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Synthesis of a Bulky Bis(carbene)borate Ligand – Contrasting Structures of Homoleptic Nickel(II) Bis(pyrazolyl)borate and Bis(carbene)borate Complexes

Ismael Nieto,[a] Ranko P. Bontchev,[b] and Jeremy M. Smith*[a]

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Twofold deprotonation of the "boronium" cation $H_2B(tBuImH)_2^+I^-$ provides access to the bulky bis(carbene)borate ligand $H_2B(tBuIm)_2^-$. Transfer of the ligand to Ni^{II} sources affords the square-planar, diamagnetic complex $Ni[H_2B(tBuIm)_2]_2$. The properties of this complex are contrasted with the related bis(pyrazolyl)borate complex $Ni[H_2B(tBupyr)_2]_2$, which is octahedral and paramagnetic. Density functional theory has been used to evaluate the reasons for the structural differences. Stabilization of the square-planar geometry by the bis(carbene)borate ligand can be ascribed to its greater donor ability.

Introduction

While not as common as the ubiquitous tris(pyrazolyl)borates, bis(pyrazolyl)borate (Bp) ligands (Figure 1, A) have also found application in coordination and organometallic chemistry.[1] For example, metal complexes supported by Bp ligands have been used to model the active sites of metalloenzymes,[2] as catalysts for the formation of polyketones[3] and in studies of C–H activation.[4]

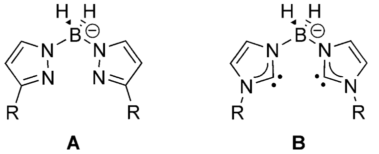

Figure 1. Bis(pyrazolyl)borate (A) and bis(carbene)borate (B) ligands.

Bis(carbene)borate ligands (Figure 1, B), which coordinate to metal centers through N-heterocyclic carbenes, were first reported by Fehlhammer.[5] These ligands were prepared in two steps from potassium bis(imidazol-1-yl)dihydridoborate. Alkylation of the borate yielded "boronium" salts that were subsequently deprotonated at low temperature to provide the anionic bis(carbene)borate ligands.

We have previously reported synthetic routes to a variety of tris(carbene)borate ligands.[6] These syntheses use substituted imidazoles to introduce functional groups into the borate ligand. We wondered whether a similar approach could be used to prepare bis(carbene)borates, which would allow for a greater diversity of these bidentate ligands. This report demonstrates our success in this endeavour, in which a bulky bis(carbene)borate ligand is prepared from 1-*tert*-butylimidazole. This strongly donating ligand reacts with a variety of nickel(II) starting materials to yield a diamagnetic square-planar complex. The structure of this complex contrasts with that of the related bis(3-*tert*-butylpyrazolyl)borate nickel(II) complex, which is octahedral and paramagnetic. Density functional theory has been used to provide insights into these structural differences.

Results and Discussion

Synthesis of the bulky bis(carbene)borate ligand and its nickel(II) complex are shown in Scheme 1. The ligand precursor salt, $H_2B(tBuImH)_2^+I^-$ (**1**), was prepared by a similar synthetic method to that reported for the synthesis of "boronium"-based ionic liquids.[7] Two equivalents of 1-*tert*-butylimidazole were heated in refluxing toluene with in situ prepared $Me_3N{:}BH_2I$, to form a colourless air- and moisture-stable solid.

The spectral and analytical data of this compound are consistent with the formulation $H_2B(tBuImH)_2^+I^-$. In the ^1H NMR spectrum ($CDCl_3$) the acidic 2-H protons resonate at $\delta = 9.15$ ppm, while the other imidazolium ring protons are found at $\delta = 7.20$ and 7.17 ppm. The BH_2 group resonates as a broad signal at $\delta = 3.45$ ppm and the *tert*-butyl groups as a singlet at $\delta = 1.67$ ppm.

Deprotonation of **1** to yield the lithium complex $H_2B(tBuIm)_2Li$ (**2**) is achieved by the room-temperature reaction with two equivalents of LDA in THF. The ^1H NMR spectrum of **2** in C_6D_6 has two resonances from the imid-

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[a] Department of Chemistry and Biochemistry, New Mexico State University,
Las Cruces NM 88003, USA
Fax: +1-575-646-2649
E-mail: jesmith@nmsu.edu
[b] Sandia National Laboratories,
P.O. Box 5800, MS 0779, Albuquerque, NM 87185

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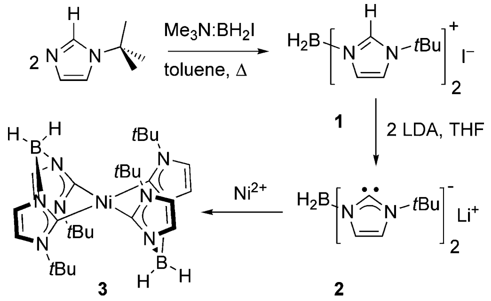

Scheme 1. Synthesis of complexes **1**–**3**.

azol-2-ylidene groups (7.28 and 6.72 ppm), a broad resonances due to the BH_2 group at δ = 4.57 and 4.32 ppm, and a single resonance due to the *tert*-butyl groups at δ = 1.30 ppm.

Diffusion of pentane into an Et_2O solution of **2** yielded single crystals suitable for X-ray crystallography. In contrast to the solution structure, which has C_{2v} symmetry by ^1H NMR spectroscopy, the complex crystallizes as a lower symmetry dimer (Figure 2, A). Two of the potentially bidentate ligands span two lithium centers, which are related by an inversion center. Two-coordinate Li(1) is bound to two symmetry-related carbon atoms, while three-coordinate Li(2) is bound to two symmetry-related carbon atoms as well as a disordered Et_2O solvent molecule. The Li–C bond lengths of this complex [2.111(4)–2.186(4) Å] are within the range reported for other lithium N-heterocyclic carbene complexes.[8] There are also contacts that are less than the sum of the van der Waals radii between Li(1) and C(11) [2.575(5) Å] as well as Li(1) and Li(2) [2.74(1) Å].

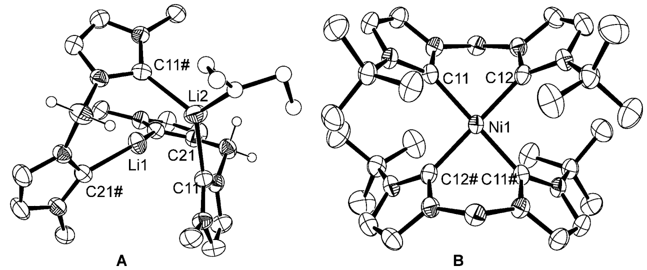

Figure 2. A: X-ray crystal structure of **2**, *tert*-butyl groups and hydrogen atoms on carbon atoms are omitted for clarity. Disordered Et_2O solvent shown in ball-and-stick format. Selected bond lengths [Å] and angles [°]: Li(1)–C(21) 2.111(4); Li(1)–C(11) 2.575(5); Li(1)–Li(2) 2.74(1); Li(2)–C(11) 2.186(4); C(21)–Li(1)–C(21#) 134.1(4); C(21)–Li(1)–Li(2) 112.9(2); C(11)–Li(2)–C(11#) 123.6(4). Symmetry transformation used to generate equivalent atoms: $-x + 2, y, -z + 1/2$. B: X-ray crystal structure of **3**. One of two molecules in the asymmetric unit is shown. Solvent molecules and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ni–C(11) 1.940(3), Ni–C21 1.949(3), C11–Ni–C12 85.5(1), C11–Ni–C12# 94.5(2). Symmetry transformation used to generate equivalent atoms: $-x + 1, -y, -z + 1$.

The reaction of **2** with $NiCl_2(dme)$, $NiCl_2(PPh_3)_2$ or $NiCl_2(PMe_3)_2$ results in the formation of an orange, air-stable product that has been characterized as the square-planar complex $Ni[H_2B(tBuIm)_2]_2$ (**3**) by X-ray crystallography (Figure 2, B). The asymmetric unit consists of two half molecules with the nickel atoms lying on inversion centers. The metrical parameters of both units are similar; one will be discussed in detail. The nickel atom is coordinated to two bis(carbene)borate ligands that are related by a crystallographic inversion center. Each of the six-membered bis(carbene)borate chelate rings adopts a boat conformation.

The *trans* double-boat conformation of **3** is reminiscent of the previously reported complex **4** (Figure 3), where nickel is coordinated to neutral bis(carbene)methane ligands.[9] Despite the difference in charge between the complexes **3** and **4**, the nickel coordination environment in these two complexes is very similar. Thus, the Ni–C bond lengths [1.940(3) and 1.949(3) Å] and the C–Ni–C bond angles [85.5(1)° and 94.5(2)°] in **3** are similar to those of **4** [bond lengths 1.936(4) and 1.928(4) Å, bond angles 83.6(2)° and 96.4(2)°]. The twist angles between the NHC rings and the metal–ligand coordination plane are also similar in both molecules; 57.30(8)° and 56.09(8)° in **3**, and 54.6(6) and 56.5(7)° in **4**. Thus, the steric pressures of the bulky chelating bis(carbene) ligands in **3** and **4** are similar, and both complexes adopt a conformation that minimizes the interactions between the bulky *tert*-butyl groups.[9]

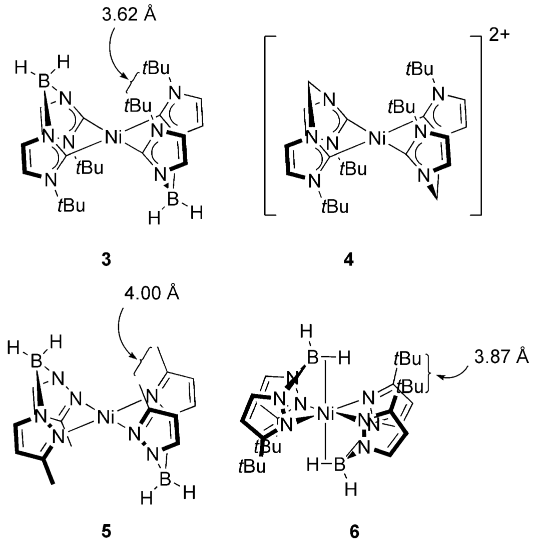

Figure 3. Structures of complexes **3**–**6**. The indicated intraligand distances are measured from the closest C···C distances between the respective ring substituents.

The ^1H NMR spectrum of **3** is consistent with the solid-state structure. The ^1H NMR spectrum has a single set of resonances for both of the bis(carbene)borate ligands, consistent with the *trans* double-boat conformation. Two resonances at δ = 5.42 and 4.30 ppm are observed for the diastereotopic BH_2 groups and a single resonance is observed for the *tert*-butyl groups at δ = 1.30 ppm. No change in the ^1H spectrum is observed in the temperature range –60–90 °C (C_7D_8).

It is also interesting to compare the properties of **3** with the related bis(pyrazolyl)borate complexes **5** and **6** (Figure 3). With small pyrazolyl substituents (i.e. H, Me), square-planar nickel(II) bis(pyrazolyl)borate complexes such as **5** are formed,[10] similar to the structure of **3**. However, where the pyrazolyl substituents are bulky *tert*-butyl groups, the resulting nickel complex **6** is paramagnetic and octahedral. In addition to the two bis(pyrazolyl)borate ligands, two agostic Ni–H–B bonds complete the metal's coordination sphere.[11]

The metrical parameters for the complexes **3**, **5** and **6** suggest that these structural differences are due to an interplay between the steric pressures of the ligand substituents and the donor ability of the bidentate ligand (Table 1). The square-planar complexes **3** and **5** have shorter bond lengths between the bidentate ligands and nickel than in the octahedral complex **6**. In the case of **3**, the short bond lengths and rigid heterocyclic rings create steric pressure between the bulky *tert*-butyl groups of the bis(carbene)borate ligand, which is reflected in the short C···C distance between the *tert*-butyl groups (3.62 Å). The longer Ni–N bonds in complex **6** and increased N–B–N angle reduce these interactions, although this is somewhat mitigated by the larger twist angles between the pyrazolyl rings and metal–ligand coordination plane (63.6 and 66.6°). The interaction between the *tert*-butyl groups in **6** is reduced, with a longer C···C distance between the *tert*-butyl groups (3.87 Å). Thus for the less strongly donating bis(pyrazolyl)borate ligand, the unfavorable steric interactions between the bulky *tert*-butyl groups are sufficient to destabilize the square-planar geometry. These interactions are not nearly as severe for **5**.

Table 1. Selected bond lengths [Å] and angles [°] from the X-ray crystal structures of **3**, **5** and **6**.

Distance/angle	**3**	**5**	**6**
Ni–C/N	1.940(3)	1.893(2)	2.113(3)
Ni–C/N	1.949(3)	1.889(2)	2.120(3)
C/N–Ni–C/N	85.5(1)	89.11(9)	86.6(1)
C/N–Ni–C/N	94.5(2)	90.89(9)	
N–B–N	105.1(3)	105.0(3)	109.3(3)

Density functional theory (B3LYP/SDD) was used to investigate the ability of the bis(carbene)borate ligand to stabilize the square-planar geometry. Geometry optimization of square planar **3** ($S = 0$) and octahedral **6** ($S = 1$) gave structures in good agreement with those determined crystallographically. The structures of the hypothetical octahedral bis(carbene)borate ($S = 1$) and square-planar bis(pyrazolyl)borate ($S = 0$) nickel(II) complexes were similarly optimized.[12]

Frequency calculations have been used to compare the relative free energies for nickel(II) complexes of both ligands in octahedral and square-planar geometries (Table 2). The theoretical calculations reproduce the qualitative experimental observations; i.e. the square-planar geometry has a lower free energy in the case of the bis(carbene)borate ligand, and the octahedral geometry has a lower free energy in the case of the bis(pyrazolyl)borate ligand. In the case of the bis(pyrazolyl)borate ligand the square-planar geometry is significantly higher in energy than the octahedral geometry (> 100 kcal/mol).[13] Analysis of the thermodynamic values reveals that changes in *enthalpy* dominate the observed free-energy differences. The relative ΔH values indicate that the strongly donating bis(carbene)borate ligand stabilizes the square-planar geometry by forming stronger bonds to nickel.

Table 2. Relative energies of the octahedral ($S = 1$) and square-planar ($S = 0$) isomer for the bis(carbene)borate and bis(pyrazolyl)borate nickel(II) complexes calculated by DFT.

Thermodynamic quantity[a]	Bis(carbene)borate	Bis(pyrazolyl)borate
ΔG	15	–113
ΔH	20	–110
ΔS	–5	–3

[a] Energies in kcal/mol. Energies are relative to that of the square planar ($S = 0$) structure.

Therefore, the combined crystallographic and computational data provides evidence that the stronger donor properties of the bis(carbene)borate ligand are sufficient to overcome the unfavourable steric interactions in the square-planar geometry.

Conclusions

In summary, we have reported a new synthetic route to bis(carbene)borate ligands. These ligands may provide an anionic alternative to neutral bidentate N-heterocyclic carbene based ligands.[14] Despite the bulky *tert*-butyl ring substituents, the strongly donating properties of the bis(carbene)borate ligand are able to stabilize a square-planar nickel(II) complex. In the case of the analogous bis(pyrazolyl)borate ligand, unfavorable steric interactions between the bulky *tert*-butyl groups are sufficient to destabilize the square-planar geometry.

Experimental Section

General Procedures: All manipulations were performed under dinitrogen by standard Schlenk techniques or in an M. Braun Labmaster glove box maintained at or below 1 ppm of O_2 and H_2O. Glassware was dried at 150 °C overnight. Diethyl ether, toluene and tetrahydrofuran were purified by the Glass Contour solvent purification system. Deuterated benzene was first dried with CaH_2, then over Na/benzophenone, and then vacuum transferred into a storage container. Before use, an aliquot of each solvent was tested with a drop of sodium benzophenone ketyl in THF solution. Celite was dried overnight at 200 °C under vacuum. Iodine, $NiCl_2(DME)$, CH_2Cl_2 and CD_3Cl were purchased from commercial suppliers and used as received. Trimethylamine–borane ($Me_3N:BH_3$) was sublimed before use. 1-*tert*-Butylimidazole[6b] and $NiCl_2(PR_3)_2$ (R = Me,[15] PPh_3[16]) were prepared using published procedures. Solid LDA was prepared by addition of *n*BuLi to a solution of diisopropylamine in pentane at –78 °C, filtered and stored at –35 °C. ^1H and $^{13}C\{^1H\}$ NMR spectroscopic data were recorded with a Varian Unity 400 spectrometer (400 MHz) at 22 °C. Resonances in the ^1H NMR spectra are referenced either to residual $CHCl_3$ at $\delta = 7.26$ ppm or C_6D_5H at $\delta = 7.15$ ppm, resonances in the $^{13}C\{^1H\}$ spectra are referenced to the $CDCl_3$ signal at $\delta = 77.2$ ppm. Elemental analysis data was collected by Desert Analytics, Tucson, AZ.

Synthesis of $H_2B(tBuImH)_2{}^+I^-$: This compound was prepared by adapting a literature procedure.[7] Under a stream of N_2, $Me_3N{\cdot}BH_3$ (4.79 g, 65.6 mmol) was added to toluene (100 mL) in a 500-mL round-bottom flask and stirred until the borane had completely dissolved. Iodine (8.33 g, 32.8 mmol) was added in small portions over a period of 10 min. After stirring for 30 min, 1-*tert*-butylimidazole (16.29 g, 131.2 mmol) was added in one portion. The mixture was stirred at room temperature for 1 h and then heated at reflux for 1 d. The reaction was cooled to room temperature, leading to the formation of a white precipitate, which was filtered, washed with CH_2Cl_2 and dried under vacuum (24.27 g, 95%), m.p. 166 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 9.15 (s, 2 H, Im-H), 7.20 (s, 2 H, Im-H), 7.17 (s, 2 H, Im-H), 3.45 (br., 2 H, BH_2), 1.67 [s, 18 H, $C(CH_3)_3$] ppm. $^{13}C\{^1H\}$ NMR (400 MHz, $CDCl_3$): δ = 135, 125, 118, 57, 29 ppm. $C_{14}H_{26}BIN_4$ (388.10): calcd. C 43.28, H 6.75, N 14.43; found C 42.83, H 6.47, N 14.11.

Synthesis of $H_2B(tBuIm)_2Li$: Lithium diisopropylamide (580 mg, 5.41 mmol) was added to a slurry of **1** (1.0 g, 2.58 mmol) in diethyl ether (10 mL). After stirring for 2 h, 1,4-dioxane (454 mg, 5.15 mmol) was added to the reaction. The mixture was stirred at room temperature for 1 h, filtered through Celite, and dried under vacuum to yield an off-white product (450 mg, 66%), which is both air and thermally sensitive. Crystals suitable for X-ray diffraction were grown from a saturated diethyl ether solution at –35 °C. ^1H NMR (C_6D_6): δ = 7.28 (s, 2 H, Im-H), 6.72 (s, 2 H, Im-H), 4.57 (br., 1 H, BH_2), 4.32 (br., 1 H, BH_2), 1.30 [s, 18 H, $(CH_3)_3C$] ppm. Despite repeated attempts, we have been unable to obtain reliable elemental analyses for this complex.

Synthesis of $Ni[H_2B(tBuIm)_2]_2$: Lithium diisopropylamide (580 mg, 5.41 mmol) was added to a slurry of **1** (1.00 g, 2.58 mmol) in THF (10 mL). After stirring for 2 h, a slurry of $NiCl_2(PPh_3)_2$ (843 mg, 1.29 mmol) in THF (5 mL) was added to the reaction mixture. Immediate formation of an orange-red solution occurred. The mixture was stirred at room temperature for 1 d and dried under vacuum. The residue was extracted into toluene, filtered through Celite, and dried under vacuum to yield a pale orange solid (670 mg, 90%), m.p. 235 °C (dec.). Conducting the reaction with $NiCl_2(PMe_3)_2$ and $NiCl_2(DME)$ resulted in the same product in 94% and 98% yield, respectively. The complex can also be prepared from isolated **2** and $NiCl_2(PPh_3)_2$. Crystals suitable for X-ray diffraction were grown from a saturated toluene solution at –35 °C. The complex is air stable, but decomposes slowly in CH_2Cl_2. ^1H NMR (C_6D_6): δ = 7.25 (s, 2 H, Im-H), 6.36 (s, 2 H, Im-H), 5.42 (br. s, 1 H, BH), 4.30 (br. s, 1 H, BH), 1.30 [s, 18 H, $(CH_3)_3C$] ppm. $C_{28}H_{46}B_2N_8Ni{\cdot}0.5P(C_6H_5)_3$ (706.18): calcd. C 61.42, H 7.73, N 15.49; found C 60.91, H 8.05, N 15.65.

DFT Calculations: Electronic structure calculations were performed using the quantum chemical program Gaussian 03.[17] Geometry optimizations were carried out by means of density functional theory (DFT) with the B3LYP hybrid functional which includes the Becke three-parameter exchange[18] and the Lee, Yang, and Parr correction functionals.[19] All calculations were performed using the SDD[20] basis set. Electronic energies and molecular frequencies were computed for the fully optimized structures of the singlet and triplet states of **3** and **6** in the gas phase. The latter, together with the standard expressions for an ideal gas in the canonical ensemble, were used to calculate the Gibbs free energies for different complexes in the gas phase by Gaussian 03. Unrestricted DFT was use to investigate the triplet spin states. Spin contaminations were estimated from deviations of the computed $\langle S^2 \rangle = S(S+1)$ with respect to the corresponding theoretical values.

CCDC-602792 (for **2**), and -287652 (for **3**), contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

Supporting Information (see footnote on the first page of this article): Full results of the computational investigation.

Acknowledgments

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