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Reactivity of the Metal→BX_3 Dative σ-Bond: 1,2-Addition Reactions of the Fe→BX_3 Moiety of the Ferraboratrane Complex $[\kappa^4\text{-B(mim}^{\text{Bu}^\text{t}})_3]\text{Fe(CO)}_2$

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The ferraboratrane $[\kappa^4\text{-B(mim}^{\text{Bu}^\text{t}})_3]\text{Fe(CO)}_2$ ($\text{mim}^{\text{Bu}^\text{t}}$ = 2-mercapto-1-*tert*-butylimidazolyl), the first example of a complex which possesses a retrodative (i.e., metal-to-ligand) Fe→B bond, is obtained via reaction of the tris(2-mercapto-1-*tert*-butylimidazolyl)hydroborato complex $[\text{Tm}^{\text{Bu}^\text{t}}]\text{FeCl}$ with $LiCH_2SiMe_3$ followed by treatment with CO. Significantly, $[\kappa^4\text{-B(mim}^{\text{Bu}^\text{t}})_3]\text{Fe(CO)}_2$ exhibits novel reactivity towards a variety of reagents that results in eradication of the Fe→B bond via a formal 1,2-addition process and the formation of B-functionalized tris(mercaptoimidazolyl)borate derivatives, $[\text{XTm}^{\text{Bu}^\text{t}}]\text{FeY}$.

The coordination chemistry of the transition metals is dominated by ligands that are electron-pair donors in their closed-shell form and interact with the metal via M−X covalent and M←L dative covalent σ-interactions.[1,2] Correspondingly, transition metal complexes which feature electron-pair *acceptor* ligands (i.e., Lewis acids, Z) that coordinate via metal-to-ligand M→Z retrodative σ-interactions are rare.[1,3] Such compounds are, nevertheless, of considerable interest because the σ-acceptor character of the ligand is anticipated to have a profound effect on the nature of a metal center. In this regard, trivalent boron compounds of the class BX_3 offer considerable potential as acceptor ligands. However, while the existence of transition metal−BX_3 complexes has been postulated for some time,[4] the nature of some of these complexes has been called into question[5,6] and the first definitive evidence was reported in 1999 with Hill's structural characterization of the "ruthenaboratrane" complex, $[\kappa^4\text{-B(mim}^{\text{Me}})_3]\text{Ru(CO)(PPh}_3)$ (mim^{Me} = 2-mercapto-1-methylimidazolyl).[7,8] Several other metallaboratrane complexes $\{[\kappa^4\text{-B(mim}^{\text{R}})_3]\text{M}\}$,[9−11] as well as related $\{[\kappa^3\text{-}S,S,B\text{-XB(mim}^{\text{R}})_2]\text{M}\}$[11,12] and $\{[\kappa^3\text{-PhB(C}_6\text{H}_4\text{-PPr}^\text{i}{}_2)_2]\text{M}\}$ derivatives,[13−15] have been subsequently reported, but despite these studies, the reactivity associated with the M→BX_3 moiety remains unexplored. Therefore, in this paper, we describe the synthesis and structural characterization of the first ferraboratrane derivative and demonstrate that the Fe→B bond in this complex is reactive towards a variety of reagents, thereby providing new examples of boron-func-

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[1] For an account of the L, X, and Z classification of metal−ligand interactions, see: Green, M. L. H. *J. Organomet. Chem.* **1995**, *500*, 127−148.

[2] For a discussion of the distinction between covalent and dative covalent bonds, see: Haaland, A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 992−1007.

[3] It must be emphasized that, while retrodative M→Z σ-interactions are rare, π- and δ-back-bonding interactions are well known (e.g., CO, C_2H_4, and C_6H_6), but these are supplements to the dative M←L interactions.

[4] For example, the adduct $\text{Ir(PPh}_3)_2\text{(CO)Cl(BF}_3)$ has been spectroscopically characterized but dissociates BF_3 upon removal of the solvent. See: Scott, R. N.; Shriver, D. F.; Vaska, L. *J. Am. Chem. Soc.* **1968**, *90*, 1079−1080.

[5] Early claims of complexes containing M→BX_3 interactions have been shown to be either incorrect or called into question due to lack of structural characterization. See, for example: (a) Braunschweig, H. *Angew. Chem., Int. Ed.* **1998**, *37*, 1786−1801. (b) Braunschweig, H.; Colling, M. *Coord. Chem. Rev.* **2001**, *223*, 1−51.

[6] Structurally characterized M→BX_3 complexes are, nevertheless, known for the main group metals, e.g., $\text{Cp*MB(C}_6\text{F}_5)_3$ (M = Al, Ga). See: Cowley, A. H. *Chem. Commun.* **2004**, 2369−2375 and references therein.

[7] (a) Hill, A. F.; Owen, G. R.; White, A. J. P.; Williams, D. J. *Angew. Chem., Int. Ed.* **1999**, *38*, 2759−2761. (b) Foreman, M. R. St.-J.; Hill, A. F.; Owen, G. R.; White, A. J. P.; Williams, D. J. *Organometallics* **2003**, *22*, 4446−4450.

[8] Piers has also reported complexes with M→B interactions derived from an anionic closed shell borataalkene, namely $\text{Cp}_2\text{Ta}[\eta^2\text{-CH}_2\text{-B(C}_6\text{F}_5)_2]\text{L}$ (L = CO, CNBu^t). See: (a) Cook, K. S.; Piers, W. E.; Woo, T. K.; McDonald, R. *Organometallics* **2001**, *20*, 3927−3937. (b) Cook, K. S.; Piers, W. E.; Rettig, S. J. *Organometallics* **1999**, *18*, 1575−1577.

[9] Crossley, I. R.; Hill, A. F.; Willis, A. C. *Organometallics* **2006**, *25*, 289−299 and references therein.

[10] Mihalcik, D. J.; White, J. L.; Tanski, J. M.; Zakharov, L. N.; Yap, G. P. A.; Incarvito, C. D.; Rheingold, A. L.; Rabinovich, D. *Dalton Trans.* **2004**, 1626−1634.

[11] Landry, V. K.; Melnick, J. G.; Buccella, D.; Pang, K.; Ulichny, J. C.; Parkin, G. *Inorg. Chem.* **2006**, *45*, 2588−2597.

[12] Crossley, I. R.; Hill, A. F.; Willis, A. C. *Organometallics* **2005**, *24*, 1062−1064.

[13] Bontemps, S.; Gornitzka, H.; Bouhadir, G.; Miqueu, K.; Bourissou, D. *Angew. Chem., Int. Ed.* **2006**, *45*, 1611−1614.

[14] For a boratrane derived from B(taz)_3 (taz = 4-ethyl-3-methyl-5-thioxo-1,2,4-triazolyl), see: Blagg, R. J.; Charmant, J. P. H.; Connelly, N. G.; Haddow, M. F.; Orpen, A. G. *Chem. Commun.* **2006**, 2350−2352.

[15] For dinuclear compounds with bridging boryl ligands that feature a M→B component to the bonding, see: (a) Braunschweig, H.; Radacki, K.; Rais, D.; Whittell, G. R. *Angew. Chem., Int. Ed.* **2005**, *44*, 1192−1193. (b) Westcott, S. A.; Marder, T. B.; Baker, R. T.; Harlow, R. L.; Calabrese, J. C.; Lam, K. C.; Lin, Z. *Polyhedron* **2004**, *23*, 2665−2677. (c) Curtis, D.; Lesley, M. J. G.; Norman, N. C.; Orpen, A. G.; Starbuck, J. *J. Chem. Soc., Dalton Trans.* **1999**, 1687−1694.

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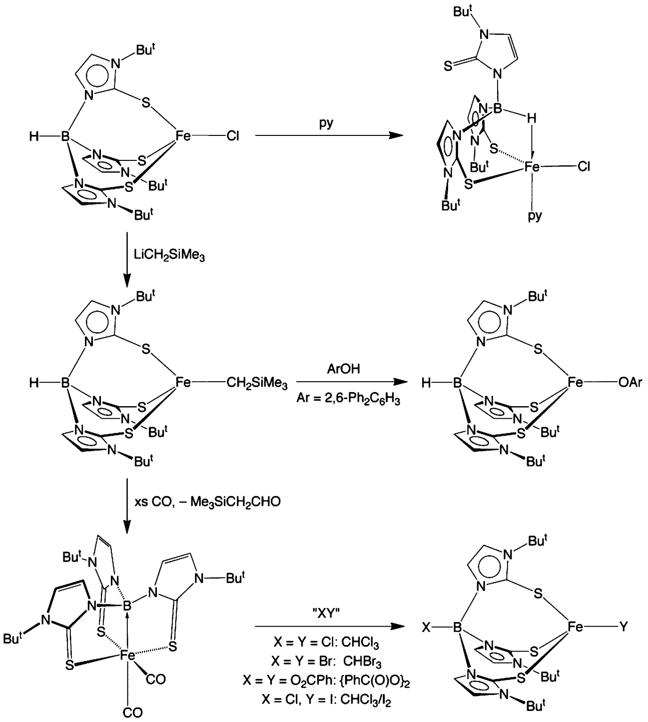
Scheme 1



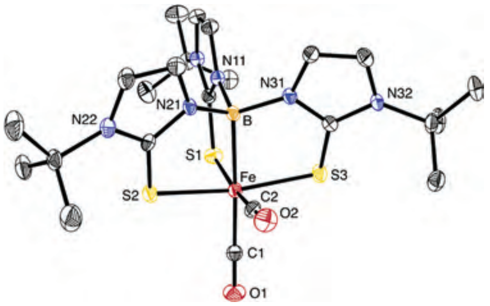


Figure 1. Molecular structure of $[\kappa^4\text{-B(mim}^{\text{Bu}^t})_3]\text{Fe(CO)}_2$.

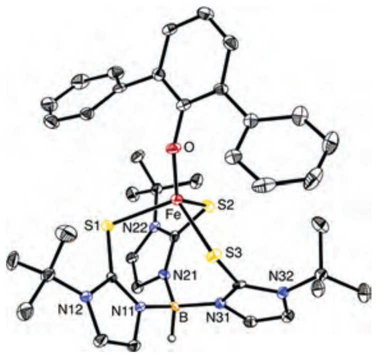


Figure 2. Molecular structure of $[\text{Tm}^{\text{Bu}^t}]\text{FeOAr}$ (Ar = 2,6-$\text{Ph}_2\text{C}_6\text{H}_3$).

tionalized ligands that are presently inaccessible by other synthetic methods.

While metallaboratranes have so far been synthesized for many of the later transition metals (Ru, Os, Co, Rh, Ir, and Pt), noticeably missing from this list is iron, despite the fact that its congener ruthenium afforded the first metallaboratrane.[7] The synthesis of a ferraboratrane was, therefore, considered a worthy objective. Since metallaboratrane complexes $\{[\kappa^4\text{-B(mim}^{\text{R}})_3]\text{M}\}$ are typically obtained via a B−H cleavage reaction of the corresponding tris(2-mercapto-1-R-imidazolyl)hydroborato ligand, $[\text{HB(mim}^{\text{R}})_3] = [\text{Tm}^{\text{R}}]$, we sought $[\text{Tm}^{\text{R}}]\text{FeX}$ derivatives to serve as appropriate precursors. In this regard, our previous studies concerned with the $\{[\text{Tm}^{\text{Ph}}]\text{Fe}\}$ system suggested that phenyl substituents are not suitable for our objective because of the facile formation of 2:1 derivatives, namely $[\kappa^3\text{-}S,S,H\text{-Tm}^{\text{Ph}}]_2\text{Fe}$ and $\{[\text{Tm}^{\text{Ph}}]_2\text{Fe}\}^+$.[16] For this reason, we turned our attention to the $[\text{Tm}^{\text{Bu}^t}]$ ligand, with the notion that the bulkier Bu^t substituents could reduce the tendency to form 2:1 complexes. Indeed, the 1:1 complex $[\text{Tm}^{\text{Bu}^t}]\text{FeCl}$ may be readily obtained by reaction of $[\text{Tm}^{\text{Bu}^t}]\text{Tl}$[10] with FeCl_2.[17]

Significantly, $[\text{Tm}^{\text{Bu}^t}]\text{FeCl}$ is readily converted to the divalent octahedral d^6 ferraboratrane $[\kappa^4\text{-B(mim}^{\text{Bu}^t})_3]\text{Fe(CO)}_2$[18,19] via a two-step sequence involving (i) alkylation with $\text{LiCH}_2\text{SiMe}_3$ followed by (ii) reaction with CO (Scheme 1). The molecular structure of $[\kappa^4\text{-B(mim}^{\text{Bu}^t})_3]\text{Fe(CO)}_2$ has been determined by X-ray diffraction, which clearly reveals the presence of an $\text{Fe}\rightarrow\text{BX}_3$ σ-interaction (Figure 1). Indeed, the Fe−B bond length of 2.108(6) Å is only slightly longer than the corresponding values for iron boryl and borylene derivatives,[20] e.g., $\text{CpFe(CO)}_2(\text{BPh}_2)$ [2.034(3) Å][21] and $(\text{CO})_4\text{FeBCp*}$ [2.010(3) Å].[22,23]

With respect to the mechanism of formation of $[\kappa^4\text{-B(mim}^{\text{Bu}^t})_3]\text{Fe(CO)}_2$, the first step of the sequence is believed to involve the formation of $[\text{Tm}^{\text{Bu}^t}]\text{FeCH}_2\text{SiMe}_3$, although the latter has not been isolated because concentrating the solution results in ligand redistribution and the formation of $[\kappa^3\text{-}S,S,H\text{-Tm}^{\text{Bu}^t}]_2\text{Fe}$. However, good evidence for the formulation of $[\text{Tm}^{\text{Bu}^t}]\text{FeCH}_2\text{SiMe}_3$ is provided by the observation that addition of ArOH (Ar = 2,6-$\text{Ph}_2\text{C}_6\text{H}_3$) yields the aryloxide $[\text{Tm}^{\text{Bu}^t}]\text{FeOAr}$ and Me_4Si (Scheme 1 and Figure 2).

The second step of the sequence, i.e., the formation of the ferraboratrane $[\kappa^4\text{-B(mim}^{\text{Bu}^t})_3]\text{Fe(CO)}_2$ upon treatment of

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(16) Kimblin, C.; Churchill, D. G.; Bridgewater, B. M.; Girard, J. N.; Quarless, D. A.; Parkin, G. *Polyhedron* **2001**, *20*, 1891−1896.

(17) Related examples of tetrahedral iron(II) chloride complexes employing C_3-symmetric tripodal ligands include $[\text{Tp}^{\text{Bu}^t}]\text{FeCl}$,[a] $[\text{PhTp}^{\text{Bu}^t}]\text{FeCl}$,[b] and $[\text{PhB(CH}_2\text{PPr}^i{}_2)_3]\text{FeCl}$.[c] (a) Gorrell, I. B.; Parkin, G. *Inorg. Chem.* **1990**, *29*, 2452−2456. (b) Kisko, J. L.; Hascall, T.; Parkin, G. *J. Am. Chem. Soc.* **1998**, *120*, 10561−10562. (c) Betley, T. A.; Peters, J. C. *Inorg. Chem.* **2003**, *42*, 5074−5084.

(18) While some proponents of oxidation state formalisms may view the d^6 configuration to imply that the compound is a derivative of a dianionic $[\text{BX}_3]^{2-}$ ligand with an $\text{Fe}^{2+}\leftarrow\text{BX}_3{}^{2-}$ dative bond, it must be emphasized that the $\text{Fe}\rightarrow\text{B}$ retrodative bond description provided here is in complete accord with Covalent Bond Classification method of ref 1.

(19) For a discussion of the bonding in boratrane compounds, see ref 11.

(20) For recent reviews of complexes with M−B bonds, see: (a) Irvine, G. J.; Lesley, M. J. G.; Marder, T. B.; Norman, N. C.; Rice, C. R.; Robins, E. G.; Roper, W. R.; Whittell, G.; Wright, L. J.*Chem. Rev.* **1998**, *98*, 2685−2722. (b) Braunschweig, H. *Angew. Chem., Int. Ed.* **1998**, *37*, 1786−1801. (c) Braunschweig, H.; Colling, M. *Coord. Chem. Rev.* **2001**, *223*, 1−51. (d) Aldridge, S.; Coombs, D. L. *Coord. Chem. Rev.* **2004**, *248*, 535−559.

(21) Hartwig, J. F.; Huber, S. *J. Am. Chem. Soc.* **1993**, *115*, 4908−4909.

(22) Cowley, A. H.; Lomelí, V.; Voight, A. *J. Am. Chem. Soc.* **1998**, *120*, 6401−6402.

(23) It is pertinent to note that $\text{Fe}\rightarrow\text{B}$ interactions have been considered to account for the displacement of boron from the cyclopentadienyl plane in ferrocenylboranes, but recent calculations suggest there is no direct bonding interaction. See: Scheibitz, M.; Bolte, M.; Bats, J. W.; Lerner, H.-W.; Nowik, I.; Herber, R. H.; Krapp, A.; Lein, M.; Holthausen, M. C.; Wagner, M. *Chem. Eur. J.* **2005**, *11*, 584−603.

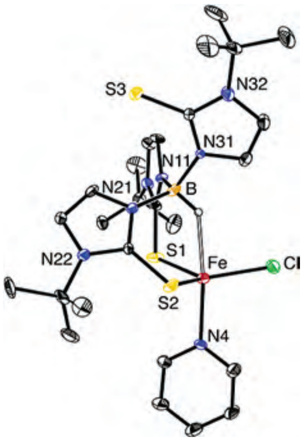

Figure 3. Molecular structure of $[\kappa^3\text{-}H,S,S\text{-}[Tm^{Bu^t}]FeCl(py)$.

$[Tm^{Bu^t}]FeCH_2SiMe_3$ with CO, is accompanied by liberation of Me_3SiCH_2CHO rather than Me_4Si. Furthermore, deuterium labeling employing $[DTm^{Bu^t}]FeCH_2SiMe_3$ demonstrates it is the hydrogen on boron that becomes a component of the formyl group.

A critical aspect of the proposed mechanism for boratrane formation is activation and cleavage of the B−H bond. Insight into this step is provided by the structural characterization of the pyridine adduct $[\kappa^3\text{-}H,S,S\text{-}Tm^{Bu^t}]FeCl(py)$ obtained by treatment of $[Tm^{Bu^t}]FeCl$ with pyridine (Scheme 1). Significantly, coordination of pyridine results in dissociation of one of the mercaptoimidazolyl arms and replacement with a 3-center-2-electron B−H−Fe interaction (Figure 3). On this basis, we suggest that coordination of CO induces rearrangement of the $[Tm^{Bu^t}]$ ligand, thereby promoting cleavage of the B−H bond.

The most novel aspect of $[\kappa^4\text{-}B(mim^{Bu^t})_3]Fe(CO)_2$ is concerned with its reactivity, especially with respect to reactions that involve eradication of the Fe→B bond. For example, $[\kappa^4\text{-}B(mim^{Bu^t})_3]Fe(CO)_2$ reacts with dibenzoyl peroxide $[PhC(O)O]_2$ to undergo a formal 1,2-addition across the Fe→B bond to give $[PhC(O)OTm^{Bu^t}]Fe[\kappa^2\text{-}OC(O)Ph]$ in which the benzoate function is installed at both iron and boron, as illustrated in Figure 4. This reaction is particularly significant because it provides a means of synthesizing a new class of B-functionalized tris(mercaptoimidazolyl)borate ligands, $[XTm^{Bu^t}]$. In this regard, other B-functionalized $[XTm^{Bu^t}]FeX$ complexes are also available from $[\kappa^4\text{-}B(mim^{Bu^t})_3]Fe(CO)_2$. For example, $[\kappa^4\text{-}B(mim^{Bu^t})_3]Fe(CO)_2$ reacts with CHX_3 (X = Cl, Br) to yield $[XTm^{Bu^t}]FeX$.[24] In addition to symmetric 1,2-addition reactions that install the same X substituent on iron and boron, asymmetric variants are also possible. Thus, treatment of $[\kappa^4\text{-}B(mim^{Bu^t})_3]Fe(CO)_2$ with I_2 (0.5 equiv) in $CHCl_3$ gives $[ClTm^{Bu^t}]FeI$ in which the iodine and chlorine selectively add to the iron and boron, respectively.

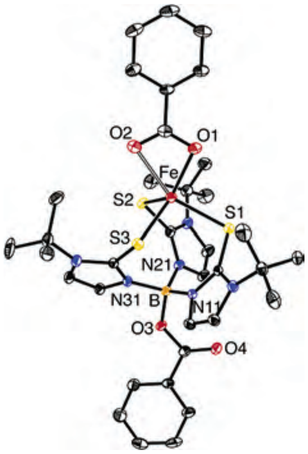

Figure 4. Molecular structure of $[PhC(O)OTm^{Bu^t}]Fe[\kappa^2\text{-}OC(O)Ph]$.

While the mechanisms of these formal 1,2-addition reactions are not known, the formation of the mixed complex $[ClTm^{Bu^t}]FeI$ suggests that the reaction does not involve a direct concerted addition across the Fe→B bond. Regardless of the mechanism, however, the ability to transform a $[Tm^{Bu^t}]$ ligand into $[XTm^{Bu^t}]$ ligands with diverse susbtituents on boron is particularly noteworthy because only methyl and phenyl substituents have been previously incorporated into $[RTm^{Me}]$ ligands. The ability to vary the substituent on boron thus represents a potentially powerful method for tuning the chemistry of pseudo-tetrahedral $[XTm^R]M$ complexes.[25] Such modular control is also appealing in view of the fact that the $[Tm^R]$ platform has found widespread recent applications in providing an $[S_3]$ donor environment in coordination chemistry[26] and substituted derivatives $[XTm^R]$ provide a means of probing electronic effects in such systems.

In summary, the ferraboratrane $[\kappa^4\text{-}B(mim^{Bu^t})_3]Fe(CO)_2$ exhibits novel reactivity of the Fe→B bond, thereby allowing access to a series of unprecedented B-functionalized complexes of the type $[XTm^{Bu^t}]FeY$. Furthermore, it is anticipated that the ability to interconvert $[XTm^R]$ and $[\kappa^4\text{-}B(mim^R)_3]$ ligands may provide a powerful strategy for modulating the reactivity of a metal center, a feature that is not available for tris(pyrazolyl)borate counterparts

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Supporting Information Available: Experimental details for all new compounds and crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(24) It is worth noting that complexes with a chloro bis(mercaptoimidazolyl) ligand, namely $CpM[\kappa^2\text{-}H(Cl)B(mim^{Me})_2]Cl_2$ (M = Nb, Ta), have been obtained via degradation of the $[Tm^{Me}]$ ligand upon treatment of $CpMCl_4$ (M = Nb, Ta) with $[Tm^{Me}]SnPh_3$. See: Hill, A. F.; Smith, M. K. *Chem. Commun.* **2005**, 1920−1922.

(25) For a recent discussion concerned with the influence of ligand substituents in tuning the electronic properties of pseudo-tetrahedral cobalt complexes, see: Jenkins, D. M.; Peters, J. C. *J. Am. Chem. Soc.* **2005**, *127*, 7148−7165.

(26) For example, as applied to synthetic analogues of zinc enzymes. See: Parkin, G. *Chem. Rev.* **2004**, *104*, 699−767 and references therein.