Reactivity of the Ni → B dative σ-bond in the nickel boratrane compounds $[\kappa^4\text{-B}(\text{mim}^{\text{Bu}^t})_3]\text{NiX}$ (X = Cl, OAc, NCS, N_3): synthesis of a series of *B*-functionalized tris(2-mercapto-1-*tert*-butylimidazolyl)borato complexes, $[\text{YTm}^{\text{Bu}^t}]\text{NiZ}$†

Keliang Pang,[a] Joseph M. Tanski[b] and Gerard Parkin*[a]

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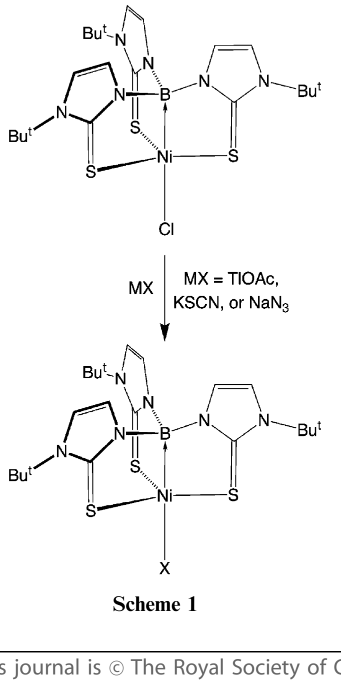
The nickel boratrane complexes $[\kappa^4\text{-B}(\text{mim}^{\text{Bu}^t})_3]\text{Ni}(\kappa^1\text{-OAc})$, $[\kappa^4\text{-B}(\text{mim}^{\text{Bu}^t})_3]\text{NiNCS}$ and $[\kappa^4\text{-B}(\text{mim}^{\text{Bu}^t})_3]\text{NiN}_3$ are obtained *via* metathesis of the chloride ligand of $[\kappa^4\text{-B}(\text{mim}^{\text{Bu}^t})_3]\text{NiCl}$ with TlOAc, KSCN and NaN_3, respectively; the Ni → B bond in these complexes is a site of reactivity, thereby providing a means of synthesizing nickel complexes that feature *B*-functionalized tris(mercaptoimidazolyl)borate derivatives, $[\text{YTm}^{\text{Bu}^t}]\text{NiZ}$.

Metallaboratrane compounds are a class of molecules with a cage-like structure that feature metal-to-ligand M → B σ-dative bonds, examples of which are known for the late transition metals Fe, Ru, Os, Co, Rh, Ir, Ni, Pd and Pt.[1,2] The initial significance of this class of molecules pertained to the fact that they provided the first structurally characterized examples of transition metal compounds with M → B σ-dative bonds; as such, the nature of the M → B bonding interaction in these complexes was of considerable interest.[3] By comparison to the many synthetic and structural studies, however, the reactivity of the M → B bond in metallaboratranes has received very little attention. Therefore, we have started to investigate the chemistry of metallaboratranes, with the intention of uncovering new reactivity that is associated with cleavage of the M → B bond.[1d] Here we report reactivity of nickel boratranes $[\kappa^4\text{-B}(\text{mim}^{\text{Bu}^t})_3]\text{NiX}$ that involves cleavage of the Ni → B bond, thereby affording a series of *B*-functionalized derivatives, $[\text{YTm}^{\text{Bu}^t}]\text{NiZ}$.

The nickel boratrane compound $[\kappa^4\text{-B}(\text{mim}^{\text{Bu}^t})_3]\text{NiCl}$, recently synthesized *via* the reaction of $[\text{Tm}^{\text{Bu}^t}]\text{Li}$ with NiCl_2,[1f] provides a means to obtain a variety of other boratrane derivatives. For example, $[\kappa^4\text{-B}(\text{mim}^{\text{Bu}^t})_3]\text{Ni}(\kappa^1\text{-OAc})$, $[\kappa^4\text{-B}(\text{mim}^{\text{Bu}^t})_3]\text{NiNCS}$ and $[\kappa^4\text{-B}(\text{mim}^{\text{Bu}^t})_3]\text{NiN}_3$ may be obtained *via* metathesis of the chloride ligand with TlOAc, KSCN and NaN_3, respectively (Scheme 1). The molecular structures of $[\kappa^4\text{-B}(\text{mim}^{\text{Bu}^t})_3]\text{NiX}$ (X = Cl, OAc, NCS, N_3) have been determined by X-ray diffraction, as illustrated in Fig. 1 for $[\kappa^4\text{-B}(\text{mim}^{\text{Bu}^t})_3]\text{NiNCS}$. In each case, the coordination geometry about nickel is trigonal bipyramidal with Ni–B bond lengths in the range 2.08–2.11 Å and Ni–S bond lengths in the range 2.23–2.30 Å,[4] as summarized in Table 1. The Ni–B bond lengths of the nickel boratrane compounds are comparable to the corresponding M–B values for other first row transition metal derivatives, namely the iron and cobalt complexes $[\kappa^4\text{-B}(\text{mim}^{\text{Bu}^t})_3]\text{Fe(CO)}_2$ [2.108(6) Å][1d] and $\{[\kappa^4\text{-B}(\text{mim}^{\text{Bu}^t})_3]\text{Co(PPh}_3)\}^+$ [2.132(4) Å].[1b] A more interesting comparison, however, is with the palladium compound $[\kappa^4\text{-B}(\text{mim}^{\text{Bu}^t})_3]\text{Pd(PMe}_3)$, for which the Pd–B bond [2.050(8) Å][1e] is actually *shorter* than the Ni–B bonds in $[\kappa^4\text{-B}(\text{mim}^{\text{Bu}^t})_3]\text{NiX}$ derivatives (2.08–2.11 Å). In contrast, the Pd–S and Ni–S bond lengths for $[\kappa^4\text{-B}(\text{mim}^{\text{Bu}^t})_3]\text{Pd(PMe}_3)$ (2.33–2.54 Å) and $[\kappa^4\text{-B}(\text{mim}^{\text{Bu}^t})_3]\text{NiX}$ (2.23–2.30 Å) show the expected trend with the Pd–S bonds being longer than the Ni–S bonds. Since the covalent radius of nickel is 0.1 Å smaller than that of palladium,[4] the shorter Pd–B bond length indicates that the M → B interaction is more significant for the second row metal.

We recently described that the Fe → B bond of the ferraboratrane $[\kappa^4\text{-B}(\text{mim}^{\text{Bu}^t})_3]\text{Fe(CO)}_2$ could be cleaved by a variety of reagents to give *B*-functionalized tris(mercaptoimidazolyl)borate complexes of the type $[\text{YTm}^{\text{Bu}^t}]\text{FeZ}$.[1d] For example, $[\kappa^4\text{-B}(\text{mim}^{\text{Bu}^t})_3]\text{Fe(CO)}_2$ reacts with (i) CHX_3 (X = Cl, Br) to give $[\text{XTm}^{\text{Bu}^t}]\text{FeX}$, and (ii) I_2 in CHCl_3 to give $[\text{ClTm}^{\text{Bu}^t}]\text{FeI}$.[5] In a similar manner, the Ni → B bond of the nickel boratrane



Scheme 1

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[a] *Department of Chemistry, Columbia University, New York, New York 10027, USA. E-mail: parkin@columbia.edu*
[b] *Department of Chemistry, Vassar College, 124 Raymond Avenue, Box 601, Poughkeepsie, New York 12604, USA*

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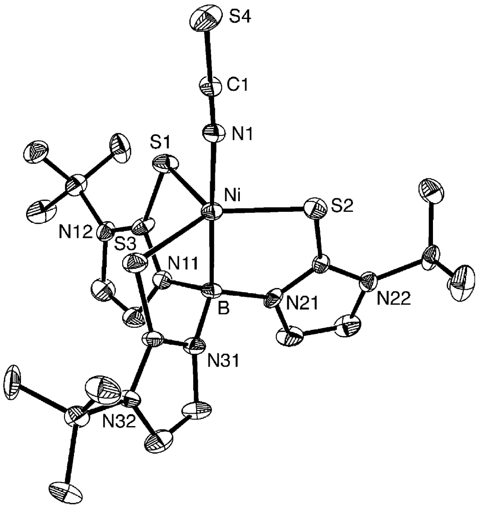


Fig. 1 Molecular structure of [κ^4-B(mim$^{Bu^t}$)$_3$]NiNCS.

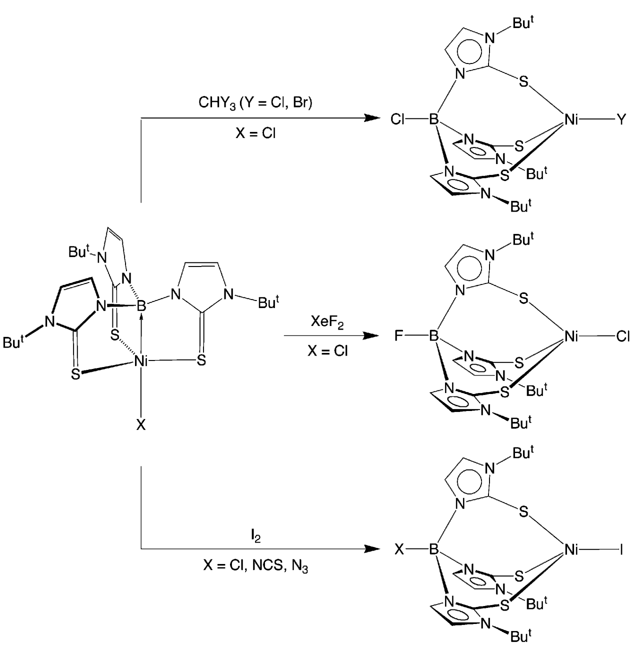
compounds [κ^4-B(mim$^{Bu^t}$)$_3$]NiX (X = Cl, OAc, SCN, N_3) may also be cleaved by suitable reagents to afford *B*-functionalized derivatives, [YTm$^{Bu^t}$]NiZ, as illustrated in Scheme 2.[6,7] For example, [κ^4-B(mim$^{Bu^t}$)$_3$]NiCl reacts with $CHCl_3$, $CHBr_3$ and I_2 to give [ClTm$^{Bu^t}$]NiCl, [ClTm$^{Bu^t}$]NiBr and [ClTm$^{Bu^t}$]NiI, respectively. Likewise, the azide and isothiocyanate complexes [κ^4-B(mim$^{Bu^t}$)$_3$]NiN_3 and [κ^4-B(mim$^{Bu^t}$)$_3$]NiNCS react with I_2 to give [N_3Tm$^{Bu^t}$]NiI and [SCNTm$^{Bu^t}$]NiI. In each of these examples, the boron is functionalized by the ligand originally attached to nickel, as illustrated in Fig. 2 for [SCNTm$^{Bu^t}$]NiI. It is, therefore, significant that [κ^4-B(mim$^{Bu^t}$)$_3$]NiCl reacts with XeF_2 to yield [FTm$^{Bu^t}$]NiCl in which the boron is functionalized by the reagent and the chloride ligand remains attached to nickel.

In principle, the observed isomeric form of the products resulting from cleavage of the Ni → B bonds, *i.e.* [YTm$^{Bu^t}$]NiZ *vs.* [ZTm$^{Bu^t}$]NiY, may provide insight into the nature of the mechanism; however, such mechanistic interpretation is only possible if the observed isomer is known to be the kinetic product. Therefore, we have performed DFT calculations to establish the relative stabilities of the [YTm^{Me}]NiZ and [ZTm^{Me}]NiY isomers in a computationally simpler system in which the *tert*-butyl groups are replaced by methyl. The data are summarized in Table 2 and indicate that the thermodynamically more stable isomer is the one in which the more electronegative substituent resides on boron. This observation is in line with the fact that B–X bond energies increase dramatically in the sequence I < Br < Cl < F, with the B–F bond being particularly strong.[8] As such, the thermodynamically more stable isomer resulting from cleavage of the Ni → B bond is largely dictated by the B–X bond energy.

Table 1 Ni–B and Ni–S bond lengths for [κ^4-B(mim$^{Bu^t}$)$_3$]NiX and [ZTm$^{Bu^t}$]NiY derivatives

	d(Ni–B)/Å	*d*(Ni–S)/Å
[κ^4-B(mim$^{Bu^t}$)$_3$]NiCl	2.110(8)[a]	2.252(1)
[κ^4-B(mim$^{Bu^t}$)$_3$]NiN_3	2.092(5)	2.244(1), 2.254(1), 2.275(1)
[κ^4-B(mim$^{Bu^t}$)$_3$]NiNCS	2.079(13)	2.228(3), 2.261(4), 2.298(4)
[κ^4-B(mim$^{Bu^t}$)$_3$]NiOAc	2.112(3)	2.2275(8) 2.2505(8), 2.2599(7)
[FTm$^{Bu^t}$]NiCl		2.2872(4)
[ClTm$^{Bu^t}$]NiCl		2.299(1)
[ClTm$^{Bu^t}$]NiBr		2.292(2)
[ClTm$^{Bu^t}$]NiI		2.290(2), 2.295(2), 2.312(2); 2.293(2), 2.295(2), 2.302(2)[b]
[SCNTm$^{Bu^t}$]NiI		2.292(1), 2.296(1) 2.301(1)
[N_3Tm$^{Bu^t}$]NiI		2.282(3), 2.289(3), 2.325(3); 2.276(3), 2.306(3), 2.306(3)[b]

[a] A comparable value of *d*(Ni–B) = 2.108(4) Å has been reported for a crystal of composition [κ^4-B(mim$^{Bu^t}$)$_3$]NiCl·CH_2Cl_2. See ref. 1*f*. [b] Values for two crystallographically independent molecules.



Scheme 2

A simple illustration in support of the notion that the thermodynamics is dictated by the B–X bond energy is provided by a series of "snap" bond enthalpy calculations pertaining to the Ni–X and B–X (X = Y, Z) bonds of the various [YTm^{Me}]NiZ and [ZTm^{Me}]NiY isomers. Specifically, these calculations indicate that the B–X "snap" bond enthalpy is more sensitive to the nature of X than is the Ni–X "snap" bond enthalpy. For example, the B–X "snap" bond enthalpies range from 76.6 kcal mol^{-1} for X = I to 160.8 kcal mol^{-1} for X = F, whereas the corresponding Ni–X "snap" bond

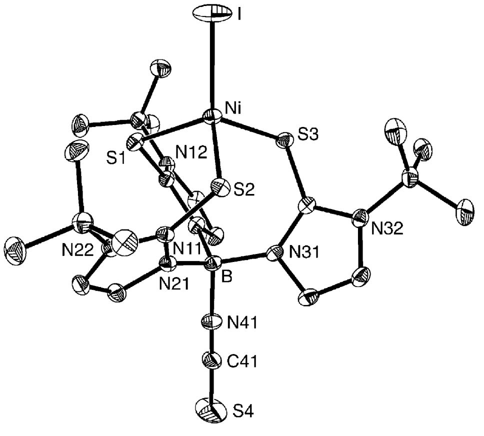


Fig. 2 Molecular structure of [SCNTm$^{Bu^t}$]NiI.

Table 2 Relative energies of [YTm$^{\mathrm{Me}}$]NiZ and [ZTm$^{\mathrm{Me}}$]NiY isomers (DFT calculations performed for $S = 1$ spin state with the B3LYP functional and cc-pVTZ(-f)/LACV3P/LAV3P basis sets)

	H^{SCF}\{[YTm$^{\mathrm{Me}}$]NiZ\} − H^{SCF}\{[ZTm$^{\mathrm{Me}}$]NiY\}/kcal mol^{-1}
Y = F, Z = Cl	−28.4
Y = Cl, Z = Br	−7.5
Y = Cl, Z = I	−14.7
Y = NCS, Z = I	−24.7

enthalpies only range from 61.6 kcal mol^{-1} for X = I to 102.5 kcal mol^{-1} for X = F. This variation indicates that there is an intrinsic thermodynamic preference for the more electronegative halogen to be attached to boron rather than to nickel. In this regard, it is pertinent to note that there is precedent for this preference. For example, halogen metathesis employing $\mathrm{BI_3}$ has been used to prepare transition metal iodide compounds from their chloride derivatives, as illustrated by the reaction of $\mathrm{Cp^*{}_2HfCl_2}$ with $\mathrm{BI_3}$ to yield $\mathrm{Cp^*{}_2HfI_2}$ and $\mathrm{BCl_3}$.[9]

In each case, the calculations listed in Table 2 indicate that the thermodynamically more stable of the two isomers of [YTm$^{\mathrm{Me}}$]NiZ corresponds to the product observed for the experimental system, [YTm$^{\mathrm{Bu^t}}$]NiZ. As such, consideration of the structure of the isomer obtained cannot be used to infer mechanistic details pertaining to the overall reaction involving cleavage of the Ni → B bond.

Finally, it is worth noting that the E–N–CS (E = Ni, B) bond angles in the isothiocyanate complexes [κ^4-B(mim$^{\mathrm{Bu^t}}$)$_3$]-NiNCS [175(1)°] and [SCNTm$^{\mathrm{Bu^t}}$]NiI [170.7(5)°] are both close to linear, whereas the corresponding E–N–NN bond angles for the azide derivatives [κ^4-B(mim$^{\mathrm{Bu^t}}$)$_3$]NiN$_3$ [120.8(4)°] and [N$_3$Tm$^{\mathrm{Bu^t}}$]NiI [122(1) and 119(1)° for two crystallographically independent molecules] are substantially bent. This observation is in accord with data in the Cambridge Structural Database which indicates that E–N–CS bond angles (mean = 164.9°) are typically greater than E–N–NN bond angles (mean = 125.7°).[10] For example, the B–N–CS bond angle in the isothiocyanate species $[(\mathrm{C_6F_5})_3\mathrm{BNCS}]^-$ is 173°,[11] while the B–N–NN bond angle in the corresponding azide derivative $[(\mathrm{C_6F_5})_3\mathrm{BNNN}]^-$ is 122°.[12] The greater bond angle for isothiocyanate derivatives may be rationalized in simple valence bond terms by recognizing that the resonance structure for a linear isothiocyanate $\mathrm{E{-}N^+{\equiv}C{-}S^-}$ has a favorable formal charge distribution whereas the formal charge distribution for a linear azide interaction (neglecting π-bonding with E) $\mathrm{E{-}N^+{\equiv}N^+{-}N^{2-}}$ is unfavorable. As such, azide compounds typically have bent E–N–NN groups corresponding to the geometries expected for the resonance structures $\mathrm{E{-}N{=}N^+{=}N^-}$ and $\mathrm{E{-}N^-{-}N^+{\equiv}N}$.[13,14]

In summary, a variety of nickel boratrane derivatives, namely [κ^4-B(mim$^{\mathrm{Bu^t}}$)$_3$]Ni(κ^1-OAc), [κ^4-B(mim$^{\mathrm{Bu^t}}$)$_3$]NiNCS and [κ^4-B(mim$^{\mathrm{Bu^t}}$)$_3$]NiN$_3$, may be obtained *via* metathesis of the chloride ligand of [κ^4-B(mim$^{\mathrm{Bu^t}}$)$_3$]NiCl. The Ni → B bond in these complexes is a site of reactivity and thereby provides a means of synthesizing nickel complexes that feature *B*-functionalized tris(mercaptoimidazolyl)borate derivatives, [YTm$^{\mathrm{Bu^t}}$]NiZ, specific examples of which include [FTm$^{\mathrm{Bu^t}}$]-NiCl, [ClTm$^{\mathrm{Bu^t}}$]NiCl, [ClTm$^{\mathrm{Bu^t}}$]NiBr, [ClTm$^{\mathrm{Bu^t}}$]NiI, [N$_3$Tm$^{\mathrm{Bu^t}}$]NiI and [SCNTm$^{\mathrm{Bu^t}}$]NiI.

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4 For comparison, these dative covalent bond lengths are only slightly longer than the respective single covalent bonds predicted on the basis of the covalent radii of the atoms: d(Ni–B) = 2.03 Å and d(Ni–S) = 2.23 Å; r_{cov}(Ni) = 1.21 Å, r_{cov}(Pd) = 1.31 Å, r_{cov}(B) = 0.82 Å and r_{cov}(S) = 1.02 Å. Source: WebElements [http://www.webelements.com/].

5 Reactivity of a M → B bond has also been invoked to account for the formation of [η^2-(*C*,*S*),κ^2-*S*′,*S*″-SC(PPh$_3$)BH(mim$^{\mathrm{Me}}$)$_2$]-Rh(PPh$_3$)H upon reaction of [RhCl(CS)(PPh$_3$)$_2$] with Na[Bm$^{\mathrm{Me}}$]; however, the postulated intermediate with a M → B bond was not observed. See: I. R. Crossley, A. F. Hill and A. C. Willis, *Organometallics*, 2007, **26**, 3891–3895.

6 Another example of a *B*-functionalized tris(2-mercaptoimidazolyl)borate ligand is provided by [κ^2-AcOB(mim$^{\mathrm{Bu^t}}$)$_3$]$_2$Pd. See ref. 1*e*.

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