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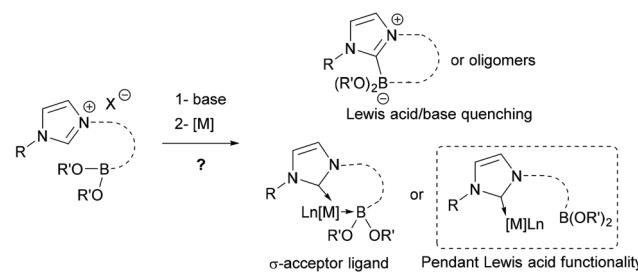
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Bifunctional Ag(I), Pd(II), Rh(I), Ru(II) and Au(I) complexes containing a NHC ligand and a pendant trivalent boron moiety have been synthesized in high yields. Fine-tuned reaction conditions were used to prevent potential ligand self-quenching or 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 electronic diversity allowing for different coordination modes 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 which was first authenticated in 1999 by Hill *et al.* through the isolation of a metallaboratrane.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 the boronic ester moiety disclosed so far are the bridging borane–boryl compounds.¹⁰ Because the structural feature of these 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, a strong σ -donor N-heterocyclic carbene (NHC) ligand was chosen to enhance the Lewis base character of the transition



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

metal. Synthesis of such NHC-boron transition metal complexes was highly challenging due to the necessary generation of a coexisting free NHC (Lewis base) and not the hindered boron derivative (Lewis acid) *in situ* (Scheme 1).

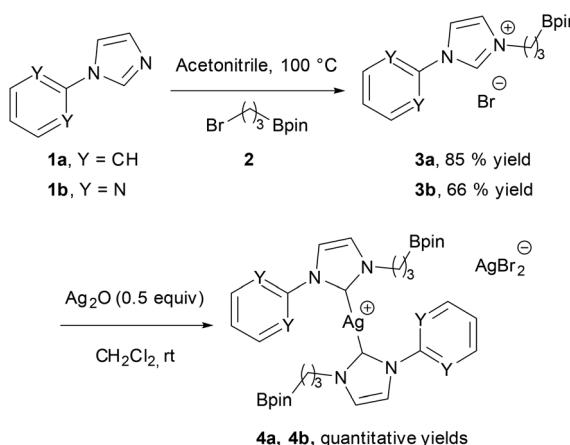
Here, we report the synthesis and the characterization of the original stable bifunctional NHC-boronic ester silver, palladium, rhodium, ruthenium and gold complexes. Despite several modifications, the boronic ester moiety remained pendant and no Z-type interaction to the metal center was observed in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

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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**. CCDC 864270, 880506, 880508, 1023303 and 1023304. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5dt00814j





Scheme 2 Synthesis of Ag-NHC boronic ester complexes.

[M – AgBr₂]⁺ 731.4). Subsequent treatment of **4a** with 2.5 equiv. of PdCl₂(CH₃CN)₂ at room temperature in dichloromethane afforded binuclear dichloride complexes **5a** in 84% yield. Transmetallation of the silver complex with other transition metals was also investigated. The reactivity of **4a** towards [Rh(*n*⁴-cod)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 shifts of the boron atom in ¹¹B NMR (128 MHz, CDCl₃) 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

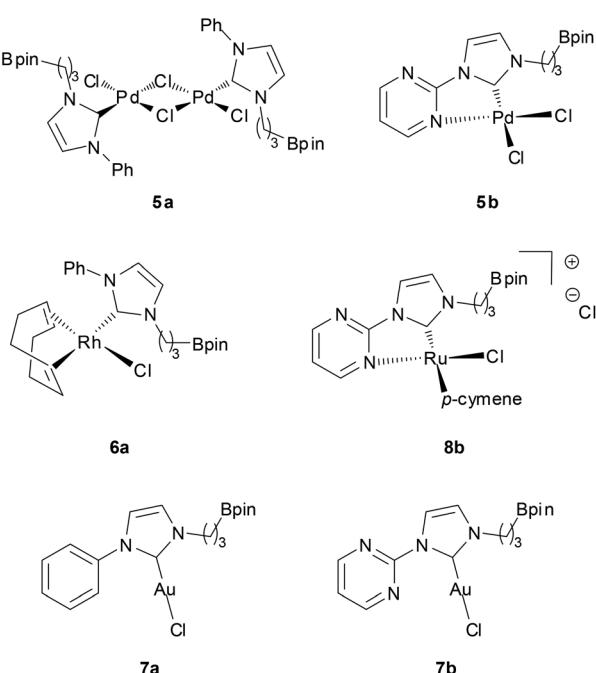
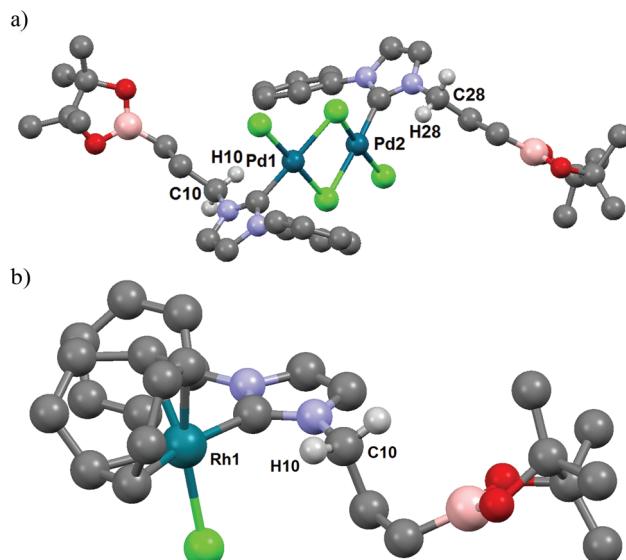


Fig. 1 Structures of palladium, rhodium, gold and ruthenium NHC boronic ester complexes.

Fig. 2 ORTEP diagrams of (a) [PdCl₂NHC]₂ complex **5a**; (b) [RhClNHC] complex **6a** are depicted with thermal ellipsoids at 50% probability. Hydrogen atoms are omitted for clarity.

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 interactions (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, CDCl₃). Hydrogen atoms of this CH₂ 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 CD₂Cl₂ solution, this signal splits 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 signal 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 interactions. The existence of such interactions in **5a** and **6a** was confirmed in the solid state by an 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, Rh1–C10 = 3.449(3) Å and angle (Rh1–H10–C10) = 114.65(2)°) are in good agreement with those of anagostic interactions in transition metal d⁸ complexes (lit.¹⁴ *d*(M–H) ≈ 2.3–2.9 Å, M–H–C ≈ 110–170°). 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 performed (see ESI† for details). Two distinct interactions were found, one involving the sp^3 C-H orbitals and the antibonding rhodium s-orbital and a second interaction between the antibonding sp^3 C-H 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 atoms 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 an interaction was not observed in the corresponding silver or gold complexes **4a** and **7a**, respectively.

The presence of privileged conformers having equivalent (**4a**, **7a**) or non-equivalent (**5a**, **6a**) protons bearing 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 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 to 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 ¹³C NMR spectra of palladium dichloride complex **5b** showed clearly three non-equivalent pyrimidine hydrogens and carbon atoms with a downfield shift ($\delta_H > 1$) 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 atoms of the pyrimidine moiety. In the solid state,

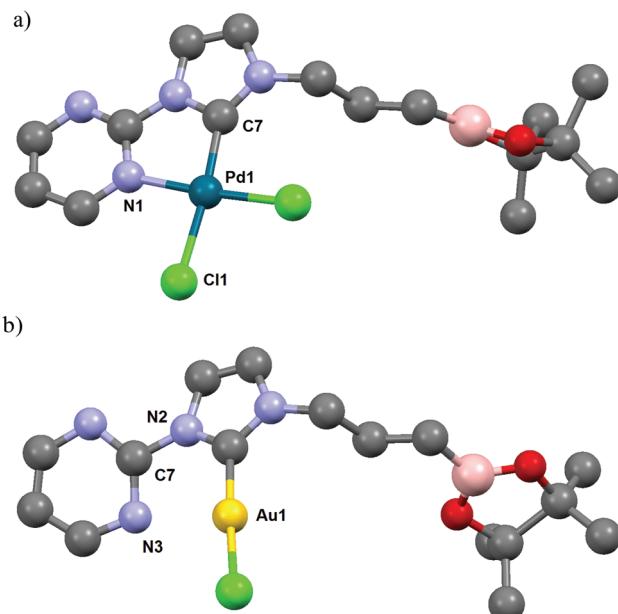
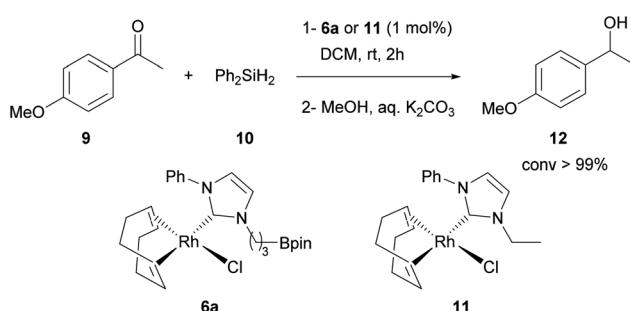


Fig. 3 ORTEP diagrams of (a) $[PdCl_2NHC]$ complex **5b**; (b) $[AuClNHC]$ complex **7b** are depicted with thermal ellipsoids at 50% probability. Hydrogen atoms are omitted for clarity.

complex **5b** features a pseudo square planar geometry with a Pd1–N1 distance of $2.049(2)$ Å and N1–Pd1–C7 and N1–Pd1–Cl1 angles of $80.18(1)$ ° and $93.47(7)$ °, respectively, which confirms the spectroscopic NMR data (Fig. 3). Unfortunately, attempts to synthesize the rhodium complex analogue from $[Rh(\eta^4\text{-cod})Cl_2]$ gave an undetermined complex mixture.

Alternatively, the treatment of **4b** with $[Ru(p\text{-cymene})Cl_2]_2$ gave quantitatively the corresponding 18-electron ruthenium(II) complex **8b**. The cationic nature of the complex was correlated by high-resolution mass spectrometry (ESI, MeOH, m/z 585.1742 [$M - Cl^-$]). 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 (¹¹B NMR, 128 MHz, in $CDCl_3$, 34.0 ppm). As expected, reaction of **4b** with an 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–N3–C7–N2 dihedral angle, $-34.91(1)$ °). 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** (¹¹B NMR, 128 MHz, in $CDCl_3$, 33.8 ppm) (Fig. 3).

Despite some evidence in the literature of transition metal-Z interactions with the boronic ester moiety,¹⁰ or a related reaction intermediate found in the borylation reaction mechanism,¹³ such interactions were not observed in this series of flexible complexes, owing to a less buttress structure that does 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



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



serve as an additional binding site in bifunctional catalysis. An initial 1 : 1 equivalent mixture of complex **5a** and Et₃N was analyzed by ¹¹B NMR (128 MHz, CDCl₃) 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 gave us confidence 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 kinetics (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.

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 Ag₂O 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 ¹¹B NMR and X-ray diffraction that the boron moiety is not coordinated to 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 shape systems,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 hypotheses will be examined in further detail in due course.

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