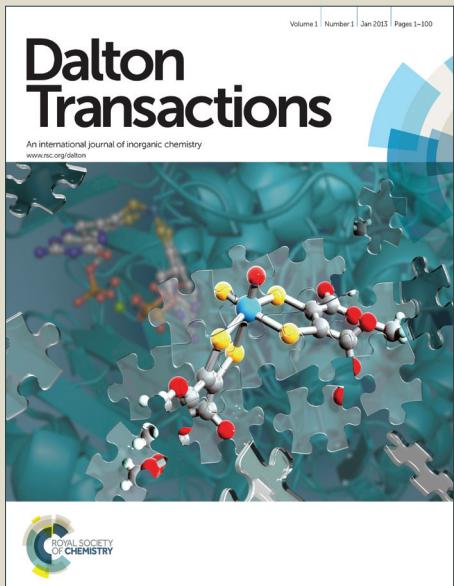


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Cite this: DOI: 10.1039/x0xx00000x

Synthesis and structure of Ag(I), Pd(II), Rh(I), Ru(II) and Au(I) NHC-complexes with pendant Lewis acidic boronic ester moiety†

Received 00th January 2012,
Accepted 00th January 2012

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DOI: 10.1039/x0xx00000x

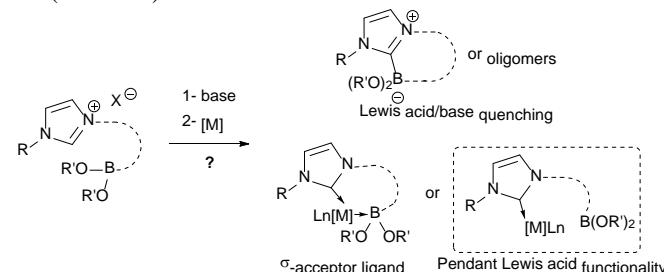
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Bifunctional Ag(I), Pd(II), Rh(I), Ru(II) and Au(I) complexes containing a NHC ligand and pendant trivalent boron moiety have been synthesized in high yields. Fine-tuned reaction conditions were used to prevent potential ligand self-quenching or polymerization due to the eventual co-existence *in situ* of free NHC (Lewis base) and boronic ester (Lewis acid) in the same molecule.

Boron-centered ligands have relatively large structural and electronical diversity allowing for different coordination mode to a metal center, as found, in borane, boryl, borylene or boride complexes.¹ In some particular cases of Lewis-basic metals, the Lewis-acidic trivalent boron atom can be coordinated to the metal center by a dative bond, becoming a σ -acceptor Z-type ligand,² mainly with borane derivatives,³ first authenticated by Hill *et al.* through the isolation of a metallaboratrane in 1999.⁴ Complexes featuring this supported M–B Z-type interactions are derived from the B–H activation of hydrido tris(methimazolyl)borates and related systems, or are obtained directly from ambiphilic phosphine borane ligands⁵ where the boron atom moiety is structurally maintained close to the metal center.

There are rare examples of bidentate or bifunctional ligands containing a boronic ester moiety that are reported in the literature,^{6–9} and the only observed transition metal–Z interactions with boronic ester moiety disclosed so far are the bridging borane-boryl compounds.¹⁰ Because the structural feature of those bifunctional ligands does not allow the boronic ester moiety to coordinate to the metal center, we designed a more flexible bifunctional ligand allowing the possibility of such an interaction. To increase the interaction, strong σ -donor N-heterocyclic carbene (NHC) ligand was chosen to enhance the Lewis base character of the transition metal. Synthesis of such NHC-boron transition metal complexes was highly challenging due to the necessary generation of coexisting free

NHC (Lewis base) and not hindered boron derivative (Lewis acid) *in situ* (Scheme 1).

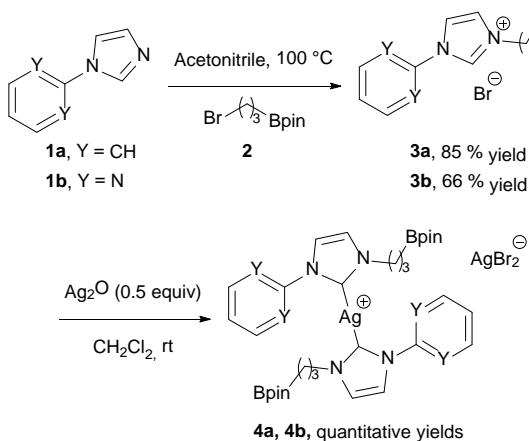


Scheme 1 Possible NHC/boronic ester/metal combined product pathways.

Here, we report the synthesis and the characterization of original stable bifunctional NHC-boronic ester silver, palladium, rhodium, ruthenium and gold complexes. Despite several modifications, the boronic ester moiety remained pendant and no Z-type interaction to the metal center was observed in this series of complexes (Scheme 1).

In the initial attempts, NHC-boron salts were obtained by reacting phenyl-substituted imidazole **1a** with the bromopropyl dioxaborolane **2** that was prepared in one step through hydroboration of allylboronide.¹¹ Attempts to prepare the complex **5a** directly from imidazolium salt **1a** and classic bases such as *n*-BuLi,¹² KHMDS, NaH or *t*-BuOK did not succeed and only degradation of the starting material was observed. No self-quenching resulting in cyclic NHC-boranes, polymerization processes or frustrated Lewis pair was detected. To generate the carbenoid species and avoid decomposition, we decided to use silver oxide as a soft base. Gratifyingly the reaction between Ag₂O and the imidazolium salt **1a** gave the desired cationic bis-NHC silver complex **4a** in quantitative yield, demonstrating the importance of the silver oxide mediated approach (Scheme 2). The structure was confirmed by NMR and mass spectrometry analysis (ESI, MeOH, m/z for [M-AgBr]⁺

731.4). Subsequent treatment of **4a** with 2.5 equiv of $\text{PdCl}_2(\text{CH}_3\text{CN})_2$ at room temperature in dichloromethane afforded binuclear dichloride complexes **5a** in 84% yield. Transmetallation of the silver complex with other transition



Scheme 2 Synthesis of Ag-NHC boronic ester complexes.

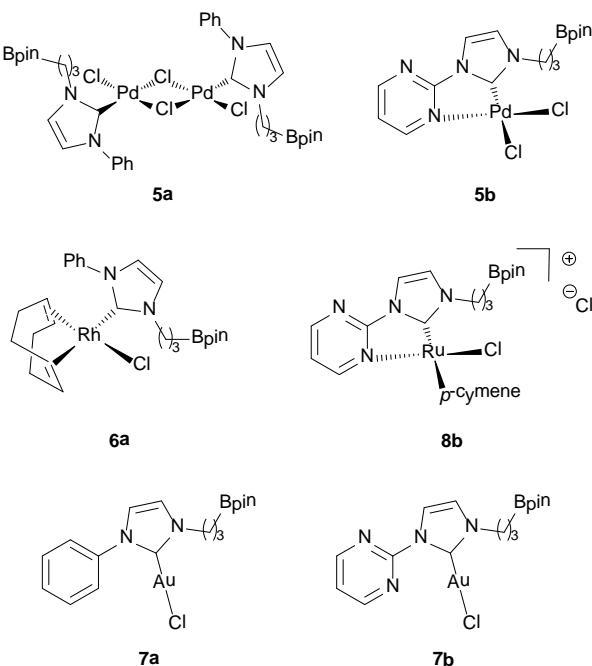


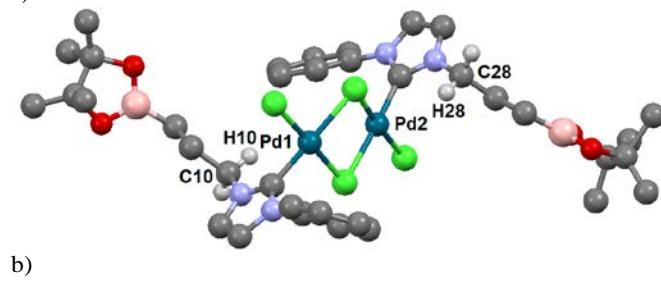
Fig. 1 Structures of palladium, rhodium, gold and ruthenium NHC-boronic ester complexes.

metals was also investigated. The reactivity of **4a** towards $[\text{Rh}(\eta^4\text{-cod})\text{Cl}]_2$ or AuCl metallic sources afforded the stable neutral complexes **6a** and **7a** in 74% and 87% yield respectively (Fig. 1). Negligible difference in chemical shift of the boron atom in ^{11}B NMR (128 MHz, CDCl_3) for imidazolium salts **3a** (33.3 ppm) and all complexes prepared (33.3–34.0 ppm) showed that the boron moiety was not ligated to the metal center and remained pendant. This initial evidence was further confirmed for **5a**, **6a** and **7a** in the solid state by X-ray diffraction studies (Fig. 2).

Interestingly, for complexes **5a** and **6a** the existence of hydrogen bonding or anagostic interaction (three-centers / four-electrons) between the metal and the hydrogen atom of the methylene group in α to the NHC was suspected by ^1H NMR (400 MHz, CDCl_3). Hydrogen atoms of this CH_2 group were equivalent both in **3a** (4.57

ppm, 2H, t, $^3J = 7.3$ Hz) and **4a** (4.13 ppm, 2H, t, $^3J = 7.3$ Hz) but a downfield shift of these protons in an unresolved broad signal appeared for **5a** at room temperature (4.40–4.95 ppm, 2H, m). Upon cooling to 243 K in CD_2Cl_2 solution, this signal split into two distinct sets attributed respectively to the hydrogen atom participating in an interaction with the palladium atom (4.57–4.91 ppm, 1H, m) and to the one that is not (4.27–4.57 ppm, 1H, m) (See ESI). In the case of rhodium complex **6a** the ^1H NMR signals of one of these two protons is strongly shifted downfield and these protons appeared as two distinct sets of broad signals at room temperature (4.32 and 4.89 ppm for non-coordinated and coordinated hydrogen atoms respectively) (see ESI). The downfield chemical shift of one of these protons indicated a clearer rhodium–H interaction than those observed for complex **5a**, typical of metal–hydrogen bonding or anagostic interaction. The existence of such interactions in **5a** and **6a** was confirmed in the solid state by X-ray diffraction study (Fig. 2) and their structural parameters (Pd1–H10 2.8203(4) Å, Pd1–C10 3.338(6) Å, Pd1–H10–C10 114.31(3)°; Pd2–H28 2.8580(5) Å, Pd2–C28 3.346(8) Å, Pd2–H28–C28 112.08(4)°; (Rh1–H10) 2.9297(2) Å, $\text{Rh1–C10} = 3.449(3)$ Å and angle $(\text{Rh1–H10–C10}) = 114.65(2)$ °) are in good agreement with those of anagostic interaction in transition metal d^8 complexes (litt.¹⁴ $d(\text{M–H}) \approx 2.3\text{–}2.9$ Å, $\text{M–H–C} \approx 110\text{–}170$ °). The origin of these interactions is still under debate and may involve donation of filled d_{z^2} or $d_{xz/yz}$ orbitals of the metal center into the C–H σ^* orbital.¹⁵ In order to obtain a more detailed understanding of the involved orbitals, a Natural Bond Orbital (NBO)¹⁶ analysis was computed (see ESI for details). Two distinct interactions were found, one involving the sp^3 C–H orbitals and the antibonding sp^3 C–H orbital with a rhodium lone pair with second order perturbation energies, $E_{2p} = 2.94$ and 2.44 kJ mol^{–1}, respectively. Moreover, the hydrogen atom close to the rhodium atom has a slightly higher natural charge of 0.222 than the other hydrogen atom bonded by the same carbon atom (0.204). To conclude, the M–H bond distance and the M–H–C angle values and the very low E_{2p} (<5 kJ mol^{–1}) strongly suggest the establishment of a very weak hydrogen bond,¹⁷ probably led to the alkyl chain conformation. Such interaction was not observed in the corresponding silver or gold complex **4a** and **7a** respectively.

The presence of privileged conformers having equivalent (**4a**, **7a**) or not equivalent (**5a**, **6a**) protons bearing by the methylene group α to the NHC is of interest. In the last case, this effect is strongly pronounced in complex **6a** and to estimate the participation of the rhodium complex geometry and/or the boronic ester moiety in such a)



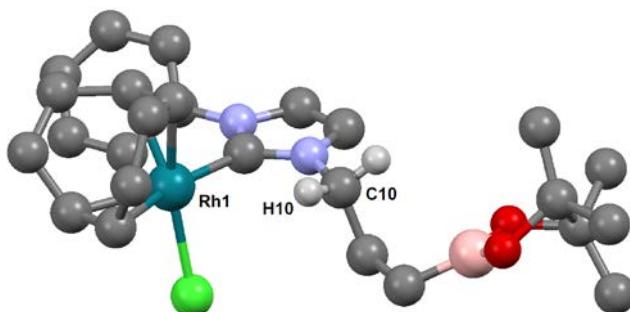


Fig. 2 ORTEP diagram of a) $[\text{PdCl}_2\text{NHC}]_2$ complex **5a**; b) $[\text{RhClNHC}]$ complex **6a** were depicted with thermal ellipsoids at 50% probability. Most of hydrogen atoms are omitted for clarity.

preferential conformation the analogous rhodium complex **11** (scheme 3) was synthesized. It was observed in **11** that these two protons were downfield shifted and not equivalent, but the effect was not as important as observed in **6a** (see ESI). Clearly, the boronic ester moiety has an effect on the conformation of the alkyl chain, leading in a rhodium complex **6a** more stabilized by an additional C–H hydrogen interaction. This, could generate a difference in the reactivity of **6a** and **11** complexes (see further).

Furthermore, to increase the Lewis basicity at the metallic center and the possibility of Z-interaction to the boron atom, a donor pyrimidine hemilabile ligand was incorporated at the *N*-position of the NHC instead of the phenyl group (Scheme 2). ^1H NMR and ^{13}C NMR spectra of palladium dichloride complex **5b** showed clearly three non-equivalent pyrimidine hydrogen and carbon atoms with a downfield shift ($\delta\text{H} > 1$) of one aromatic hydrogen atom in the α position to the nitrogen atom. As expected, these observations clearly indicate bidentate coordination of the metal to the NHC and one of the nitrogen atom of the pyrimidine moiety. In the solid state, complex **5b** features a pseudo square planar geometry with a Pd1–N1 distance of 2.049(2) Å and a N1–Pd1–C7 and N1–Pd1–Cl1 angles of 80.18(1) $^\circ$ and 93.47(7) $^\circ$, respectively, that confirms the spectroscopic NMR data (Fig. 3). Unfortunately, attempts to synthesize the rhodium complex analogue from $[\text{Rh}(\eta^4\text{-cod})\text{Cl}]_2$ gave an undetermined complex mixture.

Alternatively, the treatment of **4b** with $[\text{Ru}(\text{p-cymene})\text{Cl}_2]$ gave quantitatively the corresponding 18-electrons ruthenium(II) complex **8b**. The cationic nature of the complex was correlated by high-resolution mass spectrometry (ESI, MeOH, m/z 585.1742 $[\text{M}-\text{Cl}]^+$). Unfortunately, all attempts to crystallize complex **8b** failed, but the NMR spectroscopic data, as seen previously in the complex **5b**, provided evidence for the bidentate nature of the NHC-pyrimidine ligand as well as the pendant nature of the boron moiety (^{11}B NMR, 128 MHz, in CDCl_3 , 34.0 ppm). As expected, reaction of **4b** with AuCl gold source gave the linear geometric complex **7b**, where the pyrimidine aromatic ring was twisted to hold the gold metal center far from the nitrogen atom of the pyrimidine (Au1–N3, 3.118(1) Å, Au1–

a)

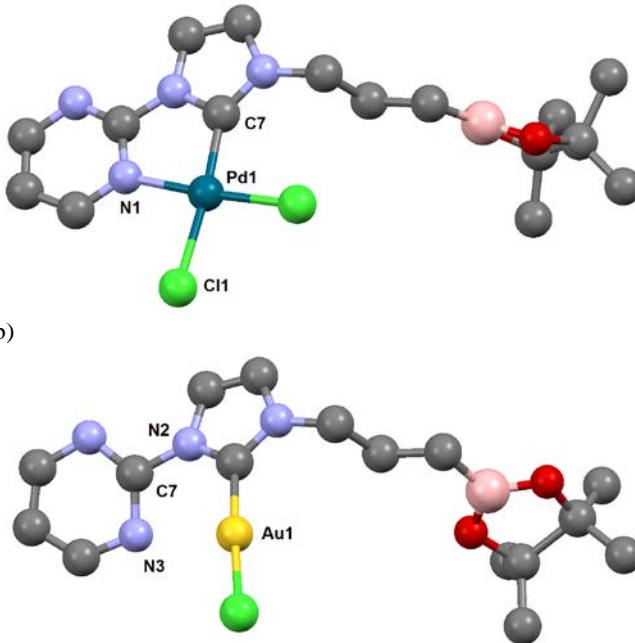
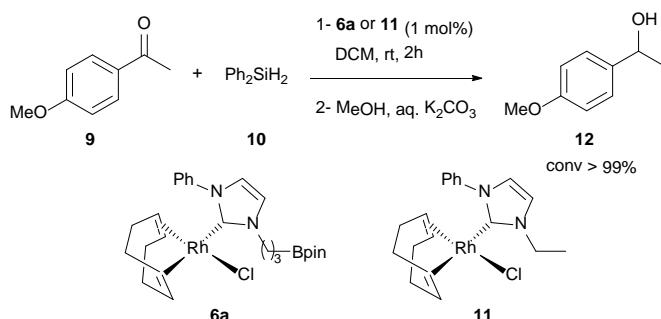


Fig. 3 ORTEP diagram of a) $[\text{PdCl}_2\text{NHC}]$ complex **5b**; b) $[\text{AuClNHC}]$ complex **7b** were depicted with thermal ellipsoids at 50% probability. Hydrogen atoms are omitted for clarity.

N3–C7–N2 dihedral angle, -34.91(1) $^\circ$). As previously observed in this series of complexes, NMR data and X-ray characterization revealed again the pendant character of the boron moiety in the complex **7b** (^{11}B NMR, 128 MHz, in CDCl_3 , 33.8 ppm) (Fig. 3). Despite some evidence in the literature of transition metal–Z interactions with boronic ester moiety,¹⁰ or related reaction intermediate found in borylation reaction mechanism,¹³ such interactions were not observed in this series of flexible complexes, owing to a less buttress structure that do not allow potential recruitment of the boron atom moiety close to the metal center. Interestingly, these stable complexes exhibit a Lewis acidic pendant boronic ester moiety that could serve as an additional binding site in bifunctional catalysis. An initial 1:1 equivalent mixture of complex **5a** and Et_3N was analyzed by ^{11}B NMR (128 MHz, CDCl_3) showing a complete upfield chemical shift of the boron atom (from 33.5 to 2.85 ppm) corresponding to a borate species that revealed an unambiguous covalent B–N bond. This information let us confident to use the boron atom in these complexes as an additional electrophilic activating site. In this context, stability and reactivity of complex **6a** were evaluated in a preliminary hydrosilylation reaction and **6a** was found to be a very efficient catalyst (conv > 99 % by ^1H NMR) (Scheme 3). However, the analogous complex **11** gave the same results in terms of kinetic (see ESI), meaning that the boronic part of the ligand seems to behave only as a spectator in this reaction. Nevertheless, the use of the stable palladium, rhodium, ruthenium and gold complexes described here as potential catalysts for the synergistic activation of reaction partners will be explored soon, as well as extension to structurally analogous more electrophilic NHC-borane ligands.



Scheme 3. Catalytic hydrosilylation of ketone **9** with analogous rhodium-NHC complexes **6a** and **11**.

Conclusions

In summary, we have reported the synthesis and characterization of novel bifunctional NHC-boronic ester ligands and their corresponding silver(I), palladium(II), rhodium(I), ruthenium(II) and gold(I) complexes.¹⁸ It was observed that only the use of Ag_2O as a base allowed us to obtain these complexes in very good yields, and without either a self-quenching or a polymerization process taking place during the generation of the *in situ* Lewis base (NHC) and Lewis acid (boronic ester). It was confirmed by ^{11}B NMR and X-ray diffraction that the boron moiety is not coordinated at the metal center and remained pendant. Complexes bearing pendant trivalent borane derivatives are of interest¹⁹ and could be an alternative to enhance potential electrophilic activation of a substrate. Reported examples are essentially built on metallocene shapes system,²⁰ but many of them must be stabilized *in situ* as borate derivatives,²¹ to avoid potential intramolecular rearrangement.²² The stable complexes developed here would let us confidently use them in bifunctional catalysis in the cooperative activation of small molecules.⁹ These hypothesis will be examined in further detail in due course.

Acknowledgments

This work was supported by grant from the French Research Ministry to M.T., Aix-Marseille Université, CNRS UMR 7313. We thanks M. Giorgi (www.spectropole.fr) for the X-ray diffraction studies.

Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental procedures, spectroscopic data, detailed calculations and CIF for complexes **5a**, **5b**, **6a**, **7a** and **7b**. DOI: 10.1039/c000000x/

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