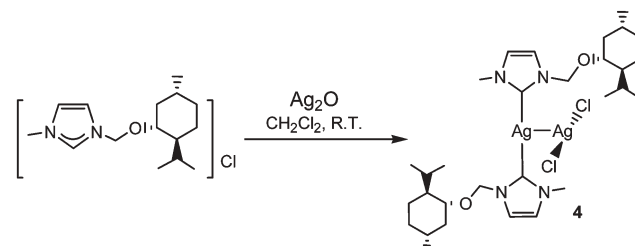
1-Methyl-3-(+)-methylmenthoxide imidazolium chloride (mentimidH) was obtained by direct reaction of *N*-methylimidazole and (+)-chloromethyl menthyl ether. The reaction is performed at room temperature in the absence of solvent, yielding a white solid in high yield (*ca.* 92%). The resulting imidazolium salt was characterized by ¹H NMR and ¹³C NMR spectroscopy.

The addition of the chiral imidazolium chloride to a suspension of an excess of Ag₂O in CH₂Cl₂ afforded the isolation of [(mentimid)₂Ag]AgCl₂, **4**, after workup (Scheme 2).

Compound **4** was characterized by NMR and mass spectroscopy.[‡] The signals of the protons of the imidazolylidene ring



Scheme 1



Scheme 2

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appear at 7.2 and 7.0 ppm. The ^{13}C NMR spectrum reveals that coordination of the NHC has occurred, as shown by the signal at 180.8 ppm, typical of a metallated Ag–NHC bond.^{11,12}

Crystals of **4** suitable for X-ray diffraction were obtained from concentrated CH_2Cl_2 /hexane solutions, and the results confirmed the structure proposed. Fig. 1 shows the ORTEP diagram of **4** and the more representative bond distances and angles. The molecule crystallizes in the non-centrosymmetric space group $P1$. The compound consists of two linear $[(\text{mentimid})_2\text{Ag}]^+$ intercalating a $[\text{Ag}_2\text{Cl}_4]^{2-}$ anion, thus providing a weak Ag(cation)⋯Ag(anion) attraction. These two ions associate through a close contact Ag–Ag interaction of 2.9 Å, similar to that shown for other Ag–NHC structures.^{11,13} The Ag–C distance is 2.1 Å.

Bis(catecholato)diboron was added to internal and terminal alkenes in presence of the precursor of catalyst **4** (5 mol%), under optimised reaction conditions (room temperature in THF). The resulting diborane compound was oxidised to the corresponding diol in presence of $\text{NaOH}/\text{H}_2\text{O}_2$. ^1H NMR and GC of the ketal derivative allowed us to determine the conversion and selectivity of the catalytic reaction. Among the terminal alkenes, we observed that the diboration/oxidation of styrene with **4** provided the single product 1-phenyl-1,2-ethanediol with 76% conversion (Table 1, entry 1). Isolated compound **4** showed a much higher catalytic activity than when prepared *in situ* from Ag_2O and the imidazolium chloride, that only showed conversions of about 5%. When the reaction was carried out at 70 °C we observed an unusually slow transformation towards the desired product, although β -H-elimination was not competitive even under these reaction conditions (Table 1, entry 2). The electron-accepting substituted vinylarenes proved to be less reactive than styrene (Table 1, entries 3–5). On the other hand, the more electron-rich vinyl-cyclohexane was by far the most active substrate in terms of conversion into the corresponding diol (Table 1, entry 6). A similar trend has been described in the diboration of *para*-substituted terminal phenylacetylenes with Pt(0) catalytic complexes where electron withdrawing substituents diminish the reaction rates.¹⁵ Remarkably, the hindered internal alkene indene was able to be cleanly transformed to the desired product, although with a low conversion (Table 1, entry 7).

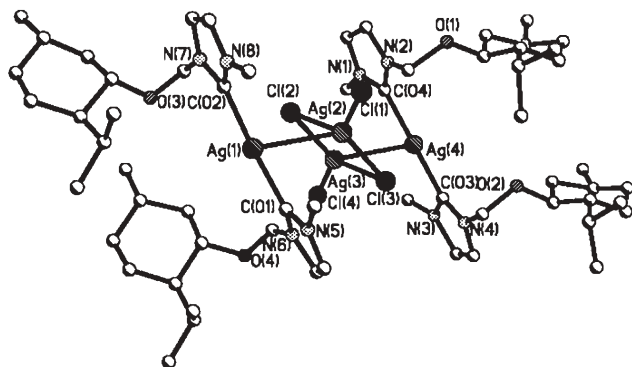


Fig. 1 X-Ray crystal structure of $[(\text{mentimid})_2\text{Ag}]\text{AgCl}_2$. Selected bond distances (Å) and angles (°): Ag(1)–Ag(2) 2.952(2), Ag(3)–Ag(4) 2.942(2), Ag(1)–C(1) 2.104(18), Ag(1)–C(2) 2.09(2), C(2)–Ag(1)–C(1) 168.7(7), C(4)–Ag(4)–C(3) 175.6(10), Cl(2)–Ag(2)–Cl(3) 95.12(19), Cl(2)–Ag(3)–Cl(3) 94.74(19).

Table 1 $[(\text{mentimid})_2\text{Ag}]\text{AgCl}_2$ catalysed diboration/oxidation of alkenes with bis(catecholato)diboron^a

Entry	Substrate	Product	Conv. (%) ^b	Diol (%) ^c
1			76	100
2 ^d	"	"	32	100
3			12	100
4			14	100
5			10	100
6			90	100
7			20	100

^a Standard conditions: alkene/diborane/Ag complex **4** = 0.5/0.55/0.025. Solvent: THF. *T*: 25 °C, 60 h. ^b Determined by ^1H NMR before oxidation. ^c Determined by GC with chiral column FS-Cyclodex B-IP, 50 m × 0.25 mm of the ketal derivatives. ^d Reflux at 70 °C, 20 h.

Despite the use of our chiral imidazolydene ligand we did not observe any asymmetric induction on the reaction products, presumably because the chiral center lies far from the metal. In addition, the lability of the Ag–C_{carbene} bond could favour some equilibrium between $[(\text{mentimid})_2\text{Ag}]\text{AgCl}_2$ and $[(\text{mentimid})\text{AgCl}]$,¹⁰ thus making it difficult to establish which is the real catalytic species. Alternatively, the use of chiral diboranes¹⁶ such as bis(diethyl-) and bis(diisopropyl-D-tartrateglycolato)-diboron and bis(+)-pinanediolato)diboron resulted in a total inhibited diboration reaction, making bis(catecholato)diboron the specific diborating reagent for this reaction with **4**.

The results of this study indicate that the new thermally and air-stable compound $[(\text{mentimid})_2\text{Ag}]\text{AgCl}_2$ cleanly catalyses the diboration of alkenes with bis(catecholato)diboron. It is noteworthy that we performed the same reaction with analogous Ag(I) complexes modified with phosphines (and diphosphines),¹⁷ but they did not allow any conversion of the alkenes towards the desired diborated products, under the same reaction conditions. Even AgNO_3 was tested in this reaction to study the possible participation of the ion Ag^+ as the catalytic species, but no reactivity was monitored.

In conclusion, this is the first time that catalytic diboration has been carried out with Ag(I) complexes. Furthermore, to our

knowledge, this is also the first example of an NHC-complex of Ag(I) being used in a catalytic process.

Additional improvements in the design of an asymmetrically inductive Ag–NHC catalytic system are in progress and may bring the reaction to the point where it becomes competitive with other methods for this chemical synthesis.†

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Notes and references

† Synthesis of 1-methyl-3-(+)-methylmenthoxide imidazolium chloride: (+)-chloromethyl menthyl ether (1.1 mL, 5 mmol) was added to *N*-methylimidazole (0.4 mL, 5 mmol) at room temperature with the ready precipitation of a white solid. The solid was purified by precipitation with CH₂Cl₂/ether. Yield: 1.315 g (92%). ¹H NMR (CDCl₃, 500 MHz) (menthyl signals omitted): 11.07 (s, 1H, NCHN), 7.43 (s, 1H, imidazole-H), 7.41 (s, 1H, imidazole-H), 5.89 (d, 1H, -CH_aH_b-O), 5.66 (d, 1H, -CH_aH_b-O), 4.12 (s, 3H, CH₃-imidazole). ¹³C NMR (DMSO-*d*₆) (menthyl and CH₃-imidazole signals omitted): 138.00 (s, NCHN), 124.66 (s, imidazole), 122.93 (s, imidazole), 78.24 (s, -CH₂-O). $\alpha = +0.5538^\circ$.

‡ Synthesis of [(mentimid)₂Ag]AgCl₂, **4**. Silver oxide (121 mg, 0.5 mmol) was added to a solution of 1-methyl-3-(+)-methylmenthoxide imidazolium chloride (200 mg, 0.7 mmol) in 10 mL of dichloromethane. The mixture was stirred at room temperature for 4 h and then filtered through Celite. The solvent was eliminated under vacuum and the resulting solid was the pure compound **2-Ag**. Yield: 200 mg (84%). ¹H NMR (CDCl₃, 300 MHz) (menthyl signals omitted): 7.18 (s, 1H, imidazole-H), 7.02 (s, 1H, imidazole-H), 5.52 (d, 1H, -CH_aH_b-O), 5.41 (d, 1H, -CH_aH_b-O), 3.85 (s, 3H, CH₃-imidazole). ¹³C NMR (CDCl₃, 300 MHz) (menthyl and CH₃-imidazole signals omitted): 180.85 (s, C-Ag), 123.20 (s, imidazole), 121.18 (s, imidazole), 78.61 (s, -CH₂-O). $\alpha = +0.3022^\circ$. Electrospray MS. Cone 30 V. *m/z* (fragment): 609 [AgL₂]⁺.

§ Crystal data for **4**: *M* = 1574.79, triclinic, space group *P*1, *a* = 9.3318(19), *b* = 11.080(2), *c* = 18.816(4) Å, $\alpha = 105.54(3)$, $\beta = 97.78(3)$, $\gamma = 94.74(3)^\circ$, *V* = 1842.6(6) Å³, *Z* = 1, *D*_c = 1.419 g cm⁻³, Mo-K α radiation ($\lambda = 0.71073$ Å), 15440 reflections collected, 12817 unique, observed reflections (*I* > 2.00 σ (*I*)), *R* = 0.0601, *R*_w = 0.1559. CCDC 264639. See <http://www.rsc.org/suppdata/cc/b5/b503239c/> for crystallographic data in CIF or other electronic format.

¶ Typical catalytic dimerization of styrene: Bis(catecholato)diboron (0.55 mmol) was added to a solution of catalyst (5 mol%, 0.025 mmol)

in THF (2 mL) under argon. The solution was stirred for 5 minutes and styrene (0.5 mmol) was then added. The mixture was stirred at ambient temperature for 60 hours, and the conversion was determined by ¹H NMR. **CAUTION:** Workup must be carried out carefully owing to the risk of explosion when using peroxides with THF. Afterwards, NaOH (3 M, 800 μ L) and H₂O₂ (800 μ L) were added and the mixture was stirred for 3 hours. After this time, 1 mL of saturated Na₂S₂O₃ was added, followed by 10 mL of NaOH (1 M). The reaction mixture was extracted into AcOEt (3 \times 25 mL) and washed with brine, dried over MgSO₄, and the products were characterized by chromatography and ¹H NMR.

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