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Tris(carbene)borate Ligands Featuring Imidazole-2-ylidene, Benzimidazol-2-ylidene, and 1,3,4-Triazol-2-ylidene Donors. Evaluation of Donor Properties in Four-Coordinate $\{NiNO\}^{10}$ Complexes

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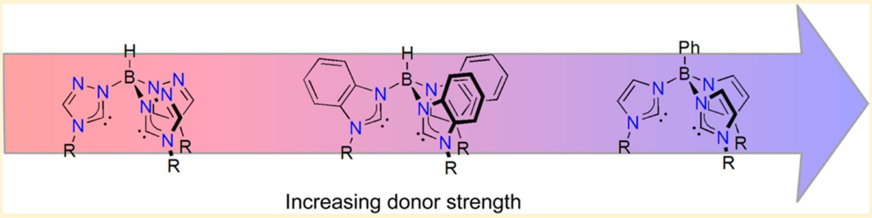
Supporting Information



ABSTRACT: The synthesis and characterization of new tris(carbene)borate ligand precursors containing substituted benzimidazol-2-ylidene and 1,3,4-triazol-2-ylidene donor groups, as well as a new tris(imidazol-2-ylidene)borate ligand precursor are reported. The relative donor strengths of the tris(carbene)borate ligands have been evaluated by the position of ν(NO) in four-coordinate $\{NiNO\}^{10}$ complexes, and follow the order: imidazol-2-ylidene > benzimidazol-2-ylidene > 1,3,4-triazol-2-ylidene. There is a large variation in ν(NO), suggesting these ligands to have a wide range of donor strengths while maintaining a consistent ligand topology. All ligands are stronger donors than Tp* and Cp*.

INTRODUCTION

The development of multidentate ligands incorporating multiple *N*-heterocyclic carbene (NHC) donors has been driven in part by the desire to develop new catalysts with increased stability. While the vast majority of multidentate NHC ligands are bidentate, higher denticity ligands, including tridentate[1] and even tetradentate[2] donors have been reported.[3] Tridentate ligands composed solely of NHC donors are mainly limited to a small number of C_3-symmetric tripodal ligands in which three imidazol-2-ylidene donors are connected through a central linker atom or group.[4−9]

Tripodal tris(carbene)borate ligands (Figure 1) connect three imidazol-2-ylidene donors through a central borate linker.[4] First generation tris(carbene)borate ligands (R = Me, Et; R′ = H) have been used to prepare octahedral manganese, iron, and cobalt complexes,[10,11] and more recently a copper(I) cluster.[12] Our group has developed synthetic routes for second generation tris(carbene)borate ligands in which the steric bulk has been increased (R = ^{t}Bu, Mes; R′ = H, Ph). As with the topologically related tris(pyrazolyl)borate ligands, the introduction of steric bulk allows for the synthesis of low coordinate transition metal complexes.[13] However, tris(carbene)borate ligands are substantially stronger donors than tris(pyrazolyl)-borates,[14] and have been shown to stabilize high valent complexes of first row transition metals,[15] including an isolable iron(V) nitride.[16]

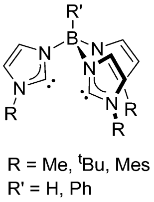


Figure 1. Tris(carbene)borate ligands based on imidazol-2-ylidene donors.

The donor strength of tris(pyrazolyl)borate ligands can be modified by suitable changes to the pyrazolyl ring substitutents.[17] Similar flexibility in the donor strength of tris(carbene)-borate ligands does not yet exist. In the case of monodentate NHC ligands, changing the *N*-substituents in imidazol-2-ylidenes does not typically have a major impact on the donor strength of the NHC ligand,[18] and thus similar changes to the donors of tris(carbene)borate ligand are not expected to have a major influence on the ligand donor strength. However, recent work has shown that NHCs based on donors other than imidazol-2-ylidene can lead to large changes in donor strength. Thus, both experimental and computational studies of

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monodentate NHC ligands show that carbenes derived from heterocycles other than imidazole can have substantially different donor strengths.[19]

In this paper we report the synthesis of new tris(carbene)-borate ligands, including ligands based on benzimidazol-2-ylidene and 1,3,4-triazol-2-ylidene donors. Studies of monodentate NHC ligands have shown that the donor strength of these ligands decreases according to the order: imidazol-2-ylidene > benzimidazol-2-ylidene > 1,3,4-triazol-2-ylidene (Figure 2) The donor properties of the new tris(carbene)borate ligands have been evaluated in four-coordinate $\{NiNO\}^{10}$ complexes, allowing their donor properties to be compared with other monoanionic facially coordinating ligands. A number of proposals regarding the nature of bonding between Ni and NO in complexes of this type have been put forth,[20] with the most comprehensive investigation describing the electronic structure as having multireference character; the dominant contributor being Ni(II) ($S_{Ni} = 1$) antiferromagnetically coupled to NO^- ($S_{NO} = 1$).[21]

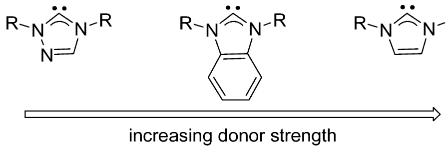


Figure 2. Relative donor strength of selected NHC ligands.

■ EXPERIMENTAL SECTION

General Considerations. Manipulations involving air-sensitive materials were performed under a nitrogen atmosphere by standard Schlenk techniques or in an M. Braun Labmaster glovebox. The quality of the glovebox atmosphere was periodically checked with a toluene solution of "titanocene".[22] Glassware was dried at 150 °C overnight. Diethyl ether, pentane, tetrahydrofuran (THF), and toluene were purified by the Glass Contour solvent purification system. Deuterated benzene was dried first over CaH_2, then over Na/benzophenone, before vacuum transfer into a storage container. Before use, aliquots of Et_2O, THF, and toluene were tested with a drop of Na/benzophenone in THF solution. *N,N*-Dimethylformamide azine dihydrochloride was prepared according to a literature procedure.[23] Florisil for column chromatography was dried by heating at 100 °C under vacuum for 8 h prior to use. The $\{NiNO\}^{10}$ synthons $Ni(PPh_3)_2(NO)Br$[24] and $Ni(NO)I(THF)_2$[25] were prepared according to literature procedures. All other reagents were purchased from commercial vendors and used as received. ^1H NMR data were recorded on a Varian Unity 400 spectrometer (400 MHz) at 22 °C. All resonances in the ^1H NMR spectra are referenced to residual $CHCl_3$ (δ 7.26 ppm), C_6D_5H (δ 7.16 ppm), C_4D_7HO (δ 3.57 and 1.72 ppm), and CD_2HCN (δ 1.94 ppm). Infrared spectra were recorded on Perkin−Elmer Spectrum One FTIR and Thermo Scientific Nicolet iS10 SMART iTR spectrophotometers, while UV−visible spectra were recorded on a Cary 100 spectrometer. Atmospheric pressure positive and negative ionization mass spectral data were collected using a Waters-Micromass ZQ2000 Mass Spectrometer. Cyclic voltammograms were recorded under a N_2 atmosphere using a CH Instruments CHI600D potentiostat in 0.1 M Bu_4PF_6 in THF with a glassy carbon working electrode, a Pt wire counter electrode, and a Ag^+/Ag reference electrode. All electrochemical data are referenced to the Cp_2Fe^+/Cp_2Fe couple. Elemental analyses were performed by Robertson Microlit Laboratories, Madison, NJ.

Synthesis of Compounds. *Preparation of 1-(Methylcyclohexyl)-imidazole (**1**).* A 250 mL flask was charged with imidazole (4.81 g, 0.700 mol, 1.0 equiv) and stirred with freshly ground KOH (5.94 g, 0.106 mol, 1.5 equiv) in dimethylsulfoxide (80 mL) for 3 h. The golden solution was cooled in ice, and then bromomethylcyclohexane (10.3 mL, 7.38 mmol, 1.05 equiv) added and maintained at 0 °C for 4 h and left to stir overnight at room temperature. Hexanes (80 mL) and diethyl ether (40 mL) were added, and the mixture was washed in a separatory funnel with saline water (3 × 150 mL). The residual dimethylsulfoxide was removed by rewashing the combined organic fractions with three more portions of water (80 mL). The solvents were removed in vacuo, and the product distilled with heating at reduced pressure to yield a hygroscopic white solid. The solid was dissolved in THF and dried over CaH_2 (11.3 g, 97%). The compound is spectroscopically identical to that reported in the literature.[26]

*Preparation of 1-(Methylcyclohexyl)benzimidazole (**2**).* A 1 L flask was charged with benzimidazole (19.1 g, 0.162 mol, 1 equiv) and stirred with freshly ground KOH (12.5 g, 0.223 mol, 1.37 equiv) in 220 mL of dimethylsulfoxide for 1 d. The yellow solution was cooled in ice, bromomethylcyclohexane (23.3 mL, 0.166 mol, 1.02 equiv) added, and the reaction allowed to warm to room temperature after 4 h. After stirring for 3 d, dichloromethane (250 mL) was added to the resultant slurry. The mixture was washed with distilled water (3 × 250 mL). The solvents were removed in vacuo, and the product sublimed with heating under reduced pressure to yield a white solid (32.1 g, 94%). ^1H NMR ($CDCl_3$): δ 7.85 (s, 1H, Bz), 7.82 (d, 1H, J_{HH} = 8.8, Bz), 7.40 (d, 1H, J_{HH} = 7.2, Bz), 7.29 (m, 2H, Bz), 4.00 (d, 2H, J_{HH} = 7.2, CH_2), 1.87 (m, 1H, Cy), 1.75−1.64 (m, 5H, Cy), 1.27−1.14 (m, 3H, Cy), 1.06−0.97 (m, 2H, Cy). ESI$^+$-MS 215 ($C_{14}H_{19}N_2^+$). Anal. Cald. for $C_{14}H_{18}N_2$: C 78.46, H 8.47, N 13.07. Found C 77.74, H 8.46, N 12.71. Multiple microanalysis trials were consistently low in carbon.

*Preparation of 4-Phenyl-1,2,4-triazole (**3**).* 4-Phenyl-1,2,4-triazole was prepared by modification of a literature procedure.[23] A 500 mL flask was charged with *N,N*-dimethylformamide azine dihydrochloride (20.9 g, 9.73 mmol, 1 equiv), freshly distilled aniline (8.87 mL, 9.73 mmol, 1 equiv), and benzene (100 mL). The reaction was heated at reflux overnight. After cooling to room temperature, the resultant mixture was dried in vacuo. Dichloromethane (100 mL) was added to the solid, and the mixture washed with alkaline water (3 × 200 mL). The solvent was removed from the organic layer under reduced pressure, and the white solid was purified by vacuum sublimation with heating to yield a white solid (8.61 g, 61%). The spectral data are identical to that reported in the literature.[27]

*Preparation of 4-(4-tert-Butylphenyl)-1,2,4-triazole (**4**).* 4-(4-*tert*-Butylphenyl)-1,2,4-triazole was prepared by modification of a literature procedure.[23] A 500 mL flask was charged with *N,N*-dimethylformamide azine dihydrochloride (16.4 g, 7.61 mmol, 1 equiv), 4-*tert*-butylaniline (12.3 mL, 7.61 mmol, 1 equiv), and benzene (80 mL). The reaction was heated at reflux overnight. After cooling the resultant mixture was dried in vacuo. Dichloromethane (100 mL) was added to the solid, and the mixture washed with alkaline water (3 × 200 mL). The solvent was removed from the organic layer under reduced pressure, and the resulting white solid was purified by vacuum distillation while heating. A white solid was obtained upon cooling (14.9 g, 97%). ^1H NMR ($CDCl_3$) δ 8.44 (s, 2H, Tz), 7.55 (d, J_{HH} = 8.4, 2H, *o*/*m*-$C_6H_4{}^tBu$), 7.32 (d, J_{HH} = 8.8, 2H, *o*/*m*-$C_6H_4{}^tBu$), 1.36 (s, 9H, ^tBu). ESI$^+$-MS 202 ($C_{12}H_{16}N_3^+$). Anal. Cald. for $C_{12}H_{15}N_3$: C 71.61, H 7.51, N 20.88. Found C 71.57, H 7.34, N 20.78.

*Preparation of 4-Mesityl-1,2,4-triazole (**5**).* 4-Mesitylene-1,2,4-triazole was prepared by modification of a literature procedure.[23] A 500 mL flask was charged with *N,N*-dimethylformamide azine dihydrochloride (20.6 g, 9.58 mmol, 1 equiv), 2,4,6-trimethylaniline (13.9 mL, 9.58 mmol, 1 equiv), and heated to 180 °C in chlorobenzene (100 mL) for 3 d. After cooling, hexanes (300 mL) was added to the vessel, and the mixture cooled to −25 °C. The supernatant was decanted from the solid that had precipitated. Dichloromethane (100 mL) was added to the solid, and the mixture washed with alkaline water (3 × 200 mL). The solvent was removed from the organic layer under reduced pressure to yield a white to off-white solid. Colored impurities were removed by recrystallization from CH_2Cl_2/Et_2O at −25 °C . The white solid obtained was purified by vacuum sublimation with heating (10.4 g, 58%). The spectral data are identical to that reported in the literature.[28]

*Preparation of [PhB(CyCH$_2$ImH)$_3$](OTf)$_2$ (**6**).* *N*-Methylcyclohexylimidazole **1** (3.50 g, 21.3 mmol, 3.04 equiv) was added to a solution of $PhBCl_2$ (1.11 g, 6.99 mmol, 1 equiv) in toluene (50 mL). After 30 min, TMSOTf (3.31 g, 14.9 mmol, 2.13 equiv) was added, and the mixture was heated at 110 °C for 1 d. After cooling to room temperature hexanes (100 mL) was added, leading to the formation of a white precipitate. The mixture was cooled to −25 °C overnight, and the resultant white solid collected by filtration and washed with hexanes. The solid was recrystallized from CH_2Cl_2/Et_2O at −25 °C. The resulting white solid collected by vacuum filtration, washed with hexanes, and dried in vacuo (5.14 g, 87%). ^1H NMR ($CDCl_3$): δ 8.49 (s, 3H, Im-H), 7.46 (s, 3H, Im-H), 7.18 (s, 3H, Im-H), 7.16 (m, 5H, B(C_6H_5)), 4.10 (d, 6H, J_{HH} = 7.6, CH_2), 1.80−1.66 (m, 17H, Cy), 1.27−1.19 (m, 10H, Cy), 1.04−0.97 (m, 6H, Cy). ESI$^+$-MS 879 ($C_{38}H_{54}N_6BF_6O_6S_2^+$). Anal. Cald. for $C_{38}H_{53}N_6BF_6O_6S_2$: C 51.94, H 6.08, N 9.56. Found C 51.88, H 6.12, N 9.39.

*Preparation of [PhB(PhTzH)$_3$](OTf)$_2$ (**7**).* 4-Phenyl-1,2,4-triazole **3** (5.83 g, 40.0 mmol, 3.05 equiv) was added to a solution of $PhBCl_2$ (2.15 g, 13.1 mmol, 1 equiv) in toluene (70 mL). After stirring for 30 min, TMSOTf (6.19 g, 27.6 mmol, 2.10 equiv) was added, and the mixture was heated at 110 °C for 1 d. After cooling to room temperature, a white solid was collected by vacuum filtration, washed with diethyl ether, and dried in vacuo (9.64 g, 94%). ^1H NMR ($CDCl_3$): δ 9.83 (s, 3H, Tz-H), 8.72 (s, 3H, Tz-H), 7.80 (m, 6H, *o*-C_6H_5), 7.58 (m, 9H, *m*/*p*-C_6H_5), 7.50 (m, 5H, B(C_6H_5)). ESI$^+$-MS 822 ($C_{32}H_{27}N_9BF_6O_6S_2^+$). Anal. Cald. for $C_{32}H_{26}N_9BF_6O_6S_2\cdot 0.25C_7H_8$: C 48.00, H 3.34, N 14.93. Found C 47.73, H 3.42, N 14.60.

*Preparation of [PhB(p-^{t}BuPhTzH)$_3$](OTf)$_2$ (**8**).* 4-(4-*tert*-Butylphenyl)-1,2,4-triazole **4** (1.98 g, 9.8 mmol, 3.03 equiv) was added to a solution of $PhBCl_2$ (0.513 g, 3.23 mmol, 1 equiv) in toluene (40 mL). After 30 min, TMSOTf (1.49 g, 6.70 mmol, 2.07 equiv) was added to the solidified reaction mixture, and the reaction heated at 110 °C for 1 d. After cooling to room temperature, the solid was collected by vacuum filtration and washed with hexanes. The white solid was then collected and dried in vacuo (2.49 g, 78%). ^1H NMR ($CDCl_3$): δ 9.76 (s, 3H, Tz-H), 8.67 (s, 3H, Tz-H), 7.71 (d, 6H, J_{HH} = 8.8, *o*/*m*-$C_6H_4{}^tBu$), 7.59 (d, 6H, J_{HH} = 8.8, *o*/*m*-$C_6H_4{}^tBu$), 7.49 (m, 5H, B(C_6H_5)), 1.33 (s, 27H, ^tBu). ESI$^+$-MS 990 ($C_{32}H_{27}N_9BF_6O_6S_2^+$). Anal. Cald. for $C_{32}H_{26}N_9BF_6O_6S_2$: C 46.78, H 3.19, N 15.34. Found C 46.58, H 3.27, N 15.07.

*Preparation of [PhB(MesTzH)$_3$](OTf)$_2$ (**9**).* 4-Mesitylene-1,2,4-triazole **5** (2.40 g, 12.8 mmol, 3.06 equiv) was partially dissolved by stirring in toluene (80 mL) overnight. Phenylboranedichloride, $PhBCl_2$ (0.665 g, 4.18 mmol, 1 equiv) was added to the mixture, and the reaction stirred for 8 h. Trimethylsilyl triflate, TMSOTf (1.91 g, 8.61 mmol, 2.06 eqiuv) was added to the cloudy solution, and the reaction heated at 110 °C for 1 d. The resultant mixture was dried in vacuo to yield a white solid. The solid was dissolved in dichloromethane (15 mL), and diethyl ether (130 mL) added to induce precipitation. The solution was stored at −25 °C overnight, and the resulting colorless crystals were dried in vacuo (3.70 g, 96%). ^1H NMR ($CDCl_3$): δ 9.99 (s, 3H, Tz), 8.55 (s, 3H, Tz), 7.46 (m, 3H, *m*/*p*-B(C_6H_5)), 7.32 (m, 2H, *o*-B(C_6H_5)), 7.03 (s, 6H, *m*-Mes), 2.34 (s, 9H, *p*-Me), 2.16 (s, 18H, *o*-Me). ESI$^+$-MS 948 ($C_{41}H_{45}N_9BF_6O_6S_2^+$). Anal. Cald. for $C_{41}H_{44}N_9BF_6O_6S_2\cdot H_2O$: C 50.99, H 4.80, N 13.05. Found C 50.93, H 4.63, N 13.30.

*Preparation of [HB(MeBzH)$_3$](Br)$_2$ (**10**).* A solution of *N*-methylbenzimidazole (3.54 g, 26.8 mmol, 3.08 eqiuv) and $Me_3N{:}BHBr_2$ (2.01 g, 8.69 mmol, 1 eqiuv) was heated in chlorobenzene (50 mL) at 150 °C for 1 d. After cooling to room temperature, the mixture was filtered to yield a white solid that was washed with diethyl ether and hexanes and then dried under reduced pressure. The white solid was dissolved in warm methanol (5 mL). Diethyl ether (50 mL) and hexanes (20 mL) were added to initiate precipitation, and the mixture was stored at −25 °C overnight. The solid that formed was separated from supernatant, and the process repeated twice more. The white solid obtained was dried in vacuo (4.6 g, 92%). ^1H NMR ($CDCl_3$): δ 10.82 (s, 3H, Bz), 7.75 (d, 3H, J_{HH} = 8.4, Bz), 7.70 (d, 3H, J_{HH} = 8.0, Bz), 7.59 (t, 3H, J_{HH} = 7.4, Bz), 7.52 (t, 3H, J_{HH} = 7.4, Bz), 5.70 (br s, 1H, B−H), 4.27 (s, 9H, Me). IR (ATR, cm^{-1}): 2482 (w, B−H). ESI$^+$-MS 568 ($C_{24}H_{25}N_6BBr_2^+$). Anal. Cald. for $C_{24}H_{25}N_6BBr_2\cdot H_2O$: C 49.18, H 4.64, N 14.34. Found C 49.18, H 4.64, N 14.35.

*Preparation of [HB(CyCH$_2$BzH)$_3$](Br)$_2$ (**11**).* A solution of *N*-methylcyclohexylbenzimidazole **2** (2.54 g, 11.8 mmol, 3.02 eqiuv) and $Me_3N{:}BHBr_2$ (0.896 g, 3.90 mmol, 1 equiv) was heated in refluxing chlorobenzene (30 mL) for 1 d. After cooling to room temperature, hexanes (60 mL) were added, and the solution was heated at 50 °C for 15 min. On cooling, the white solid was separated by vacuum filtration, washed with hexanes, and the residual solvent removed under reduced pressure The solid was purified by multiple recrystallizations from acetonitrile/Et_2O at −25 °C. The white solid was then dried in vacuo (2.8 g, 88%). ^1H NMR ($CDCl_3$): δ 10.47 (s, 3H, Bz), 8.05 (d, J_{HH} = 6.8, 3H, Bz), 7.66 (d, J_{HH} = 8.0, 3H, Bz), 7.56 (m, 6H, Bz), 5.83 (br s, 1H, B−H), 4.48 (d, J_{HH} = 7.2, 6H, CH_2), 1.97 (m, 3H, Cy), 1.74−1.62 (m, 14H, Cy), 1.15−1.06 (m, 16H, Cy). IR (ATR, cm^{-1}): 2431 (w, B−H). ESI$^+$-MS 815 ($C_{42}H_{56}N_6BBr_2^+$). Anal. Cald. for $C_{42}H_{55}N_6BBr_2\cdot H_2O$: C 60.59, H 6.90, N 10.09. Found C 60.21, H 6.76, N 9.98.

*Preparation of [HB(p-^{t}BuPhTzH)$_3$](Br)$_2$ (**12**).* A solution of 4-(4-*tert*-butylphenyl)-1,2,4-triazole **3** (2.16 g, 10.7 mmol, 3.05 equiv) and $Me_3N{:}BHBr_2$ (0.809 g, 3.51 mmol, 1 equiv) in chlorobenzene (30 mL) was heated at 150 °C for 1 d. The solution was allowed to cool to 40 °C followed by dropwise addition of diethyl ether (30 mL) then pentane (30 mL) with stirring. The mixture was then stored at −25 °C overnight. The resulting solid was separated from supernatant and dried under reduced pressure. Dichloromethane (50 mL) was added to the solid, and the solution washed with alkaline/saline water (1 × 10 mL). The organic layer was dried under reduced pressure to yield a white to off-white solid. Impurities were removed by recrystallization from acetonitrile/Et_2O at −25 °C. The white solid obtained was dried in vacuo (1.61 g, 59%). ^1H NMR ($CDCl_3$): δ 10.99 (s, 3H, Tz-H), 8.61 (s, 3H, Tz-H), 7.94 (d, J_{HH} = 8.8, 6H *o*/*m*-$C_6H_4{}^tBu$), 7.61 (d, J_{HH} = 8.8, 6H *o*/*m*-$C_6H_4{}^tBu$), 5.28 (br s, 1H, B−H), 1.33 (s, 27H, ^tBu). IR (ATR, cm^{-1}): 2518 (w, B−H). ESI$^+$-MS 776 ($C_{36}H_{47}N_9BBr_2^+$). Anal. Cald. for $C_{36}H_{46}N_9BBr_2$: C 55.76, H 5.98, N 16.26. Found C 56.03, H 6.27, N 16.46.

*Preparation of [HB(MesTzH)$_3$](Br)$_2$ (**13**).* A toluene (100 mL) solution of 4-mesitylene-1,2,4-triazole **5** (3.44 g, 18.4 mmol, 3.10 equiv) and $Me_3N{:}BHBr_2$ (1.37 g, 5.93 mmol, 1 eqiuv) in a round-bottom flask equipped with reflux condenser was heated at vigorous reflux for 3 d under nitrogen (heating in chlorobenzene at 150 °C results in the formation of impurities). The solution was allowed to cool, and the solvent removed under reduced pressure. The resulting off-white solid was dissolved in dichloromethane (80 mL) and washed with alkaline/saline water (1 × 15 mL). The organic layer was collected, and to the aqueous wash solution was added dichloromethane (30 mL) a second time. The organic layers were combined and dried under reduced pressure; the resulting solid was purified by recrystallization from acetonitrile/Et_2O at −25 °C. The white solid was dried in vacuo (3.25 g, 74%). ^1H NMR ($CDCl_3$): δ 11.24 (s, 3H, Tz-H), 8.44 (s, 3H, Tz-H), 7.01 (s, 6H, *m*-Mes), 5.28 (br s, 1H, B−H), 2.33 (s, 9H, *p*-Me), 2.19 (s, 18H, *o*-Me). IR (ATR, cm^{-1}): 2524 (w, B−H). ESI$^+$-MS 734 ($C_{33}H_{41}N_9BBr_2^+$). Anal. Cald. for $C_{33}H_{40}N_9BBr_2$: C 54.05, H 5.50, N 17.19. Found C 54.02, H 5.76, N 17.12.

*Preparation of PhB(CyCH$_2$Im)$_3$NiNO (**14**).* A slurry of [PhB(CyCH$_2$ImH)$_3$](OTf)$_2$ **6** (304 mg, 0.345 mmol, 1 equiv) in toluene (5 mL) was cooled to −78 °C. To the mixture was added lithium diisopropylamide (112 mg, 1.04 mmol, 3.01 equiv). The solution was stirred for 1 h at −78 °C, allowed to warm to room temperature and stirred for 3 h. To the resulting yellow solution was added Ni(NO)I(THF)$_2$ (124 mg, 0.345 mmol, 1 eqiuv) . The reaction was left to stir for 3 h at room temperature. The solution was filtered through Celite, and the filtrate dried under reduced pressure. The residue was then extracted with hexanes (15 mL) and filtered. The filtrate was dried under vacuum to give an orange-red solid (72 mg, 31%). ^1H NMR ($CDCl_3$): δ 7.86−7.85 (m, 2H, *m*-B(C_6H_5)), 7.70−7.65 (m, 2H, *o*-B(C_6H_5)), 7.56−7.51 (m, 1H, *p*-B(C_6H_5)), 6.83 (d, J_{HH} = 1.6, 3H, Im-H), 6.72 (d, J_{HH} = 2.0, 3H, Im-H), 4.07 (d, 6H, J_{HH} = 6.8, CH_2), 1.73−1.71 (m, 17H, Cy), 1.20 (m, 10H, Cy), 1.09−1.03

(m, 6H, Cy) . ^{13}C NMR ($CDCl_3$): δ 201.3 (carbene-C), 134.2, 127.5 127.4, 126.9, 122.8, 118.8, 57.0, 39.5, 30.7, 26.3, 25.8. IR (THF, cm^{-1}): 1693 (s, N−O). ESI^--MS 668 ($C_{36}H_{53}N_7BNiO^-$). UV−vis (THF): 441 nm (ε = 790 M^{-1} cm^{-1}). E_{ox} = −0.22 V (irr). Despite multiple attempts, we have been unable to obtain satisfactory microanalysis results.

*Preparation of HB(MeBz)$_3$NiNO (**15**).* To a solution of [HB(MeBzH)$_3$](Br)$_2$ **10** (0.345 g, 0.607 mmol, 1 equiv) in dichloromethane (7 mL) was added Ag_2O (0.227 g, 0.979 mmol, 1.6 eqiuv). The reaction was heated at 45 °C overnight in air, dried under vacuum, and an aliquot was analyzed by ^{1}H NMR spectroscopy. Two sets of resonances associated with the deprotonated ligand are observed. This is possibly due to the formation of different silver complexes, but was not further investigated, (^{1}H NMR (CD_3Cl_3)): Species A: δ 7.92 (s, 3H, Bz), 7.79 (d, J_{HH} = 8.0, 3H, Bz), 7.44 (m, 3H, Bz), 7.35 (m, 3H, Bz), 3.86 (s, 9H, Me); Species B: δ 7.75 (d, 3H, Bz), 7.57 (d, J_{HH} = 8.0, 3H, Bz), 7.43 (m, 3H, Bz), 7.34 (m, 3H, Bz), 3.69 (s, 9H, Me)). To the tris(carbene)borate ligand synthon was added THF (7 mL), the vessel charged with Ni(NO)Br(PPh_3)$_2$ (0.463 g, 0.668 mmol, 1.1 equiv) under nitrogen at room temperature, and stirred overnight. The solvent was removed under reduced pressure, and the residue extracted with toluene and filtered through Celite. The toluene filtrate was dried, and the residual solid was purified by column chromatography under nitrogen (Florisil, THF eluent). The orange-red colored fraction was collected and dried to give an orange-red solid (101 mg, 33%). ^{1}H NMR (C_6D_6): δ 7.86 (d, J_{HH} = 8.0, 3H, Bz), 7.12−7.05 (m, 6H, Bz), 6.77 (d, J_{HH} = 8.0, 3H, Bz), 5.79 (br s, 1H, B−H), 3.69 (s, 9H, Me). ^{13}C NMR ($CDCl_3$): δ 210.7 (carbene-C), 138.34, 136.81, 121.48, 120.78, 111.79, 109.06, 34.64. IR (THF, cm^{-1}): 2462 (w, B−H), 1714 (s, N−O). ESI^--MS 492 ($C_{24}H_{22}N_7BNiO^-$). Anal. Calcd. for $C_{24}H_{22}BN_7NiO$: C 58.35, H 4.49, N 19.85. Found C 58.04, H 4.48, N 19.74. UV−vis (THF): 433 nm (ε = 1180 M^{-1} cm^{-1}). E_{red} = −1.43 V (irr).

*Preparation of HB(CyCH$_2$Bz)$_3$NiNO (**16**).* To a solution of [HB(CyCH$_2$BzH)$_3$](Br)$_2$ **11** (341 mg, 0.418 mmol, 1 equiv) in acetonitrile (6 mL) was added Ag_2O (194 mg, 0.837 mmol, 2 equiv). The reaction was heated at reflux for 1 d, dried under vacuum. The poor solubility of the residue prevented any further characterization. To the tris(carbene)borate ligand synthon was added THF (6 mL) and Ni(NO)I(THF)$_2$ (0.105 g, 0.292 mmol, 0.7 equiv).[29] The reaction was stirred overnight under nitrogen at room temperature. The solvent was removed under reduced pressure, and the residue extracted with toluene and filtered through Celite. The toluene filtrate was dried, the resultant solid extracted with hexanes and filtered. The hexanes solution was dried under vacuum, and the residue washed with acetone followed by MeOH to give a red-orange colored solid (87 mg, 40% based on Ni). ^{1}H NMR (C_6D_6): δ 7.91 (d, J_{HH} = 7.6, 3H, Bz), 7.09−7.00 (m, 12H, Bz), 5.71 (br s, 1H, B−H), 4.33 (d, J_{HH} = 7.2, 6H, CH_2), 1.66 (br m, 7H, Cy), 1.57 (br m, 12H, Cy), 1.07 (br m, 14H, Cy). ^{13}C NMR ($CDCl_3$): δ 211.7 (carbene-C), 138.5, 136.6, 121.2, 120.4, 111.9, 109.5, 54.6, 38.8, 31.2, 26.3, 25.9. IR (THF, cm^{-1}): 2463 (w, B−H), 1711 (s, N−O). ESI^--MS 739 ($C_{42}H_{52}N_7BNiO^-$). UV−vis 435 nm (ε = 1490 M^{-1} cm^{-1}). E_{red} = −1.93 V (irr).

*Preparation of HB(p-^{t}BuPhTz)$_3$NiNO (**17**).* To a solution of [HB(*p*-^{t}BuPhTzH)$_3$](Br)$_2$ **12** (59 mg, 0.07 mmol, 1 equiv) in acetonitrile (4 mL) was added Ag_2O (35 mg, 0.15 mmol, 2.1 equiv). The reaction was heated at reflux for 1 d. The reaction mixture was dried under vacuum, followed by addition of KBr (14 mg, 0.11 mmol, 1.5 equiv) in THF (4 mL) and the reaction stirred under nitrogen overnight. The solvent was removed under reduced pressure, and the residue extracted with toluene and filtered through Celite. The filtrate was dried under reduced pressure to yield "HB(*p*-^{t}BuPhTz)$_3$K" (49 mg). An aliquot of the residue analyzed by ^{1}H NMR spectroscopy is consistent with 3-fold deprotonation (^{1}H NMR (C_6D_6)): δ 7.88 (s, 3H, Tz-H), 7.00 (d, J_{HH} = 8.4, 6H, *o*/*m*-$C_6H_4{}^t$Bu), 6.50 (d, J_{HH} = 8.4, 6H, *o*/*m*-$C_6H_4{}^t$Bu), 1.11 (s, 27H, ^{t}Bu). To the tris(carbene)borate ligand synthon was added a toluene (3 mL) solution of Ni(NO)I(THF)$_2$ (27 mg, 0.07 mmol, 1 equiv) at room temperature. The reaction was stirred overnight, the solution filtered through Celite, and dried in vacuo to give a maroon colored solid (29 mg, 52% based on Ni). ^{1}H NMR (C_6D_6): δ 7.55 (s, 3H, Tz-H), 7.39 (d, J_{HH} = 8.8, 6H, *o*/*m*-$C_6H_4{}^t$Bu), 7.04 (d, J_{HH} = 8.4, 6H, *o*/*m*-$C_6H_4{}^t$Bu), 1.03 (s, 27H, ^{t}Bu). ^{13}C NMR ($CDCl_3$): δ 199.6 (carbene-C), 151.2, 141.3, 135.2, 126.4, 122.6, 34.7, 31.3. IR (THF, cm^{-1}): 2544 (w, B−H), 1746 (s, N−O). ESI^--MS 700 ($C_{36}H_{43}N_{10}BNiO^-$). UV−vis (THF): 467 nm (ε = 500 M^{-1} cm^{-1}). E_{ox} = 0.38 V (irr); E_{red} = −1.78 V (irr).Despite multiple attempts, we have been unable to obtain satisfactory microanalysis data for this complex.

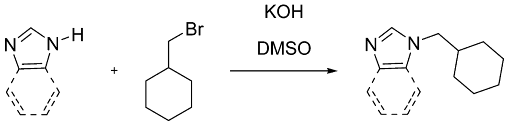
*Preparation of HB(MesTz)$_3$NiNO (**18**).* To a solution of [HB(MesTzH)$_3$](Br)$_2$ **13** (184 mg, 0.250 mmol, 1 equiv) in acetonitrile (5 mL) was added Ag_2O (93 mg, 0.40 mmol, 1.6 equiv). The reaction was heated at reflux for 1 d, the reaction mixture was then dried under vacuum, and KBr (45 mg, 0.38 mmol, 1.5 equiv) in THF (5 mL) was added to the residue and stirred under nitrogen overnight. The solvent was removed under reduced pressure, and the residue extracted with toluene and filtered through Celite. The filtrate was dried under reduced pressure to yield "HB(MesTz)$_3$K" (89 mg). An aliquot of the residue analyzed by ^{1}H NMR spectroscopy is consistent with 3-fold deprotonation (^{1}H NMR (C_6D_6)): δ 7.40 (s, 3H, Tz-H), 6.49 (s, 6H, *m*-Mes), 1.98 (s, 9H, *p*-Me), 1.48 (s, 18H, *o*-Me). To the tris(carbene)borate ligand synthon was added a toluene solution (3 mL) of Ni(NO)I(THF)$_2$ (52 mg, 0.14 mmol, 0.6 equiv).[29] The reaction was stirred overnight at room temperature. The solution was filtered through Celite and dried in vacuo to give a maroon colored solid (51 mg, 53% based on Ni). ^{1}H NMR ($CDCl_3$): δ 7.84 (s, 3H, Tz-H), 6.91 (s, 6H, *m*-Mes), 2.27 (s, 9H, *p*-Me), 1.97 (s, 18H, *o*-Me). ^{13}C NMR ($CDCl_3$): δ 202.1 (carbene-C), 142.5, 138.6, 134.6, 133.2, 129.0, 20.9, 18.0. IR (THF, cm^{-1}): 2537 (w, B−H), 1742 (s, N−O). ESI^--MS 658 ($C_{33}H_{37}N_{10}BNiO^-$). Anal. Calcd. for $C_{33}H_{37}BN_{10}NiO$: C 60.12, H 5.66, N 21.25. Found C 59.81, H 5.40, N 21.00. UV−vis (THF): 451 nm (ε = 620 M^{-1} cm^{-1}). E_{ox} = 0.40 V (irr); E_{red} = −1.83 V (irr).

Solid Angle Calculations. Solid angle calculations were performed using the program Solid-G.[30,31] The ligand coordinates used in the calculations were taken from X-ray crystal structure data of the corresponding $\{NiNO\}^{10}$ complexes. The metal ligand bond lengths were set at a distance of 2.28 Å. In cases where there was more than one molecule in the asymmetric unit, solid angles were calculated for each molecule, and the average value is reported. For the truncated calculations, ORTEP-3 (version 2.02)[32] was used to define a sphere of enclosure (4 Å, centered on Ni), and the resulting coordinates were used for solid angle calculations.

■ RESULTS AND DISCUSSION

Synthesis of Heterocycles. *N*-Methylcyclohexylimidazole **1** was prepared by the reaction of deprotonated imidazole and bromomethylcyclohexane (Scheme 1). Conducting the reaction at low temperature and allowing for long reaction times provides the product in almost quantitative yield following distillation. This procedure is a substantial improvement over that previously reported,[26] leading to substantially greater yields of product without the need for chromatography. The same procedure yields *N*-methylcyclohexylbenzimidazole as a colorless solid in almost quantitative yield. Both heterocycles have been spectroscopically characterized.

Scheme 1

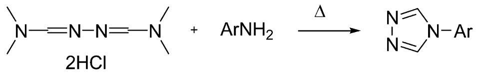


1, **2**

1-Aryl-1,3,4-triazoles were prepared by a similar procedure to that reported for the synthesis of 1-phenyl-1,3,4-triazole **3**.[23]

This synthetic route was successfully extended to the synthesis of *p*-^{t}BuPhTz **4** and MesTz **5** by reacting the dihydrochloride of *N*,*N*-dimethylformamide azine with *para-tert*-butylaniline and 2,4,6-trimethylaniline, respectively (Scheme 2).[23] Increasing the bulk of the aryl group requires longer reaction times and higher temperatures to proceed to completion, for example, for Ar = Ph, 1 d in refluxing benzene, while for Ar = Mes, 3 d heating in refluxing chlorobenzene. The colorless solids were purified by crystallization and characterized by ^{1}H NMR spectroscopy. Both PhTz **3**[23] and MesTz **5**[28] have been previously reported, while *p*-^{t}BuPhTz **4** is a new compound.

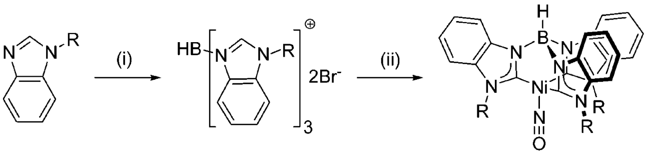
Scheme 2



Ar = Ph **3**, *p*-^{t}BuPh **4**, Mes **5**

Synthesis of Ligand Precursors. Tris(carbene)borate ligand precursors were prepared by the same synthetic routes used for the synthesis of other tris(imidazol-2-ylidene)borate ligands.[6,13] Thus, for example, tris(benzimidazolium)-hydroborane dications $HB(RBzH)_3Br_2$ (R = Me **10**, $CyCH_2$ **11**) were prepared by reaction of the appropriate benzimidazole with $Me_3N{:}BHBr_2$ in hot chlorobenzene, as with the synthesis of tris(imidazolium)hydroborane dications (Scheme 3).[13,33] As with the tris(triazolium)borane dications, the spectral data of these compounds is consistent with their proposed formulation. In the case of $HB(MeBzH)_3Br_2$ **10**, the resonance assigned to the acidic protons are observed at 10.82 ppm. Four resonances assigned to protons from the benzimidazolium group at 7.75, 7.70, 7.59, and 7.52 ppm, respectively, with the singlet at 4.27 ppm assigned to the methyl substituent.

Scheme 3. Synthesis of $HB(RBz)_3NiNO$ Complexes 15 and 16[a]



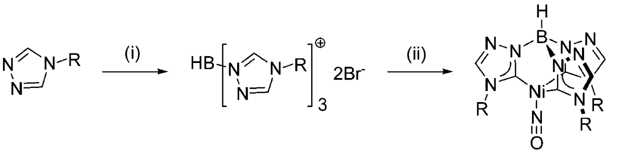
R = Me **15**, CH_2Cy **16**

[a] Reagents and conditions: (i) 0.33 $HBBr_2{:}NMe_3$, C_6H_5Cl, reflux; (ii) 1. Ag_2O, MeCN or CH_2Cl_2, Δ; 2. $Ni(NO)I(THF)_2$ or $Ni(NO)Br(PPh_3)_2$, THF.

Tris(triazolium)hydroborane dications were prepared in high yield by heating a toluene solution containing 3 equiv of the substituted triazole with $Me_3N{:}BHBr_2$ (Scheme 4).[33] We note that a bis(1,3,4-triazole)hydroborane cation has been previously reported, although a different synthetic route was used.[34] The resulting tris(triazolium)hydroborane dications **12** and **13** were characterized by ^{1}H NMR spectroscopy, ESI-MS and microanalysis. The triazolium salts are colorless air-stable compounds that are less soluble in nonpolar solvents than the related tris(imidazolium)hydroborane dications.[13] Their solubility is influenced by the nature of the triazole substituent, with the relative solubility decreasing in the order *p*-^{t}BuPh > Mes > Ph.

The spectral data for these compounds are consistent with their proposed formulation as tris(triazolium)hydroborane dications. Thus, for example, six resonances are observed in the ^{1}H NMR spectrum of $HB(MesTz)_3Br_2$ **13**. The most notable feature of the spectrum is the downfield singlet at 11.24 ppm, which is assigned to the three acidic triazole protons. As expected for the 2+ charge, all the other resonances arising from the substitued triazole moeity are shifted downfield from the corresponding triazole. Thus, the remaining triazole ring protons resonate as a singlet at 8.55 ppm, while resonances assigned to the mesityl substituent are observed at 7.01 (*m*-H), 2.33 (*p*-Me), and 2.19 ppm (*o*-Me). A broad resonance attributed to the B−H group is observed at 5.28 ppm. Similar features are observed in the ^{1}H NMR spectrum of HB(*p*-^{t}BuPhTzH)$_3$Br$_2$ **12**.

Scheme 4. Synthesis of $HB(RTz)_3NiNO$ Complexes 17 and 18[a]



R = *p*-^{t}BuC$_6$H$_5$ **17**, Mes **18**

[a] Reagents and conditions: (i) 0.33 $HBBr_2{:}NMe_3$, $C_6H_5CH_3$ or C_6H_5Cl, Δ; (ii) 1. Ag_2O, MeCN, Δ; 2. KBr, THF; 3. $Ni(NO)I(THF)_2$, THF.

We have also prepared a new tris(imidazolium)phenylborane dication starting from 1-methylcyclohexylimidazole, namely, $PhB(CyCH_2ImH)_3OTf_2$ **6**. This salt was prepared by the same method used for the synthesis of other tris(imidazolium)-phenylborane triflate salts and has similar spectral properties.[11,13] Colorless crystals of this salt were grown by diffusion of pentane into a CH_2Cl_2 solution at −25 °C. The solid state structure reveals the expected four-coordinate boron center that is bound to a phenyl and three imidazolium groups (Figure 3). Two triflate anions are also observed in the solid state structure.

NHC Formation. The new tris(carbene)borate ligands were generated by 3-fold deprotonation of the borane dications to yield the corresponding tris(carbene)borate ligands (Schemes 3 and 4). 3-fold deprotonation of the borane dications to generate the corresponding tris(carbene)borate ligands was found to be very sensitive to the nature of the base. While the tris(methylcyclohexylimidazol-2-ylidene)phenylborate ligand was readily formed by deprotonation of the corresponding imidazole borane dication with LDA, as previously reported,[13] similar attempts to generate the tris(benzimidazol-2-ylidene)-hydroborate and tris(1,3,4-triazol-2-ylidene)hydroborate ligands were unsuccessful. A library of bases was canvassed, including LDA, NaH, MeMgBr, all of which provided intractable mixtures of products, as determined by ^{1}H NMR spectroscopic analysis of the crude reaction mixtures.

The tris(benzimidazolium)hydroborane and tris(triazolium)-hydroborane dications could be deprotonated by reaction with Ag_2O in hot MeCN or CH_2Cl_2. While the insolubility of most of these materials prevented further characterization, subsequent reaction with $\{NiNO\}^{10}$ synthons confirmed that tris(benzimidazol-2-ylidene)hydroborate synthons were formed (see below).

Unfortunately, the ligand synthons formed from the tris(triazolium)hydroborane dications and Ag_2O did not cleanly transfer to nickel. These compounds were instead treated with KBr to species tentatively formulated as potassium tris(1,3,4-

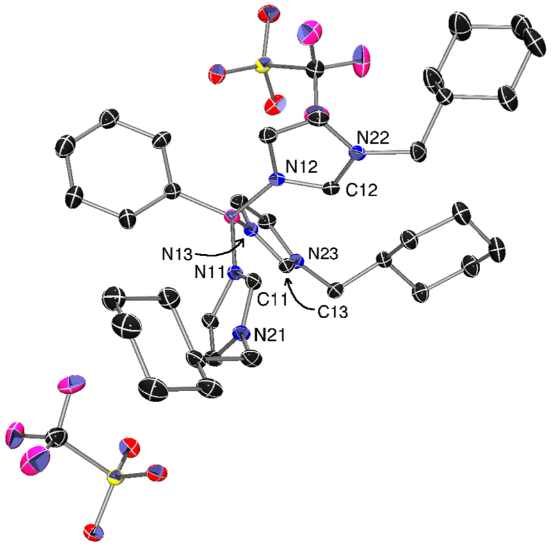


Figure 3. X-ray crystal structure of PhB(CyCH$_2$ImH)$_3$OTf$_2$ **6**. Thermal ellipsoids shown at 50% probability, hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (deg): C(11)−N(11) 1.337(3); C(11)−N(21) 1.322(3); C(12)−N(12) 1.332(3); C(12)−N(22) 1.319(3); C(13)−N(13) 1.331(3); C(13)−N(23) 1.328(3; N(11)−C(11)−N(21) 109.8(2); N(12)−C(12)−N(22) 110.1(2); N(13)−C(13)−N(23) 110.2(2).

triazol-2-ylidene)hydroborates. Because of their greater solubility, deprotonation of the carbene precursors could be confirmed by ^{1}H NMR spectroscopy. Thus, for example, four resonances are observed in the ^{1}H NMR spectrum of product prepared from [HB(*p*-^{t}BuTz)$_3$](Br)$_2$: a singlet at δ 7.88 ppm, assigned to the remaining triazolylidene proton, doublets at δ 7.00 and 6.50 ppm, assigned to the protons of the *p*-*tert*-butylphenyl ring and a singlet at δ 1.11 ppm, assigned to the *tert*-butyl group. The resonance for the B−H group is not observed, presumably because of quadrupolar broadening.

Synthesis and Characterization of Nickel Nitrosyl Complexes. The ligand synthons were not isolated, but instead were used in a one-pot reaction with the {NiNO}^{10} synthons Ni(NO)Br(PPh$_3$)$_2$[24] or Ni(NO)I(THF)$_2$,[25] leading to formation of new tris(carbene)borate {NiNO}^{10} complexes (Schemes 3 and 4). The nickel nitrosyl complexes were found to be diamagnetic, air stable complexes, characterized by a number of techniques including ^{1}H and ^{13}C{^{1}H} NMR, UV−vis, and IR spectroscopy, single crystal X-ray diffraction, CV, microanalysis, and ESI-MS. When prepared using Ni(NO)Br(PPh$_3$)$_2$, the complexes were often contaminated with PPh$_3$, PPh$_3$O, and PPh$_3$AgBr byproducts. For some complexes, these byproducts could be removed by chromatography on a Florisil column in an air-free environment. However, other complexes, for example, PhB(CyCH$_2$Im)$_3$NiNO **14**, were found to decompose on the column, even when other solid supports were used. The use of Ni(NO)I(THF)$_2$[25] as the {NiNO}^{10} synthon was not universally successful, and in some cases the use of a sub-stochiometric amount of the reagent was necessary to avoid the formation of side products, for example, in the case of HB(CyCH$_2$Bz)$_3$NiNO **16**.

The complexes PhB(CyCH$_2$Im)$_3$NiNO **14**, HB(MeBz)$_3$NiNO **15**, HB(CyCH$_2$Bz)$_3$NiNO **16**, HB(*p*-^{t}BuPhTz)NiNO **17**, and HB(MesTz)NiNO **18** were also crystallographically characterized.[35] The molecular structures of these complexes (Figure 4 and Supporting Information) reveal the expected four-coordinate metal center bound to the tripodal tris(carbene)borate ligand and terminal nitrosyl ligand. The complexes all have similar metrical parameters around the nickel center, regardless of the nature of the tripodal ligand. Thus, for example, the Ni−NO bond lengths in these complexes are in the narrow range 1.640(2)−1.646(2) Å, which compares well with the Ni−N bond length of 1.620(5) Å observed for HB(^{t}BuIm)$_3$NiNO.[14] Similarly, the Ni−C bonds show little variation between the different tripodal ligands. There is greater variability in the Ni−N−O bond angle, which varies from 169.3(2)°−176.3(3)°, compared with 178.5(4)° for HB(^{t}BuIm)$_3$NiNO.[14] However, it is likely these differences are due to packing forces in the solid state, as evidenced by the variation in the Ni−N−O bond angle (169.3(2)−174.8(2)°) for the four independent molecules of HB(MeBz)$_3$NiNO **15** in the unit cell. There do not appear to be any trends in metrical

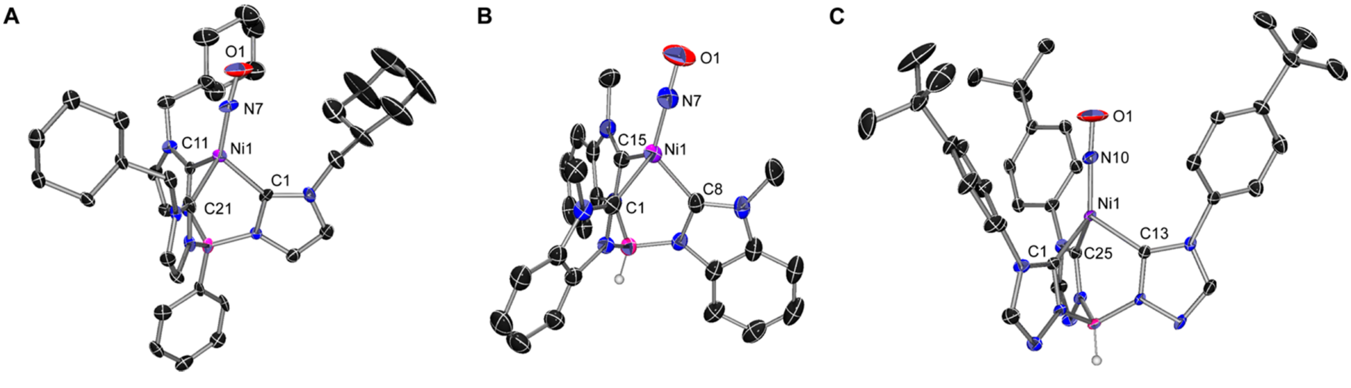


Figure 4. X-ray crystal structures of representative nickel nitrosyl complexes. Thermal ellipsoids shown at 50% probability, most hydrogen atoms omitted for clarity. (A) PhB(CyCH$_2$Im)$_3$NiNO **14**. One of three independent molecules in the asymmetric unit. Selected bond lengths (Å) and angles (deg): Ni(1)−N(7) 1.643(10); Ni(1)−C(1) 1.982(11); Ni(1)−C(11) 1.939(11); Ni(1)−C(21) 1.974(13); N(7)−Ni(1)−C(1) 122.8(5); N(7)−Ni(1)−C(11) 123.2(5); N(7)−Ni(1)−C(21) 130.3(5); Ni(1)−N(7)−O(1) 173.7(11). (B) HB(MeBz)$_3$NiNO **15**. One of four independent molecules in the asymmetric unit. Selected bond lengths (Å) and angles (deg): Ni(1)−N(7) 1.646(2); Ni(1)−C(15) 1.945(3); Ni(1)−C(1) 1.959(3); Ni(1)−C(8) 1.961(3); N(7)−Ni(1)−C(15) 118.85(11); N(7)−Ni(1)−C(1) 132.30(11); N(7)−Ni(1)−C(8) 123.90(11); O(1)−N(7)−Ni(1) 169.3(2). (C) HB(*p*-^{t}BuPhTz)$_3$NiNO **17**. Selected bond lengths (Å) and angles (deg): Ni(1)−N(10) 1.640(2); Ni(1)−C(1) 1.979(3); Ni(1)−C(13) 1.989(3); Ni(1)−C(25) 1.985(3); N(10)−Ni(1)−C(1) 125.68(12); N(10)−Ni(1)−C(13) 122.51(12); N(10)−Ni(1)−C(25) 126.90(14); O(1)−N(10)−Ni(1) 176.3(3).

parameters that are ligand-dependent, and thus X-ray crystallography is unable to differentiate the donor abilities of the different tris(carbene)borate ligands, for example, from N−O or Ni−C bond lengths.

Infrared spectroscopy was used to evaluate the relative donor ability of the tris(carbene)borate ligands in solution, specifically from ν_{NO} (Table 1). On the basis of the bonding descriptions for structurally related Tp*NiNO, the impact of the tripodal ligand donor strength on ν_{NO} can be formulated in two ways. In the traditional formulation,[20a] the magnitude of ν_{NO} is related to the extent of π-backbonding from the Ni(0) center to the π^* orbitals of coordinated NO^+.[36] Thus, increasing the electron-releasing ability of the tripodal ligand leads to a reduction in ν_{NO}. In the revised formulation, the electronic structure is described as having multireference character with $Ni^I(S = 1/2)-NO^0(S = 1/2)$, $Ni^{II}(S = 0)-NO^-(S = 0)$, and $Ni^{II}(S = 1)-NO^-(S = 1)$ configurations.[21] In this description, the magnitude of ν_{NO} can be related to the relative stabilization of these different electronic configurations. Specifically, increasing the donor strength of the tripodal ligand will stabilize the Ni(II) configurations at the expense of the Ni(I) configuration. Since the Ni(II) configurations have populated N−O π^* orbitals, this is expected to reduce the overall N−O bond order. Thus, both electronic structure descriptions predict that increasing the donor strength of the tripodal ligand will result in a lowering of ν_{NO}.

Table 1. Infrared Spectroscopic Data for Four-Coordinate Tris(carbene)borate $\{NiNO\}^{10}$ Complexes Measured in THF

tris(carbene)borate	solution ν_{NO} (cm^{-1})	reference
$PhB(CyCH_2Im)_3^-$	1693	this work
$PhB(MeIm)_3^-$	1697	14
$PhB(^tBuIm)_3^-$	1701	14
$PhB(MesIm)_3^-$	1724	14
$HB(CyCH_2Bz)_3^-$	1711	this work
$HB(MeBz)_3^-$	1714	this work
$HB(MesTz)_3^-$	1742	this work
$HB(p\text{-}^tBuPhTz)_3^-$	1746	this work

The IR data reveal that, in general, the donor strength of these tris(carbene)borate ligands decreases in the order: imidazol-2-ylidene > benzimidazol-2-ylidene > 1,3,4-triazol-2-ylidene, which correlates well with the trend observed for monodentate NHC ligands.[19a,c,35] It has been shown in at least one instance that the nature of the fourth group on the boron atom (i.e., H^- vs Ph^-) has little impact on the donor strength of the tris(carbene)borate ligand.[14] It is notable that tris(carbene)borates provide an exceptional degree of electronic tunability, with ν_{NO} varying over a range of more than 50 cm^{-1}. This should be compared with the smaller range of 25 cm^{-1} observed for $Rh(CO)_2(NHC)I$ complexes, where the monodentate NHC varied from relatively weakly donating 1,3-dimethylperimidin-2-ylidene to very strongly donating 1,2,3-trimethyl-4-isopropylpyrazolin-5-ylidene.[19]

Interestingly, and in contrast to monodentate NHC ligands, changing the ligand substituent influences the donor strength of tris(carbene)borate ligands.[19] Thus, for example, alkyl substituted ligands have a greater donor ability than aryl, as reflected in the data for the imidazol-2-ylidene series. In fact, replacing alkyl substituents in the tris(imidazol-2-ylidene)borates by an aryl group attenuates donor strength sufficiently to make them similar to the alkyl-substituted tris(benzimidazol-2-ylidene)borate. It is likely that the three NHC donors in tris(carbene)borate ligands magnify these effects as compared to the monodentate analogues, allowing for fine-tuning of the tripodal ligand donor strength. Interestingly, for the imidazol-2-ylidene based ligands, the tris(carbene)borate donor strength does not follow the trend that would be predicted from the inductive properties of the alkyl donors, with the *tert*-butyl substituted ligand being the least donating. For this ligand it is likely that steric crowding resulting from this very bulky ligand reduces orbital overlap between nickel and the tris(carbene)borate. Evidence for this hypothesis comes from the average Ni−C bond length, which is longer for $PhB(^tBuIm)_3NiNO$ (2.003(1) Å)[14] than for $PhB(CyCH_2Im)_3NiNO$ **14** (1.969(4) Å).

Comparing the donor properties of these tris(carbene)borate ligands with related facially coordinating ligands is instructive (Table 2). Thus, although the tris(1,3,4-triazol-2-ylidene)borates are the weakest of the tris(carbene)borate donors, they are still more strongly donating than either Cp* and Tp*. In fact, the tris(1,3,4-triazol-2-ylidene)borates bridge a gap in donor strength between these classical ligands and the stronger tris(phosphino)borate[39] and tris(thioimidazolyl)borate (TmR^-) donors,[36] while the tris(benzimidazol-2-ylidene)borates bridge a similar gap between these two ligands and the alkyl-substituted tris(imidazol-2-ylidene)borates. An important difference with these other ligand classes is that the ligand topology is consistent for all three types of tris(carbene)borate. Thus, the rigid tris(carbene)borates span a greater range of donor strengths than either the tris(phosphino)borate or tris(thioimidazolyl)borate ligands[6] while maintaining a consistent topology.

Table 2. Solution IR Spectroscopic Data for Selected Four-Coordinate $\{NiNO\}^{10}$ Complexes

ligand	ν_{NO} (cm^{-1})	reference
Cp*	1787	37
Tp*	1786	38
$PhB(CH_2PPh_2)_3^-$	1737	39
Tm^tBu^-	1741	36

Attempts to use other physical measurements to delineate the donor properties of the tris(carbene)borate ligands were not successful, for example, $^{13}C\{^1H\}$ NMR, UV−vis, CV. Thus, for example, while the resonances attributed to the carbene carbon of the tris(carbene)borate ligand could be readily identified in the $^{13}C\{^1H\}$ NMR spectra, the chemical shifts are similar for all complexes, and there is no systematic order related to the donor strength of the ligand.[35] This is similar to observations reported for a large series of monodentate carbene ligands in $Rh(CO)_2(NHC)I$ complexes.[19a]

The range of substituents has also allowed us to explore the steric properties of the tris(carbene)borate ligands using solid angles. The solid angle can be visualized as follows: a light source is placed at the metal center that is circumscribed by a sphere of radius r. Since the ligand blocks the light source, it will cast a shadow of area A on the inside of the sphere, allowing the solid angle to be calculated in steradians as $\Omega = A/r^2$. A convenient way of expressing the solid angle is as the percentage of the sphere's surface that is covered by the ligand shadow, $G = 100\ \Omega/4\pi$ (4π is the solid angle of a sphere in steradians).[30]

The percent coverage of a sphere (G) for the alkyl-substituted tris(carbene)borate ligands were calculated from the coordinates determined by X-ray crystallography (Table 3).[35] As expected, these calculations reveal that the methyl-subtituted tris(carbene)borate ligand is the least encompassing ligand, but somewhat surprisingly, the *tert*-butyl and methylcyclohexyl substituted ligands appear to exert a similar steric effect. However, when G was determined with the ligand artificially truncated at a radius 4 Å from the metal center, the methylcyclohexyl and methyl substituents were found to be similar in size. Similar observations have been made for some monodentate NHC ligands.[40] The truncated value of G, which approximates the steric profile of the ligand as experienced in the first coordination sphere of nickel, suggests that the methylcyclohexyl substituent provides an open environment in the immediate vicinity of the metal center, while the large value of G for the full ligand suggests that this substituent may also be sufficiently bulky to stabilize low coordination numbers.

Table 3. Solid Angle Data (G)[a] for Selected Alkyl-Substituted Tris(carbene)borate Ligands in $\{NiNO\}^{10}$ Complexes

ligand	full ligand	truncated ligand[b]
$HB(MeBz)_3^{-c}$	36.9	37.0
$HB(CyCH_2Bz)_3^-$	56.3	36.9
$PhB(CyCH_2Im)_3^{-c}$	52.8	39.0
$HB(^tBuIm)_3^-$	53.2	53.2
Tp*	37.0	37.0
$PhB(CH_2PPh_2)_3^-$	55.4	54.1

[a] Solid angles expressed as percentage coverage of a sphere. The G values were calculated using a metal ligand distance of 2.28 Å. [b] Ligand was truncated at a radius of 4 Å from the metal center. [c] Average values for the four independent molecules in the asymmetric unit.

For comparative purposes, G was also calculated for two other tripodal ligands using the X-ray crystal structure data of Tp*NiNO[20b] and $PhB(CH_2PPh_2)_3NiNO$.[39] The data suggest, not surprisingly, that the steric impact of tris(carbene)borate and tris(pyrazolyl)borate ligands are similar, as shown by the similar sizes of the methyl-substituted ligands $HB(MeBz)_3^-$ and Tp*. The solid angle data also reveal that the very bulky $HB(^tBuIm)_3^-$ ligand is similar in size to the tris(phosphino)borate ligand $PhB(CH_2PPh_2)_3^-$.[41] Interestingly, the solid angle of the tris(phosphino)borate ligand is dependent on the coordination number, and decreases to 45.96% of a sphere (truncated at 4 Å) for the six-coordinate complex $PhB(CH_2PPh_2)_3Fe(\kappa^2\text{-}OAc)(N_2H_4)$,[42] highlighting the flexibility of this ligand.

CONCLUSIONS

The synthesis and donor properties of new tris(carbene)borate ligands incorporating a range of benzimidazol-2-ylidene and 1,3,4-triazol-2-ylidene donors have been reported. Changing the nature of the carbene donor results in predictable changes to the donor properties of these ligands, with the relative donor strength following the order imidazol-2-ylidene > benzimidazol-2-ylidene >1,3,4-triazol-2-ylidene, as determined by IR spectroscopy of four-coordinate $\{NiNO\}^{10}$ complexes. Moreover, in contrast to monodentate NHCs, the nature of the carbene *N*-substituent also has an impact on the donor strength of the ligand, with alkyl substituted ligands being stronger donors than aryl-substituted. A caveat to this observation is that very bulky substituents appear to hinder effective orbital overlap, thereby reducing the effective donor strength. Similarly to tris(pyrazolyl)borates, the consistent topology of the tris(carbene)borate ligand class allows for predictable changes to their steric properties. An interesting finding in this regard is that certain *N*-substituents, for example, methylcyclohexyl, may provide an open environment close to the metal center, while still providing a sufficiently bulky profile to stabilize low coordination numbers. The combination of exceptional electronic tunability and the consistent topology of the tris(carbene)borate ligand class is likely to allow for predictable variation in the properties of their transition metal complexes.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Further details on the solid angle calculations, X-ray crystallographic data for all structurally characterized compounds, including crystallographic information files (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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