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Catalyst design based on agostic interactions: synthesis, characterization, and catalytic activity of bis(pyrazolyl)borate copper complexes†

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Agostic interactions are often used to activate inert C–H bonds, and thus facilitate new reactions. We report the first example of designed catalysts based on the agostic interaction. Novel copper(I) complexes $[BBN(pz^x)_2]Cu(PPh_3)_n$ (BBN = 9-borabicyclo[3.3.1]nonane; pz^x = 3-substituted pyrazole; x = H, n = 2; x = Me, n = 1) and $\{[BBN(pz^{iPr})_2]Cu\}_2$ have been synthesized and characterized. Single crystal studies of the three compounds show weak intramolecular C–H···Cu interactions which can be assigned as agostic or anagostic interactions. Catalytic studies of these complexes toward carbenoid insertion into N–H bonds indicate these weak interactions act as a "switch" which will be turned "on" if interacting with the substrate and "off" if eliminating the product and regenerating the weak interaction. The process of the "switch" turning "on" or "off", which is related to the catalytic effect, is found to be influenced by both steric effects and the solvent: a less sterically hindered catalyst in non-coordinating benzene results in high yield, while a more sterically hindered catalyst in coordinating THF results in relatively low yield.

Introduction

In the past few decades, transition metal organometallic complexes have been found to show some unusual bonding modes. One typical example is the agostic interaction, usually considered as a 3-center–2-electron (3c–2e) bond and formed between a C–H σ bond and an unoccupied orbital of a transition metal center.[1–4] In addition, non-agostic and anagostic or pregostic are complementary terms used to describe systems that, while showing similar close C–H···M proximity, are not considered truly agostic in nature.[5–7] Recently, these metal mediated interactions have been mainly considered candidates for possible catalytic C–H activation (further resulting in C–H bond elimination),[8] alkane oxidative addition,[9] Ziegler–Natta polymerization,[10,11] transcyclometallation,[12] and cyclometallation of benzoquinoline.[13]

Neutron diffraction data show that agostic interactions usually lead to changes in interatomic distances, with the C–H bond engaged in agostic interactions being lengthened by about 5–10% more than normal, while the M···H distance appears to be *ca.* 15–20% longer than a typical non-agostic M···H separation.[1] This observation implies that the M···H bond due to the agostic interaction may be more flexible and easily cleaved. Furthermore, solvent molecules can compete with agostic interactions to coordinate with a metal center. The dynamic exchange between solvent and agostic interactions has been studied experimentally and computationally.[14,15] On the basis of the weak agostic interaction between a metal center and a C–H bond, we have designed a new type of catalyst, in which the C–H···M interaction is considered as a "switch" between two states ("on" and "off"). In the "on" state, the interaction between a substrate (S) and a metal center (M) will result in activation of the substrate and further chemical reaction. After the reaction, the product is eliminated, the C–H···M interaction re-forms, and the catalyst switches back to the "off" state (Scheme 1).

Since first reported 50 years ago by Trofimenko,[16] polypyrazolylborate ligands have found applications in a wide range of chemistry from organic synthesis, to analytical chemistry, catalysis, and materials science.[17,18] In our study, we have chosen one class of polypyrazolylborate ligands, the bis(pyrazolyl)borate ligand ($[RR'B(pz^x)_2]^-$, Fig. 1), because most bis(pyrazolyl)borate complexes, $[RR'B(pz^x)_2]ML_n$, show C–H···M interactions and high stability, and yet the chemistry of these

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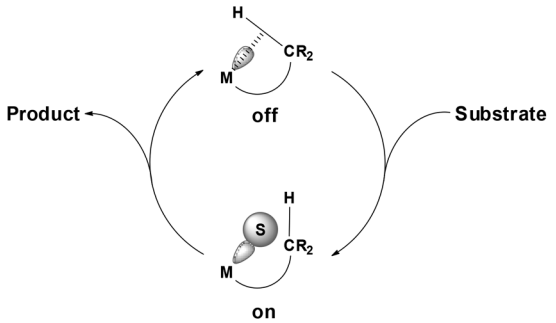


Scheme 1 A proposed mechanism of a catalytic reaction involving C–H···M agostic interactions.

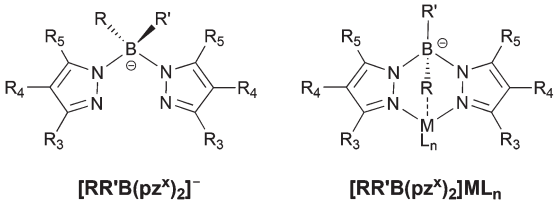


Fig. 1 Structures of the bis(pyrazolyl)borate ligand $[RR'B(pz^x)_2]^-$ and bis(pyrazolyl)borate complex $[RR'B(pz^x)_2]ML_n$.

particular ligands is still relatively poorly developed. In addition, different substituents on the pyrazole rings may permit tuning of the catalytic activity through steric and electronic effects.

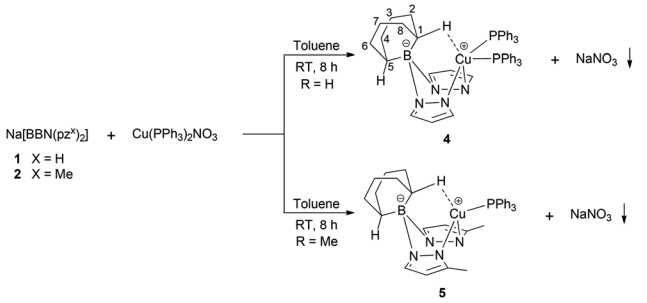
Herein we report the synthesis and characterization of the new Cu(I) complexes $[BBN(pz)_2]Cu(PPh_3)_2$ (**4**), $[BBN(pz^{Me})_2]Cu(PPh_3)$ (**5**) and $\{[BBN(pz^{iPr})_2]Cu\}_2$ dimer (**6**), and their catalytic activity toward carbene insertion into N–H bonds in different solvents. Single crystal X-ray structural analyses demonstrated that intramolecular C–H···Cu agostic or anagostic interactions occurred in all three compounds and these C–H···Cu interactions take part in catalytic cycles and act as a "switch". It is also found that the C–H···Cu interaction, the steric effect of the ligands, and the coordinating ability of the solvents synergistically influence these catalytic reactions.

Results and discussion

Syntheses and structural characterization of copper(I) complexes

Complex **4** was prepared by a direct reaction of $Na[BBN(pz)_2]$ (**1**)[19,20] with an equimolar amount of $(PPh_3)_2CuNO_3$ in toluene at room temperature (RT) (Scheme 2). The white crystalline solid **4** is stable in air for months without any change, and no obvious decomposition is observed in solution under an N_2 atmosphere after a few days. It is soluble in many common organic solvents such as toluene, dichloromethane, or THF, but has low solubility in hexane.

A single-crystal X-ray diffraction study clarified the structure of **4**. As shown in Fig. 2, the bis(pyrazolyl)borate ligand in **4**



Scheme 2 Syntheses of complexes **4** and **5**.

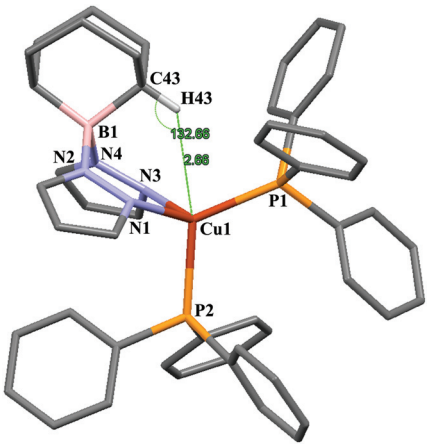


Fig. 2 The molecular structure of **4**. Hydrogen atoms on phenyl, pyrazole, and BBN rings (except C_α hydrogen) are omitted for clarity. Selected bond lengths (Å) and angles (°): Cu1–N1, 2.086(1); Cu1–N3, 2.107(1); Cu1–P1, 2.267(1); Cu1–P2, 2.317(1); N1–Cu1–N3, 94.71(5).

coordinates in a bidentate fashion with a bite angle N1–Cu1–N3 of 94.71°. The central six-membered ring, Cu1–N1–N2–N3–N4–B1, displays an approximate boat conformation.[21] The interaction between H43 on the C_α of BBN and Cu1 shows a distance of 2.66 Å and a C43–H43–Cu1 angle of 132.66°. Agostic interactions tend to have shorter H···M distances and smaller C–H···M angles than those found in anagostic interactions; these are characterized by H···M distances of 1.8–2.3 Å and C–H···M angles of 90–140° for the former, and 2.3–2.9 Å and 110–170° for the latter.[22,23] Therefore, the parameters for the interaction seen in **4** lie well within the typical range for anagostic interactions.

Consistent with the solid-state structure, the ^1H, $^{13}C\{^1H\}$ and ^{13}C-^1H HSQC NMR spectra show five aliphatic signals with relative integrals of 1 : 2 : 2 : 2 : 1 for the BBN moiety, which are comparable to those of the related $[BBN(pz^x)_2]RhL_n$ complex.[5] The inequivalence of the 1 and 5, 2 and 4, 3 and 7, and 6 and 8-positions (numbered in Scheme 2) may be attributed to the restricted flexibility of the bicyclic BBN and the H···Cu interaction, indicating that the solid structure is maintained in solution.[5]

When $Na[BBN(pz^{Me})_2]$ (**2**)[5,19,20] was treated with $(PPh_3)_2CuNO_3$ under the same synthetic conditions as that of complex **4**, the crystalline solid **5** was obtained. Compound **5**

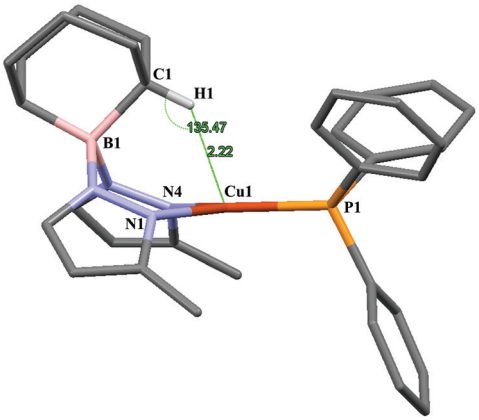
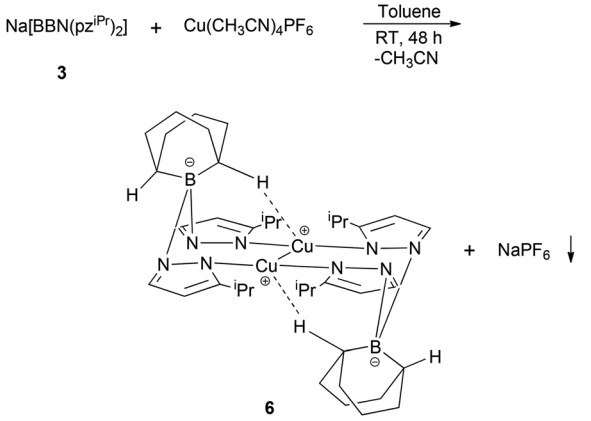


Fig. 3 The molecular structure of **5**. Hydrogen atoms on phenyl, pyrazole, and BBN rings (except the C_α hydrogen) are omitted for clarity. Selected bond lengths (Å) and angles (°): Cu1–N1, 1.975(3); Cu1–N4, 1.998(3); Cu1–P1, 2.152(1); N1–Cu1–N4, 97.16(10).

has similar air stability, solubility and spectral signatures as **4**. Single-crystal X-ray diffraction of **5** indicates that only one PPh_3 ligand is coordinated to the Cu center (Fig. 3), in contrast to **4** where two PPh_3 ligands are bonded to Cu (Fig. 2). The result is consistent with the fact that the R_3 substituent in an $[RR'B(pz^x)_2]^-$ ligand has the most critical effect on the coordination chemistry of the $[RR'B(pz^x)_2]^-$ ligand, as it defines the size of the cavity for the metal center. The Cu center in **5** adopts sp^3 hybridization to form a distorted tetrahedral geometry involving two N atoms, one P atom, and an interaction with a C–H bonding electron pair. The H1···Cu1 distance of 2.22 Å in **5** is significantly shorter than the corresponding value in **4** (H43···Cu1 = 2.66 Å), while the C1–H1···Cu1 angle of 135.47° is only slightly larger than the corresponding angle in **4** (132.66°), indicating a stronger interaction between H1 and Cu1 that should be considered an agostic interaction.

In order to further examine the impact of steric effects on the structure and catalytic activity, the reaction of a more sterically demanding complex, $Na[BBN(pz^{iPr})_2]$ (**3**),[19,20] with $(PPh_3)_2CuNO_3$ was attempted, but no reaction occurred. This may be ascribed to the steric hindrance of both the iPr substituent on the pyrazole unit and the strong coordinating ability of the PPh_3 ligand that prevent the approach of the $[BBN(pz^{iPr})_2]^-$ anion to the metal center. An alternative copper(I) starting material featuring only weakly coordinating ligands, $Cu(CH_3CN)_4PF_6$, was then investigated. After running the reaction for 48 h in toluene at room temperature, we obtained an unexpected dimeric complex $\{[BBN(pz^{iPr})_2]Cu\}_2$ (**6**) (Scheme 3). Consequently, it seemed that ligand exchange between $[BBN(pz^{iPr})_2]^-$ and PF_6^-, dissociation of CH_3CN and dimerization took place.

The solid state structure of **6** is centrosymmetric as shown in Fig. 4. Each Cu(I) center is coordinated by two pyrazole groups from two different $[BBN(pz^{iPr})_2]^-$ ligands. The interaction between α-C–H of BBN and Cu(I) belongs to the class of anagostic interactions according to its H11···Cu1 distance and C11–H11···Cu1 angle of 2.34 Å and 134.87°, respectively. Also,



Scheme 3 Synthesis of complex **6**.

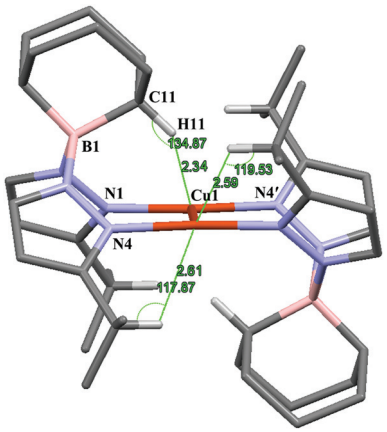


Fig. 4 The molecular structure of **6**. Most hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Cu1–N1, 1.892(1); Cu1–N4, 1.891(1); Cu1–Cu1, 2.8649(4); N1–Cu1–N4′, 163.32(5).

an additional anagostic interaction was found at each Cu(I) center with the isopropyl C–H bonds, with H···Cu distances of 2.59 Å and 2.61 Å, and C–H···Cu1 angles of 119.53° and 117.87° (Fig. 4). The Cu(I)–Cu(I) distance of 2.86 Å falls within the range of a weak intramolecular interaction.[24] The interaction is also reflected in a nonlinear N1–Cu1–N4′ angle of 163.32°. This relatively short metal–metal distance is not unusual in d^{10} complexes,[25–29] and may be due to steric effects imposed by the ligand.[30–32] As a result, the formation of the dimeric structure of **6** further supports the influence of the R_3 substituent on the chemistry of the $[RR'B(pz^x)_2]^-$ ligand.

Hence, we have observed that all three synthesized compounds contain intramolecular C–H···Cu agostic or anagostic interactions.[5,19,21,33,34] While these weak interactions stabilize the compounds, they may also play an important role in catalytic transformations.[15]

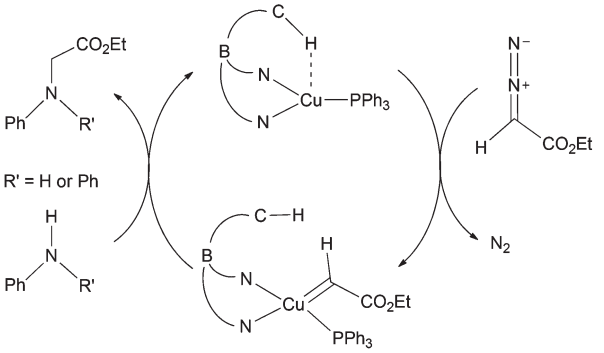
Catalytic activity of the copper(I) complexes

To verify the catalytic properties of the synthesized compounds **4–6**, we investigated the catalytic transfer of a carbene moiety

into an N–H bond, a very powerful tool for the construction of C–N bonds.[35–38] Here, the carbene was generated as a metallocarbenoid species *via* metal-catalyzed decomposition of the diazo reagent ethyl diazoacetate, (N═N═CHC(O)OC_2H_5, EDA). In the past few years, catalysts for this reaction have undergone great evolution, from noble metals Rh[39–44] and Ru[45,46] to much more low-cost Cu-[47–52] and Fe-complexes[53–58] and even metal-free systems.[59,60] In the present study, we investigated the ability of the new Cu(I) complexes prepared herein to decompose EDA and subsequently transfer the resulting carbene $CHCO_2Et$ group into the N–H bonds catalytically. All reactions were performed with EDA and arylamines ($PhNH_2$ and Ph_2NH) in the presence of 2.5 mol% (**4** and **5**) or 1.25 mol% (**6**) as catalysts at room temperature. The results are displayed in Table 1.

It should be noted that no product of insertion into the N–H bond was found in the absence of a catalyst (entries 1 and 2) and all catalytic insertion reactions were clean, proceeding without the formation of diethyl maleate or other by-products (entries 3 to 18).

Compound **5** can be considered a 16e or 18e complex, depending on whether the C–H bonding electron pair is counted. When used in the catalytic transfer of a carbene moiety into the N–H bond in the non-coordinating solvent benzene, it appears from NMR spectra that **5** still maintains its solid state structure, where C–H is believed to interact with Cu *via* an agostic interaction with an sp^3 orbital. When substrate EDA attacks the Cu center, the C–H···Cu interaction is broken to provide a vacant coordination site. The catalyst turns "on" to form the carbene intermediate Cu═$CHCO_2Et$ with concomitant elimination of N_2 (Scheme 4). Subsequently, arylamines, PhR′NH, react with the carbene to give PhR′NCH_2CO_2Et and regenerate **5**.



Scheme 4 The proposed mechanism for catalytic N–H insertion.

In comparison, compound **4** is a saturated 18e complex. This electronic saturation may preclude it from readily participating in the catalytic reaction. However, **4** did show observable catalytic activity, although its efficiency is dramatically decreased in comparison with that of **5** (entries 3 and 5). A plausible explanation is that an initial decoordination of the PPh_3 ligand takes place to give the catalytic site,[61] which is stabilized by an anagostic interaction and then undergoes a similar catalytic cycle as complex **5**. The eliminated PPh_3 was determined to form Ph_3P═$CHCO_2Et$ by analysis of the crude product by $^{31}P\{^1H\}$NMR. Hence, a side reaction might be occurring between EDA and the dissociated PPh_3.[62] To test this assumption, a supplementary run in the presence of excess PPh_3 was carried out (see the ESI† for details). Under these conditions, catalytic insertion of the N–H bonds was not observed. In contrast, Ph_3P═$CHCO_2Et$ was the dominant product. This observation indicates that EDA reacted with PPh_3 prior to interacting with the Cu catalyst to form the carbene, further confirming that it is the elimination of the PPh_3 ligand that induces the (relatively low) catalytic activity of **4**.

For the dimeric compound **6**, there are only two N atoms interacting with each Cu center through chemical bonds, with the coordination sphere of each Cu being completed by weak interactions. Therefore, it has available coordination sites that should result in increased catalytic efficiency. However, the reaction rate was slow, as shown by comparison of entries 5 and 7 in Table 1. This low catalytic efficiency is believed to be due to steric effects of the bulky iPr substituent groups. Thus, the reaction time was extended to 24 h and higher catalytic efficiency was observed (compare entries 7 and 8 in Table 1).

The mechanism was further confirmed by carrying out the catalytic reaction in the coordinating solvent THF. The catalytic efficiency of all reactions was decreased significantly in the THF solution. One reason is that the strong coordinating ability of THF disturbs or displaces agostic interactions to occupy an active site of the catalyst. Another reason may be competition between THF and the substrate to interact with Cu, decelerating the rate of formation of the copper carbene intermediate. Considering that THF has been shown to displace an

Table 1 N–H functionalization reaction by carbene insertion

Entry	Substrate	Catalyst	Solvent	Yield[d] (%)
1	$PhNH_2$	None	Benzene	0[e]
2	Ph_2NH	None	Benzene	0[e]
3	$PhNH_2$	4[a]	Benzene	55
4	$PhNH_2$	4[a]	THF	24
5	$PhNH_2$	5[a]	Benzene	>95
6	$PhNH_2$	5[a]	THF	53
7	$PhNH_2$	6[b]	Benzene	78
8	$PhNH_2$	6[c]	Benzene	>95
9	$PhNH_2$	6[b]	THF	63
10	$PhNH_2$	6[c]	THF	86
11	Ph_2NH	4[a]	Benzene	45
12	Ph_2NH	4[a]	THF	33
13	Ph_2NH	5[a]	Benzene	85
14	Ph_2NH	5[a]	THF	52
15	Ph_2NH	6[b]	Benzene	75
16	Ph_2NH	6[c]	Benzene	>98
17	Ph_2NH	6[b]	THF	48
18	Ph_2NH	6[c]	THF	84

[a] Reaction conditions: arylamine/EDA/catalyst (100 : 40 : 1) in solvent (10 mL) at room temperature for 12 h. [b] Reaction conditions: arylamine/EDA/catalyst (200 : 80 : 1) in solvent (10 mL) at room temperature for 12 h. [c] Reaction conditions: arylamine/EDA/catalyst (200 : 80 : 1) in solvent (10 mL) at room temperature for 24 h. [d] Yield of the isolated product by column chromatography. [e] No reaction.

agostic interaction in a Ti complex,[14] it is believed that the first reason may be more important but both factors cannot be ruled out as potential influences on the reaction process.

A set of analogous reactions was performed using Ph_2NH in place of $PhNH_2$, and similar results were obtained (see entries 11 to 18 in Table 1), implying that the substitution of hydrogen by the bulkier phenyl group has no significant influence on the reaction.

Conclusions

In conclusion, we report the design and syntheses of novel Cu(I) complexes with interesting catalytic properties due to the inherent structural feature of an intramolecular C–H···Cu interaction. These compounds are synthesized by the reaction of a Cu(I) precursor with the $[BBN(pz^*)_2]^-$ ligand. All the Cu(I) complexes have been structurally characterized and possess agostic or anagostic C–H···Cu interactions. Their catalytic behaviors toward carbenoid insertion into N–H bonds are examined, demonstrating that the C–H···Cu interaction acts as a "switch", with the "off" state featuring an agostic interaction and the "on" state featuring the binding of the substrate to the Cu(I) center. It is found that steric effects and the coordinating ability of the chosen solvent both influence the catalytic ability of the Cu(I) complexes: higher yields are observed for less sterically crowded catalysts in non-coordinating benzene while relatively low yields are observed for more sterically crowded catalysts in coordinating THF.

Acknowledgements

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