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Heteroleptic Nickel Complexes of a Bulky Bis(carbene)borate Ligand

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Abstract

Bis(carbene)borate ligand transfer to the nickel nitrosyl synthon $\text{Ni}(\text{NO})(\text{PPh}_3)_2\text{Br}$ provides the new nickel nitrosyl complex $\text{Ph}_2\text{B}(\text{tBuIm})_2\text{Ni}(\text{NO})(\text{PPh}_3)$. The solid state structure reveals a trigonal pyramidal nickel ion with a very long bond to the apical PPh_3 ligand. The complex reversibly dissociates PPh_3 in solution to afford three-coordinate $\text{Ph}_2\text{B}(\text{tBuIm})_2\text{Ni}(\text{NO})$, with NMR data providing evidence for PPh_3 binding at low temperatures. Ligand transfer to $\text{Ni}(\text{PMe}_3)_2\text{Cl}_2$ provides the square planar complex, $\text{Ph}_2\text{B}(\text{tBuIm})_2\text{Ni}(\text{PMe}_3)\text{Cl}$, which shows no evidence for rearranging to the form a homoleptic complex with two bis(carbene)borate ligands. This complex is a suitable synthon for the $[\text{Ph}_2\text{B}(\text{tBuIm})_2\text{Ni}]^+$ fragment, as demonstrated by the synthesis of the π -allyl complex $\text{Ph}_2\text{B}(\text{tBuIm})_2\text{Ni}(\eta^3\text{-C}_7\text{H}_7)$. The π -allyl complex reacts with O_2 to provide benzaldehyde and an unstable complex that is tentatively identified as the nickel(II) hydroxide $[\text{Ph}_2\text{B}(\text{tBuIm})_2\text{Ni}(\mu\text{-OH})]_2$.

Keywords

Nickel complexes; nitrosyl ligands, NHC complexes, bidentate ligands; dioxygen reactivity

Introduction

Among his many scientific contributions, Bill Jones has elegantly demonstrated the utility of strongly donating bulky ligands in nickel chemistry. For example, the Ni(dippe) fragment (dippe = $^i\text{Pr}_2\text{PCH}_2\text{CH}_2\text{P}^i\text{Pr}_2$) is notable for its involvement in organonitrile C-CN bond cleavage¹ as well as thiophene and benzothiophene desulfurization.² Moreover, using this same fragment, Bill's group foreshadowed a new era in metal-ligand multiple bonds³ by providing some of the first evidence for a terminal metal-ligand multiple bond involving a late 3d transition metal, in the form of a transient nickel sulfide.⁴

The strong σ -donor nature and synthetic flexibility of *N*-heterocyclic carbenes (NHC) have driven the development of these ligands well beyond their initial application as phosphine surrogates. Although the utility of nickel complexes with monodentate NHCs is relatively well established,⁵ nickel complexes with bidentate bis(carbene) donor ligands are still relatively rare.^{6,7,8,9} Despite this limited body of work, the application of bidentate bis(carbene) nickel complexes in metal-ligand multiple bond chemistry^{8e} and C-C bond cleavage^{8h} hints at the potential functionality of the nickel bis(carbene) fragment. One impediment towards realizing this potential is the highly favorable formation of undesired square planar Ni(II) complexes containing two bis(carbene) ligands, even with quite bulky bis(carbene) ligands.⁹

We have had a longstanding interest in the chemistry of 3d metals based on borate ligands containing multiple NHC donors,¹⁰ including bis(carbene)borates. While the combination of negative charge and strong σ -donors may be expected to favor higher oxidation states, these ligands have also shown affinity for low valent metals, for example in providing the first access to square planar Fe(0).¹¹ In the case of nickel, we previously reported the synthesis of the square planar homoleptic Ni(II) complex of the dihydrobis(*tert*-butylimidazol-2-ylidene)borate ligand, $[\text{H}_2\text{B}(\text{tBulm})_2]_2\text{Ni}$, however we were unable to prepare heteroleptic Ni(II) complexes containing a single bis(carbene)borate ligand.⁹ The formation of four-coordinate homoleptic complexes of this ligand is similarly facile for other 3d metals, providing complexes such as $[\text{H}_2\text{B}(\text{tBulm})_2]_2\text{Fe}$ ¹² and $[\text{H}_2\text{B}(\text{tBulm})_2]_2\text{Co}$.^{12b}

We have subsequently found that simple modification of this bis(carbene)borate ligand, namely to diphenylbis(*tert*-butylimidazol-2-yl)borate,¹³ allows for the isolation of stable low-coordinate iron complexes that show no evidence for rearrangement to the undesired homoleptic analogues (Figure 1).¹⁴ We hypothesized that this modified ligand would similarly provide access to low coordinate Ni(II) complexes in a strongly donating environment. In this paper, we report on the synthesis and reactivity of heteroleptic nickel(II) bis(carbene)borate complexes using this modified ligand. These complexes also provide additional evidence for the strong donor ability of the bis(carbene)borate ligand.

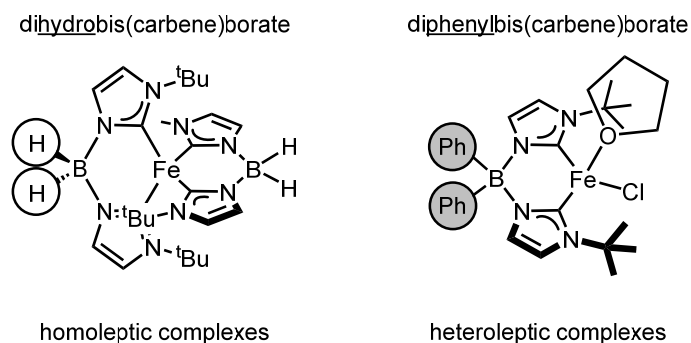


Figure 1. Bis(carbene)borate ligands to stabilize homoleptic and heteroleptic iron(II) complexes.

Experimental

General Considerations. All manipulations involving air- and moisture sensitive compounds and their preparations were performed under a nitrogen atmosphere by standard Schlenk techniques or in an M. Braun Labmaster glovebox. Glassware was dried at 130 °C overnight before cooling under dynamic vacuum in an antechamber. Diethyl ether (Et₂O), *n*-pentane, tetrahydrofuran (THF), and toluene were purified by the Glass Contour solvent purification system. Before use, an aliquot of each solvent was tested with 1 drop of solution of sodium benzophenone ketyl in THF. Celite was dried under vacuum at 130 °C overnight. The reagents Ph₂B(^tBulmH)₂(OTf)¹³ and Ni(NO)Br(PPh₃)₂¹⁵ were prepared according to literature procedures. All reagents were purchased from commercial vendors and used as received. Benzene-d₆ (C₆D₆, Cambridge Isotope Laboratories) was degassed by three consecutive freeze-pump-thaw cycles on a Schlenk line and placed over molecular sieves for at least 12 h prior to use. THF-d₈ (Sigma-Aldrich) was dried over molecular sieves overnight prior to use. ¹H NMR data were recorded on a Varian Unity 400 spectrometer (400 MHz) at 25 °C. VT IR data were recorded using a Mettler Toledo ReactIR 15.

Synthesis of Ph₂B(^tBulm)₂Ni(NO)(PPh₃)

A solution of LDA (39 mg, 0.36 mmol) in toluene (2 mL) was added to a slurry of Ph₂B(^tBulm)₂OTf (100 mg, 0.18 mmol) in toluene (3 mL). After stirring at ambient temperature for 2 h, Ni(PPh₃)₂(NO)Br was added as a solid. The resulting dark green solution was stirred for 3 h before the volatiles were removed under reduced pressure. The residue was extracted with pentane, filtered through Celite and dried *in vacuo* to yield a purple solid (86 mg, 96 %). Crystals suitable for X-ray diffraction were grown from concentrated pentane at -35 °C. The NMR spectral data is consistent with an equilibrium involving loss of PPh₃ from Ph₂B(^tBulm)₂Ni(NO)(PPh₃), see the discussion for details. ¹H NMR (400 MHz, C₆D₆, δ): 7.49 (d, *J*_{HH} = 6.8, 4H, B(C₆H₅)₂), 7.36 (m, 6H, P(C₆H₅)₃), 7.34 (d, *J*_{HH} = 7.6, 4H, B(C₆H₅)₂), 7.24 (t, *J*_{HH} = 7.2, 2H, B(C₆H₅)₂), 7.03 (m, 9H, P(C₆H₅)₃), 6.79 (d, *J*_{HH} = 1.6, 2H, ImH), 6.76 (d, *J*_{HH} = 1.6, 2H, ImH), 1.75 (s, 18H, C(CH₃)₃). ¹³C{¹H} (C₆D₆, 500 MHz): 184.47, 137.95, 137.87, 134.48, 134.27, 134.12, 128.91, 128.83, 128.78, 127.57, 126.40, 125.28, 116.97, 57.09, 31.68. ³¹P{¹H} (400 MHz, C₆D₆, δ): -4 (1P, PPh₃). IR (cm⁻¹): ν_{NO} = 1767 cm⁻¹ (THF); ν_{NO} = 1722 cm⁻¹ (KBr). HRMS (APCI/Q-TOF) *m/z* [M+H]⁺ Anal. Calcd for C₄₄H₄₈BN₅NiOP 762.3038; Found 762.3032.

Synthesis of Ph₂B(^tBulm)₂NiCl(PMe₃)

In a scintillation vial, a 1 M solution of PMe₃ in THF (5.98 mL) was added to solid NiCl₂ (0.258 g, 1.92 mmol), affording a dark purple solution. The vial was taken outside the glovebox and heated at 35 °C for 3 h before returning the mixture to the glovebox. Volatiles were removed under pressure to yield a pink solid (crude NiCl₂(PMe₃)₂).¹⁶ In a separate scintillation vial, a solution of LDA (0.39 g, 3.64 mmol) in Et₂O (5 mL) was added dropwise to a slurry of Ph₂B(^tBulmH)₂ (1.01 g, 1.79 mmol) in Et₂O (10 mL), affording a clear solution after 15 min. The carbene solution was added to solid *in situ* prepared NiCl₂(PMe₃)₂ at -78 °C. The mixture was slowly warmed to room temperature and the reaction was stirred for 14 h. Volatiles were removed under reduced pressure and the residue stirred in toluene (15 mL) for 1 h before filtering through Celite. The solvent was removed under vacuum to yield a yellow solid (0.74 g, 71 % yield based on Ph₂B(^tBulmH)₂). Crystals suitable for X-ray diffraction were grown by layering *n*-pentane onto a THF solution at -35 °C. ¹H NMR (400 MHz, C₆D₆, δ): 7.86 (s, 2H, B(C₆H₅)₂), 7.45 (m, 2H, B(C₆H₅)₂), 7.31 (m, 2H, B(C₆H₅)₂), 7.24 (s, 4H, B(C₆H₅)₂), 6.91 (s, 1H, ImH), 6.71 (s, 1H, ImH), 6.45 (s, 1H, ImH), 6.25 (s, 1H, ImH), 1.87 (s, 9H, C(CH₃)₃), 1.57 (s, 9H, C(CH₃)₃), 0.42 (d, *J*_{PH} = 9.0 Hz, 9H, P(CH₃)₃). ¹³C{¹H} (C₆D₆): 168.09, 166.92, 164.95, 164.63, 136.68,

134.24, 127.40, 127.32, 126.70, 126.22, 126.14, 117.73, 117.53, 57.18, 56.66, 32.06, 31.28, 12.97, 12.72. $^{31}\text{P}\{^1\text{H}\}$ (400 MHz, C_6D_6 , δ): -18 (1P, $\text{P}(\text{CH}_3)_3$).

Synthesis of $\text{Ph}_2\text{B}(\text{tBulm})_2\text{Ni}(\eta^3\text{-C}_7\text{H}_7)$:

A THF solution of benzyl magnesium chloride (1 M, 1.1 mL) was added to $\text{Ph}_2\text{B}(\text{tBulm})_2\text{NiCl}(\text{PMe}_3)$ (320 mg, 0.55 mmol) in THF (4 mL) and stirred for 14 h. The THF was removed under reduced pressure and the residue was redissolved in toluene (5 mL). Anhydrous 1,4-dioxane (203 mg, 2.3 mmol) was added dropwise to the toluene solution to precipitate the magnesium salts. The mixture was vigorously stirred for 1 h before filtering through Celite. Volatiles were removed under reduced pressure to yield an orange solid. Crystals suitable for X-ray diffraction were grown at room temperature from a saturated Et_2O solution in two crops (176 mg 57 % yield). ^1H NMR (400 MHz, C_6D_6 , δ): 7.75 (s, 2H, $\text{B}/\text{CH}_2(\text{C}_6\text{H}_5)$), 7.63 (m, 2H, $\text{B}/\text{CH}_2(\text{C}_6\text{H}_5)$), 7.43 (b, 1H, $\text{B}/\text{CH}_2(\text{C}_6\text{H}_5)$), 7.37-7.29 (m, 5H, $\text{B}/\text{CH}_2(\text{C}_6\text{H}_5)$), 7.20 (s, 1H, $\text{B}/\text{CH}_2(\text{C}_6\text{H}_5)$), 7.18 (s, 1H, $\text{B}/\text{CH}_2(\text{C}_6\text{H}_5)$), 7.16 (C_6D_6 overlap, $\text{B}/\text{CH}_2(\text{C}_6\text{H}_5)$), 7.09 (d, $J_{\text{HH}} = 1.7$ Hz, 1H, ImH), 7.0-6.87 (m, 4H, $1\text{ImH}+3$ $\text{B}/\text{CH}_2(\text{C}_6\text{H}_5)$), 6.56 (d, $J_{\text{HH}} = 1.6$ Hz, 1H, ImH), 6.44 (d, $J_{\text{HH}} = 1.5$ Hz, 1H, ImH), 4.38 (d, $J_{\text{HH}} = 6.7$ Hz, 1H, $\text{CH}_2(\text{C}_6\text{H}_5)$), 2.04 (d, $J_{\text{HH}} = 3.6$ Hz, 1H, $\text{CH}_2(\text{C}_6\text{H}_5)$), 1.47 (s, 9H, $\text{C}(\text{CH}_3)_3$), 0.94 (s, 9H, $\text{C}(\text{CH}_3)_3$). $^{13}\text{C}\{^1\text{H}\}$ (C_6D_6 , 500 MHz): 178.01, 172.65, 137.07, 136.60, 134.01, 131.06, 127.46, 127.33, 127.19, 127.01, 126.70, 126.20, 125.91, 117.81, 116.89, 116.84, 92.45, 56.09, 54.88, 33.02, 31.74, 30.69. HRMS (APCI/Q-TOF) m/z $[\text{M}+\text{H}]^+$ Anal. Calcd for $\text{C}_{33}\text{H}_{40}\text{BN}_4\text{Ni}$ 561.2700; Found 561.2710.

Reaction of $\text{Ph}_2\text{B}(\text{tBulm})_2\text{Ni}(\eta^3\text{-C}_7\text{H}_7)$ with O_2 :

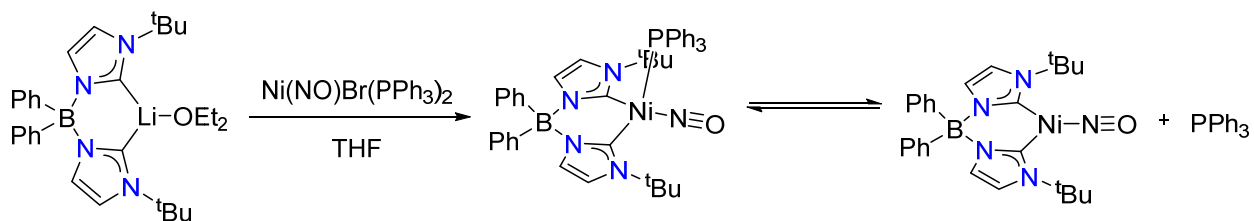
A solution of $\text{Ph}_2\text{B}(\text{tBulm})_2\text{Ni}(\eta^3\text{-C}_7\text{H}_7)$ (8.0 mg) in C_6D_6 (1 mL) was added to a J. Young NMR tube. The tube was degassed with three freeze-pump-thaw cycles and 1 atm of O_2 was added to the frozen solution. The proposed nickel hydroxide complex can be observed within the first 30 min of reaction before the onset of significant decomposition. Decomposition is observed even in the absence of excess O_2 . Benzaldehyde was isolated by vacuum transfer.

Results and Discussion

Synthesis and Characterization of $\text{Ph}_2\text{B}(\text{tBulm})_2\text{Ni}(\text{NO})(\text{PPh}_3)$

Reaction of the bis(carbene)borate ligand transfer agent $\text{Ph}_2\text{B}(\text{tBulm})_2\text{Li}(\text{OEt}_2)$ with $\text{Ni}(\text{NO})\text{Br}(\text{PPh}_3)_2$ provides the $\{\text{NiNO}\}^{10}$ complex¹⁷ $\text{Ph}_2\text{B}(\text{tBulm})_2\text{Ni}(\text{NO})(\text{PPh}_3)$ as a purple solid in high yield after workup (Scheme 1). This complex has been structurally and spectroscopically characterized. The solid state structure of the complex, as revealed by single crystal X-ray diffraction, reveals a four-coordinate Ni center bound by the bis(carbene)borate, nitrosyl and PPh_3 ligands (Figure 2). The nickel ion has a trigonal pyramidal geometry and is 0.508 Å out of the plane defined by the bis(carbene)borate and nitrosyl donors. A notable feature of the structure is the long Ni-P distance (2.3099(5) Å), which is almost 0.1 Å longer than in the related tris(thioimidazolyl)borate and tris(selenoimidazolyl)borate complexes $\text{Bm}^{\text{Me}}\text{Ni}(\text{PPh}_3)(\text{NO})$ ¹⁸ and $\text{Bse}^{\text{Me}}\text{Ni}(\text{PPh}_3)(\text{NO})$.¹⁹ In fact, this distance is also significantly longer than the average Ni-P distance in CSD for all four-coordinate nickel PPh_3 complexes (2.21(5) Å). This long distance suggests a weak interaction between nickel and phosphine ligand,²⁰ which has been evaluated in solution (see below).

Scheme 1



It is also worth noting that the Ni-N-O angle in Ph₂B(^tBulm)₂Ni(NO)(PPh₃) is close to linear at 173.2(2) °, whereas the related complexes Bm^{Me}Ni(PPh₃)(NO)¹⁸ and Bse^{Me}Ni(PPh₃)(NO)¹⁹ both feature bent nitrosyl ligands (*ca.* 150 °). While the latter complexes are nominally five-coordinate due to a weak interaction between the ligand B-H group and nickel, this is not consequential for nitrosyl ligand bending. Rather, bending stabilizes these low symmetry molecules, firstly by reducing overlap in the M-N σ* orbital, and secondly by allowing this orbital to mix with an NO π* orbital.^{19,21} The fact that similar bending is not observed in Ph₂B(^tBulm)₂Ni(NO)(PPh₃) suggests the complex may be better described as a three-coordinate complex where the weak Ni-PPh₃ interaction has only a minor perturbation on the electronic structure. All structurally characterized three-coordinate nickel nitrosyl complexes reported to date feature linear Ni-N-O linkages.^{22,23,24,25,26}

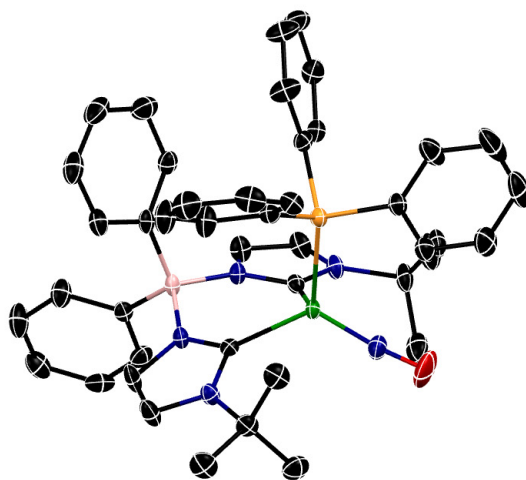
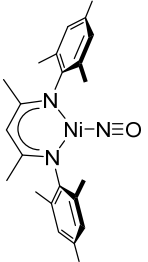
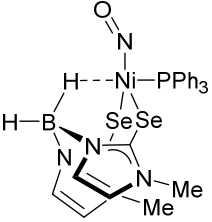
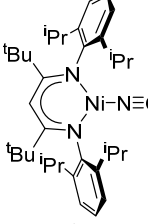
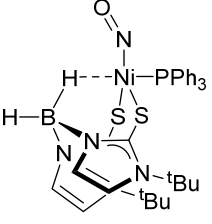
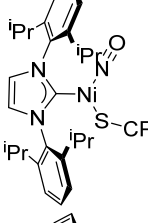
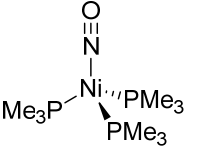
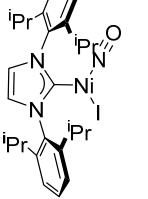
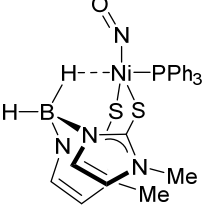


Figure 2. X-ray crystal structure of Ph₂B(^tBulm)₂Ni(NO)(PPh₃), thermal ellipsoids shown at 50 % probability, hydrogen atoms omitted for clarity. Black, blue, red, pink, green and orange ellipsoids correspond to C, H, O, B, Ni and P atoms, respectively. Selected bond lengths (Å) and angles (°): Ni-P 2.3099(5), Ni-C 1.981(2), 1.990(2), Ni-N 1.659(2), N-O 1.177(2); Ni-N-O 173.2(2).

Table 1. IR data (ν_{NO}) for selected neutral three- and four-coordinate $\{\text{NiNO}\}^{10}$ complexes

Three-coordinate complexes			Four-coordinate complexes		
Complex	ν_{NO} (cm^{-1})	ref	Complex	ν_{NO}	ref
$\text{Ph}_2\text{B}(\text{}^t\text{Bulm})_2\text{Ni}(\text{NO})(\text{PPh}_3)$	1767, 1730 (THF)	this work	$\text{Ph}_2\text{B}(\text{}^t\text{Bulm})_2\text{Ni}(\text{NO})(\text{PPh}_3)$	1722 (KBr)	this work
	1785 (ATR) ^b	23		1731, 1692 (KBr)	19 ^a
	1784 (C ₆ H ₆)	24		1728 (KBr)	18 ^a
	1772 (NaCl)	26		1718 (C ₆ H ₆)	25
	1766 (NaCl)	26		1688 (KBr)	18 ^a

^a - Interaction of B-H and nickel is weak.

^b - ATR = Attenuated Total Reflectance.

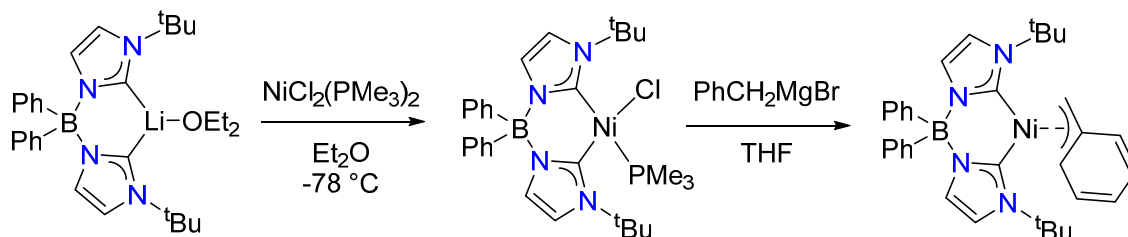
In the solid state, the NO ligand of $\text{Ph}_2\text{B}(\text{tBuIm})_2\text{Ni}(\text{NO})(\text{PPh}_3)$ is characterized by a strong band in the IR spectrum ($\nu_{\text{NO}} = 1722 \text{ cm}^{-1}$). The position of this band compares favorably with that observed for $(\text{Bm}^{\text{tBu}})\text{Ni}(\text{PPh}_3)(\text{NO})$ in the solid state (Table 1), although the latter complex was not characterized by single crystal X-ray diffraction. It is notable that ν_{NO} for both of these complexes is at a significantly higher frequency than for $(\text{Bm}^{\text{Me}})\text{Ni}(\text{PPh}_3)(\text{NO})$, where the nitrosyl ligand is bent.¹⁸ Intriguingly, two bands are observed in the solid state spectrum of $(\text{Bse}^{\text{Me}})\text{Ni}(\text{PPh}_3)\text{NO}$, one at a frequency similar to $\text{Ph}_2\text{B}(\text{tBuIm})_2\text{Ni}(\text{NO})(\text{PPh}_3)$ and one similar to $(\text{Bm}^{\text{Me}})\text{Ni}(\text{PPh}_3)(\text{NO})$. These similarities suggest the presence of both linear and bent nitrosyl ligands in the solid state structure of $(\text{Bse}^{\text{Me}})\text{Ni}(\text{PPh}_3)\text{NO}$, as was hypothesized by the authors.¹⁹

While four-coordinate in the solid state, spectroscopic studies reveal the loss of PPh_3 in solution to provide three-coordinate $\text{Ph}_2\text{B}(\text{tBuIm})_2\text{Ni}(\text{NO})$. Thus, the solution IR spectrum shows a large change in the nitrosyl stretching frequency ($\nu_{\text{NO}} = 1767 \text{ cm}^{-1}$) from that observed in the solid state ($\nu_{\text{NO}} = 1722 \text{ cm}^{-1}$). It is notable that this frequency is similar to that observed for other three-coordinate nickel nitrosyl complexes (Table 1). The addition of excess PPh_3 (up to 500 mM) to a 5 mM solution of $\text{Ph}_2\text{B}(\text{tBuIm})_2\text{Ni}(\text{NO})$ complex has no effect on the intensity and position of this band, and moreover does not lead to the appearance of new ν_{NO} bands, leading us to estimate an upper bound for PPh_3 binding, $K_{\text{eq}} < 10^{-4} \text{ M}^{-1}$.²⁷ Although the room temperature IR spectrum does not show evidence for the formation of $\text{Ph}_2\text{B}(\text{tBuIm})_2\text{Ni}(\text{NO})(\text{PPh}_3)$ in solution, even in the presence of excess of PPh_3 , decreasing the temperature leads to the growth of a new band at 1730 cm^{-1} , consistent with the formation of $\text{Ph}_2\text{B}(\text{tBuIm})_2\text{Ni}(\text{NO})(\text{PPh}_3)$ at low temperature. This conclusion is supported by VT ^1H NMR spectroscopy, where coalescence of the resonances associated with PPh_3 is observed at $-60 \text{ }^\circ\text{C}$ in C_7D_8 . These spectroscopic changes are concomitant with the blue solution changing to the purple color observed for $\text{Ph}_2\text{B}(\text{tBuIm})_2\text{Ni}(\text{NO})(\text{PPh}_3)$ in the solid state.²⁸

Synthesis and Reactivity of Square Planar Complexes

The square planar nickel(II) complex $\text{Ph}_2\text{B}(\text{tBuIm})_2\text{NiCl}(\text{PMe}_3)$ is formed in good yield from the reaction of $\text{Ph}_2\text{B}(\text{tBuIm})_2\text{Li}(\text{OEt}_2)$ and the nickel(II) complex $\text{NiCl}_2(\text{PMe}_3)_2$ (Scheme 2). The low temperature and nickel source are both critical to successful metalation, with unidentified side products observed at higher temperatures, and other nickel reagents, including NiX_2 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), $\text{NiCl}_2(\text{dme})$, $\text{NiCl}_2(\text{PCy}_3)_2$ and $\text{NiBr}_2(\text{PPh}_3)_2$ providing intractable materials.

Scheme 2.



Single crystal X-ray diffraction reveals the expected square planar geometry, in which nickel has the same coordination sphere as the cationic bis(carbene)methane complex $[\text{H}_2\text{C}(\text{tBuIm})_2\text{NiCl}(\text{PMe}_3)]^+$.⁷ Indeed, the two complexes have comparable bond lengths to the nickel ion, despite the charge differences. Apart from the bent C-Ni-P angle ($163.20(9)^\circ$), which is likely due to steric interactions between PMe_3 and *tert*-butyl group of the bis(carbene)borate ligand, and is similarly observed for $[\text{H}_2\text{C}(\text{tBuIm})_2\text{NiCl}(\text{PMe}_3)]^+$, the

structure of $\text{Ph}_2\text{B}(\text{}^t\text{BuIm})_2\text{NiCl}(\text{PMe}_3)$ is unremarkable. This structure is maintained in solution, as determined by ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy.

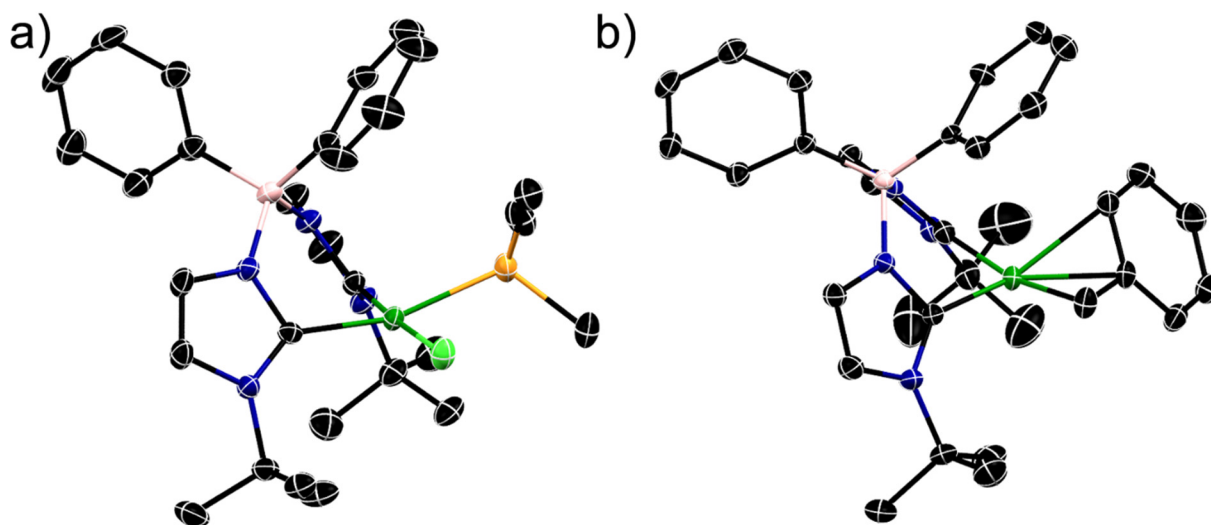


Figure 3. X-ray crystal structures of (a) $\text{Ph}_2\text{B}(\text{}^t\text{BuIm})_2\text{NiCl}(\text{PMe}_3)$, selected bond lengths (\AA): Ni-Cl 2.2205(9); Ni-P 2.219(1); Ni-C 1.921(3); 1.862(3); and (b) $\text{Ph}_2\text{B}(\text{}^t\text{BuIm})_2\text{Ni}(\eta^3\text{-C}_7\text{H}_7)$, selected bond lengths (\AA) and angles ($^\circ$): Ni-C (carbene) 1.916(2); 1.876(2). Ni-C (benzyl) 1.974(2), 2.100(2), 2.228(2) Thermal ellipsoids shown at 50 % probability, hydrogen atoms omitted for clarity. Black, blue, red, light green, pink, green and orange ellipsoids correspond to C, H, O, Cl, B, Ni and P atoms, respectively.

While the structure of $\text{Ph}_2\text{B}(\text{}^t\text{BuIm})_2\text{NiCl}(\text{PMe}_3)$ is in itself unremarkable, it is worth noting that this complex shows no tendency to rearrange to a homoleptic analogue containing two bis(carbene)borates. For example, no change in the ^1H NMR spectrum is observed when the complex is heated at 110°C . This stability should be contrasted with observations for the related dihydrobis(carbene)borate and dihydrobis(carbene)methane ligands, where there is a strong driving force to forming the homoleptic Ni(II) complexes.⁹ Thus, $\text{Ph}_2\text{B}(\text{}^t\text{BuIm})_2\text{NiCl}(\text{PMe}_3)$ is expected to serve as a suitable platform for the further development of nickel chemistry with the bis(carbene)borate behaving as a spectator ligand.

In an initial demonstration of this potential synthetic utility, we treated $\text{Ph}_2\text{B}(\text{}^t\text{BuIm})_2\text{NiCl}(\text{PMe}_3)$ with PhCH_2MgBr to afford orange $\text{Ph}_2\text{B}(\text{}^t\text{BuIm})_2\text{Ni}(\eta^3\text{-C}_7\text{H}_7)$ in moderate isolated yield (Scheme 2). This complex has also been structurally characterized (Figure 3). The structural metrics regarding the benzyl ligand are similar to those of other structurally characterized nickel(II) η^3 -benzyl complexes,²⁹ however the angle between plane of the allyl ligand and that defined by nickel and bis(carbene)borate donors (46.2°) is relatively small. We attribute this small angle to the steric influence of the *tert*-butyl groups of the bis(carbene)borate ligand, which prevents the η^3 -benzyl ligand from binding with a more perpendicular orientation.

The solid state structure of $\text{Ph}_2\text{B}(\text{}^t\text{BuIm})_2\text{Ni}(\eta^3\text{-C}_7\text{H}_7)$ is maintained in solution, as determined by ^1H NMR spectroscopy. A distinctive feature of the ^1H NMR spectrum are the resonances attributed to the two benzylic protons, which are observed as doublets at δ 4.38 and 2.04 ppm. The chemical inequivalence of these two protons, along with the chemical inequivalence of the resonances assigned to the *tert*-butyl

groups (δ 1.47 and 0.94 ppm), suggests that there are no fluxional processes involving the η^3 -benzyl ligand.

The benzyl complex $\text{Ph}_2\text{B}(\text{tBuIm})_2\text{Ni}(\eta^3\text{-C}_7\text{H}_7)$ is sensitive to O_2 , reacting cleanly to yield a new diamagnetic nickel complex. While the thermal instability of this complex has hindered efforts at crystallographic characterization, we propose that this product is a Ni(II) hydroxide on the basis of ^1H NMR spectroscopy, likely the dimer $[\text{Ph}_2\text{B}(\text{tBuIm})_2\text{Ni}(\mu\text{-OH})]_2$. Most notably, the ^1H NMR spectrum of this complex reveals a single resonance for the *tert*-butyl groups of the bis(carbene)borate ligand at δ 1.52 ppm, consistent with a two-fold symmetric structure. In addition, a new upfield shifted resonance integrating for a single proton is observed at δ -6.62 ppm, which we tentatively assign to the hydroxide ligand, based on its similarity to $[\text{IPrNi}(\text{Cl})(\mu\text{-OH})]_2$.³⁰ In addition to the nickel complex, the reaction also yields an equivalent of benzaldehyde, which was characterized by ^1H NMR spectroscopy following vacuum transfer of the reaction volatiles.

This transformation is similar to observations for (NHC)Ni(η^3 -allyl)Cl complexes, where O_2 oxidizes the π -allyl ligands to α,β -unsaturated carbonyls.³⁰ This oxidation reaction has been proposed to follow a mechanism involving initial formation of a Ni(III) peroxo intermediate that abstracts a hydrogen atom from the allyl ligand to yield a hydroperoxo ligand. Homolysis of the O-O bond leads to intramolecular hydroxylation of the allyl ligand, which is followed by hydrogen atom transfer to provide the carbonyl and nickel hydroxide products. The reaction of $\text{Ph}_2\text{B}(\text{tBuIm})_2\text{Ni}(\eta^3\text{-C}_7\text{H}_7)$ with O_2 likely follows a similar mechanism.

Summary and Conclusions

Similarly to our observations for iron, introducing phenyl groups for the boron hydrides of a bulky bis(carbene)borate ligand allows access to heteroleptic Ni(II) complexes. Specifically, the conformation of the borate ligand orients the phenyl groups such that they prevent another bis(carbene)borate ligand from binding to the metal, as we have previously observed for iron.¹⁴ The square planar complex $\text{Ph}_2\text{B}(\text{tBuIm})_2\text{Ni}(\text{PMe}_3)_3\text{Cl}$ is an entry point to Ni(II) chemistry in which the bis(carbene)borate ligand is expected to behave as a spectator ligand. Ligand substitution provides the corresponding allyl complex $\text{Ph}_2\text{B}(\text{tBuIm})_2\text{Ni}(\eta^3\text{-C}_7\text{H}_7)$ that reacts with O_2 to provide benzaldehyde and a putative Ni(II) hydroxide complex. The stability of the Ni bis(carbene)borate fragment in all of these transformations worth noting.

The bulky bis(carbene)borate ligand also provides access to a three-coordinate nickel nitrosyl complex through the reversible loss of PPh_3 from $\text{Ph}_2\text{B}(\text{tBuIm})_2\text{Ni}(\text{NO})(\text{PPh}_3)$. While PPh_3 binding is weak at room temperature, low temperature spectroscopic data suggest that the four coordinate complex observed in the solid state is also formed in solution. While this ligand binding and uncertainty regarding the linearity of the nitrosyl ligand in reference complexes are a complicating factor, the frequency of ν_{NO} in the IR spectrum is consistent with previous reports¹⁴ that bis(carbene)borates are a very strongly donating bidentate ligands.

Appendix A. Supplementary data

CCDC 1859951-1859953 contains the supplementary crystallographic data for $\text{Ph}_2\text{B}(\text{tBuIm})_2\text{Ni}(\text{NO})(\text{PPh}_3)$, $\text{Ph}_2\text{B}(\text{tBuIm})_2\text{NiCl}(\text{PMe}_3)$ and $\text{Ph}_2\text{B}(\text{tBuIm})_2\text{Ni}(\eta^3\text{-C}_7\text{H}_7)$. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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Supporting Information

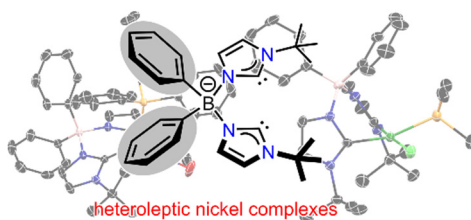
Additional spectroscopic data, X-ray crystallographic data.

References

- ¹ (a) Garcia, J.J.; Jones, W.D. *Organometallics* **2000**, *19*, 5544-5545; (b) Garcia, J.J.; Brunkan, N.M.; Jones, W.D. *J. Am. Chem. Soc.* **2002**, *124*, 9547-9555; (c) Brunkan, N.M.; Bretensky, D.M.; Jones, W.D. *J. Am. Chem. Soc.* **2004**, *126*, 6327-3641; (d) Garcia, J.J.; Arevalo, A.; Brunkan, N.M.; Jones, W.D. *Organometallics* **2004**, *23*, 3997-4002; (e) Atesin, T.A.; Li, T.; Lachaize, S.; Brennessel, W.W.; Garcia, J.J.; Jones, W.D. *J. Am. Chem. Soc.* **2007**, *129*, 7562-7569; (f) Atesin, T.A.; Li, T.; Lachaize, S.; Garcia, J.J.; Jones, W.D. *Organometallics* **2008**, *15*, 3811-3817; (g) Swartz, B.D.; Reinartz, N.M.; Brennessel, W.W.; Garcia, J.J.; Jones, W.D. *J. Am. Chem. Soc.* **2008**, *130*, 8548-8554; (h) Li, T.; Garcia, J.J. Brennessel, W.W.; Jones, W.D. *Organometallics* **2010**, *29*, 2430-2445; (i) Swartz, B.D.; Brennessel, W.W.; Jones, W.D. *Synlett* **2018**, *29*, 747-753.
- ² (a) Vicic, D.A.; Jones, W.D. *J. Am. Chem. Soc.* **1997**, *119*, 10855-10856; (b) Vicic, D.A.; Jones, W.D. *Organometallics* **1998**, *17*, 3411-3413; (c) Vicic, D.A.; Jones, W.D. *J. Am. Chem. Soc.* **1999**, *121*, 7606-7617; (d) Torres-Nieto, J.; Brennessel, W.W.; Jones, W.D.; Garcia, J.J. *J. Am. Chem. Soc.* **2009**, *131*, 4120-4126; (e) Grochowski, M.R.; Li, T.; Brennessel, W.W.; Jones, W.D. *J. Am. Chem. Soc.* **2010**, *132*, 12412-12421.
- ³ Selected reviews: (a) Saouma, C.T.; Peters, J.C. *Coord. Chem. Rev.* **2011**, *255*, 920-937; (b) Ray, K.; Heims, F.; Pfaff, F.F. *Eur. J. Inorg. Chem.* **2013**, 3784-3807.
- ⁴ Vicic, D.A.; Jones, W.D. *J. Am. Chem. Soc.* **1999**, *121*, 4070-4071.
- ⁵ Prakasham, A.P.; Ghosh, P. *Inorg. Chim. Acta* **2015**, *431*, 61-100.
- ⁶ Charra, V.; de Frémont, P.; Braunstein, P. *Coord. Chem. Rev.* **2017**, *341*, 53-176.
- ⁷ Douthwaite, R.E.; Haüssinger, D.; Green, M.L.H.; Silcock, P.J.; Gomes, P.T.; Martins, A.M.; Danopoulos, A.A. *Organometallics* **1999**, *18*, 4584-4590.
- ⁸ (a) Douthwaite, R.E.; Green, M.L.H.; Silcock, P.J.; Gomes, P.T. *Organometallics* **2001**, *20*, 2611-2615; (b) Berding, J.; Lutz, M.; Spek, A.L.; Bouwman, E. *Organometallics* **2009**, *28*, 1845-1854; (c) Huynh, H.V.; Jothibas, R. *Eur. J. Inorg. Chem.* **2009**, 1926-1931; (d) Paulose, T.A.P.; Wu, S.-C.; Olson, J.A.; Chau, T.; Theaker, N.; Hassler, M.; Quail, J.W.; Foley, S.R. *Dalton Trans.* **2012**, *41*, 251-260; (e) Harrold, N.D.; Hillhouse, G.L. *Chem. Sci.* **2013**, *4*, 4011-4015; (f) Guo, J.; Lv, L.; Wang, X.; Cao, C.; Pang, G.; Shi, Y.; *Inorg. Chem. Commun.* **2013**, *31*, 74-78; (g) Huffer, A.; Jeffrey, B.; Waller, B.J.; Danopoulos, A.A. *C.R. Chimie* **2013**, *16*, 557-565; (h) Brendel, M.; Braun, C.; Rominger, F.; Hofmann, P. *Angew. Chem. Int. Ed.* **2014**, *53*, 8741-8745; (i) Huynh, H.V.; Koh, C.H.M.; Nguyen, V.H. *Dalton Trans.* **2017**, *46*, 11318-11326; (j) Nirmala, M.; Saranya, G.; Viswanathamurthi, P.; Bertani, R.; Sgarbossa, P.; Malecki, J.G. *J. Organomet. Chem.* **2017**, *831*, 1-10.
- ⁹ (a) Nieto, I.; Bontchev, R.P.; Smith, J.M. *Eur. J. Inorg. Chem.* **2008**, 2476-2480; (b) Santini, C.; Marinelli, M.; Pellei, M. *Eur. J. Inorg. Chem.* **2016**, 2312-2331.
- ¹⁰ Smith, J.M. *Comments Inorg. Chem.* **2008**, *28*, 189-233.
- ¹¹ Hickey, A.K.; Lutz, S.A.; Chen, C.-H.; Smith, J.M. *Chem. Commun.* **2017**, *53*, 1245-1248.
- ¹² (a) Lee, W.-T.; Jeon, I.-R.; Xu, S.; Dickie, D.A.; Smith, J.M. *Organometallics*, **2014**, *33*, 5654-5659; (b) Liu, Y.-Z.; Wang, J.; Zhao, Y.; Chen, L.; Chen, X.-T.; Xue, Z.-L. *Dalton Trans.* **2015**, *44*, 908-911.
- ¹³ (a) Shishkov, I.V.; Rominger, F.; Hofmann, P. *Organometallics* **2009**, *28*, 3532-3536; (b) Xiong, Y.; Szilvási, T.; Yao, S.; Tan, G.; Driess, M. *J. Am. Chem. Soc.* **2014**, *136*, 11300-11303.
- ¹⁴ Hickey, A.K.; Lee, W.-T.; Chen, C.-H.; Pink, M.; Smith, J.M. *Organometallics* **2016**, *35*, 3069-3073.
- ¹⁵ Feltham, R.D. *Inorg. Chem.* **1964**, *3*, 116-119.
- ¹⁶ Dahl, O. *Acta Chem. Scand.* **1969**, *23*, 2342-2354.

- ¹⁷ Enemark, J.H.; Feltham, R.D. *Coord. Chem. Rev.* **1974**, *13*, 339-406.
- ¹⁸ Maffett, L.S.; Gunter, K.L.; Kreisel, K.A.; Yap, G.P.A.; Rabinovich, D. *Polyhedron* **2007**, *26*, 4758-4764.
- ¹⁹ Landry, V.K.; Parkin, G. *Polyhedron* **2007**, *26*, 4751-4757.
- ²⁰ An important caveat to such an analysis: Kaupp, M.; Danovich, D.; Shaik, S. *Coord. Chem. Rev.* **2017**, *344*, 355-362.
- ²¹ Mingos, D.M.P. *Inorg. Chem.* **1973**, *12*, 1209-1211.
- ²² (a) Chong, K.S.; Rettig, S.J.; Storr, A.; Trotter, J. *Can. J. Chem.* **1979**, *57*, 3090-3098; (b) Iluc, V.M.; Miller, A.J.M.; Hillhouse, G.L. *Chem. Commun.* **2005**, 5091-5093; (c) Wright, A.M.; Wu, G.; Hayton, T.W. *J. Am. Chem. Soc.* **2012**, *134*, 9930-9933; (d) Wright, A.M.; Zaman, H.T.; Wu, G.; Hayton, T.W. *Inorg. Chem.* **2013**, *52*, 3207-3216; (e) Tskhovrebov, A.G.; Solari, E.; Scopelliti, R.; Severin, K. *Inorg. Chem.* **2013**, *52*, 11688-11690.
- ²³ Puiu, S.C.; Warren, T.H. *Organometallics* **2003**, *22*, 3974-3976.
- ²⁴ Hartmann, N.J.; Wu, G.; Hayton, T.W. *J. Am. Chem. Soc.* **2016**, *138*, 12352-12355.
- ²⁵ Kriege-Simonsen, J.; Elbaze, G.; Dartiguenave, M.; Feltham, R.D.; Dartiguenave, Y. *Inorg. Chem.* **1982**, *21*, 230-236.
- ²⁶ Varonka, M.S.; Warren, T.H. *Organometallics* **2010**, *29*, 717-720.
- ²⁷ This is based on the estimate that 5% conversion would provide an observable band for $\text{Ph}_2\text{B}(\text{tBulm})_2\text{Ni}(\text{NO})(\text{PPh}_3)$ in the IR spectrum.
- ²⁸ While adding one equivalent of $\text{B}(\text{C}_6\text{F}_5)_3$ to a solution of $\text{Ph}_2\text{B}(\text{tBulm})_2\text{Ni}(\text{NO})(\text{PPh}_3)$ in benzene does lead to the formation of $\text{Ph}_2\text{B}(\text{tBulm})_2\text{Ni}(\text{NO})$, as detected by ^1H NMR and IR spectroscopy, a number of other products are also observed.
- ²⁹ (a) Anderson, T.J.; Vicic, D.A. *Organometallics* **2004**, *23*, 623-625; (b) Wasilke, J.-C.; Komon, Z.J.A.; Bu, X.; Bazan, G.C. *Organometallics* **2004**, *23*, 4174-4177; (c) Sujith, S.; Noh, E.K.; Lee, B.Y.; Han, J.W. *J. Organomet. Chem.* **2008**, *693*, 2171-2176; (d) Matsubara, R.; Gutierrez, A.C.; Jamison, T.F. *J. Am. Chem. Soc.* **2011**, *133*, 19020-19023.
- ³⁰ (a) Dible, B.R.; Sigman, M.S. *J. Am. Chem. Soc.* **2003**, *125*, 872-873; (b) Dible, B.R.; Sigman, M.S. *Inorg. Chem.* **2006**, *45*, 8430-8441.

TOC picture



A bulky diphenylbis(carbene)borate ligand provides access to heteroleptic nickel complexes

Highlights

Unlike its dihydrobis(carbene)borate analogue, which unavoidably provide homoleptic Ni(II) complexes, a bulky diphenylbis(carbene)borate ligand stabilizes heteroleptic Ni(II) complexes.

A four-coordinate $\{\text{NiNO}\}^{10}$ complex provides access to the three-coordinate species via phosphine loss.

Reaction of a π -benzyl complex with O_2 leads to the formation of benzaldehyde.