

# Synthesis and structural characterization of a new class of organoborato ligands containing imidazolyl functional groups [MeB(Im<sup>N-Me</sup>)<sub>2</sub>(X)]<sup>-</sup>

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A series of alkylborate compounds containing imidazolyl functional groups [MeB(Im<sup>N-Me</sup>)<sub>2</sub>(X)]<sup>-</sup> (X = OPr<sup>i</sup> **1**, Cl **2**, Pz **3** or Ph **4**) has been synthesized and characterized. Reaction of di(isopropoxy)methylborane with 2 equivalents of 2-lithio-1-methylimidazole yielded the lithium isopropoxymethylbis(2-methyl-1-imidazolyl)borate, Li[**1**]. The chlorobis(imidazolyl)methylborate **2**, which was obtained by treatment of **1** with HCl, could be transformed to the pyrazolyl and phenyl derivatives **3** and **4**, respectively, by nucleophilic substitution of the B-bound chlorine atom. The molecular structures of {H<sub>2</sub>[**2**]}Cl, H[**3**] and Ni[**4**]<sub>2</sub> have been successfully determined by X-ray crystallography. In {H<sub>2</sub>[**2**]}Cl both the imidazolyl groups are protonated, forming an intermolecular hydrogen bonding interaction with the chloride anion and giving a dimeric structure. In H[**3**] an intramolecular hydrogen bond between the non-coordinated nitrogen atoms of the two imidazolyl groups is formed. Structural properties of the protonated imidazole rings in {H<sub>2</sub>[**2**]}<sup>+</sup> and H[**3**] indicate delocalization of positive charge over the rings, which results in strong interaction with the negatively charged boron center. Formation of Ni[**4**]<sub>2</sub> clearly indicates the chelation ability of the bis(imidazolyl)-borate framework. Therefore, the imidazolyl groups in [MeB(Im<sup>N-Me</sup>)<sub>2</sub>(X)]<sup>-</sup> act as a proton acceptor and metal-binding site as found for poly(pyrazolyl)borates.

## Introduction

A family of poly(pyrazolyl)borates [X<sub>4-n</sub>B(Pz<sup>R</sup>)<sub>n</sub>]<sup>-</sup> (n = 2–4; X = H or alkyl; HPz<sup>R</sup> = pyrazole where R denotes substituents on the pyrazole ring) has been extensively utilized in study of the co-ordination chemistry of transition metal complexes.<sup>1</sup> In general, the poly(pyrazolyl)borate ligands produce a relatively stable metal–ligand fragment (=M[X<sub>4-n</sub>B(Pz<sup>R</sup>)<sub>n</sub>]) due to electrostatic interaction as well as the chelate effect derived from their monoanionic, multidentate properties. We have been investigating the chemistry of various transition metal complexes with hydrotris(pyrazolyl)borate ligands Tp<sup>R</sup> (= [HB(Pz<sup>R</sup>)<sub>3</sub>]<sup>-</sup>) from bioinorganic and organometallic viewpoints.<sup>2</sup> Recently, we have developed a brand-new monoanionic ligand system on the basis of the B–C<sub>alkyl</sub> linkage which should be resistant to nucleophilic attack on the boron atom leading to decomposition of the ligands. Herein we report the synthesis and characterization of a new class of borate compounds containing a methylbis(1-methyl-2-imidazolyl)borane framework [MeB(Im<sup>N-Me</sup>)<sub>2</sub>(X)]<sup>-</sup> (X = OPr<sup>i</sup> **1**, Cl **2**, Pz **3** or Ph **4**; see Chart 1).

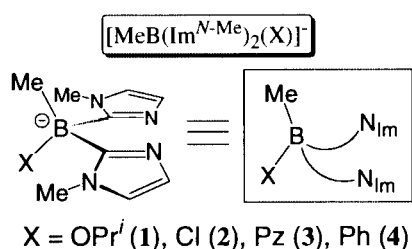


Chart 1

Especially, the chloride group in **2** was readily replaced by another nucleophile; transformation from **2** to **3** and **4** was achieved by treatment with sodium pyrazolate (NaPz) and

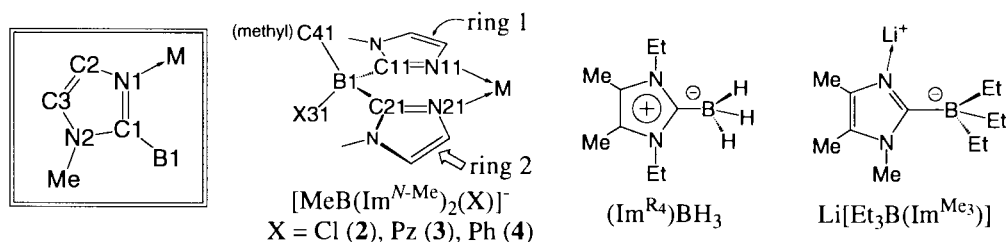
phenyllithium (PhLi), respectively, and the molecular structures of their derivatives {H<sub>2</sub>[**2**]}Cl, H[**3**] and Ni[**4**]<sub>2</sub> were determined by X-ray crystallography. In this paper, we will also discuss a unique structural property of the boron–imidazole linkage.

## Results and discussion

### 1. Synthesis and characterization of chlorobis(imidazolyl)-methylborate (**2**)

It is known that the alkoxide moiety of tri(alkoxy)borane B(OR)<sub>3</sub> can be replaced by an alkyl group by reaction with alkyl-lithium.<sup>3</sup> In fact, reaction of tri(isopropoxy)borane B(OPr<sup>i</sup>)<sub>3</sub> with 1 equivalent of methylolithium and subsequent treatment with benzoyl chloride yielded di(isopropoxy)methylborane, MeB(OPr<sup>i</sup>)<sub>2</sub>, as reported by Venanzi and his co-workers.<sup>4</sup> We examined introduction of imidazolyl groups, which can act as metal co-ordination sites, on the B atom with a similar synthetic procedure (*i.e.*, reaction of alkoxyborane with lithio-imidazole). Addition of 0.5 equivalent of MeB(OPr<sup>i</sup>)<sub>2</sub> to *in situ* generated 2-lithio-1-methylimidazole (in THF) followed by heating at the refluxing temperature of THF resulted in formation of lithium isopropoxymethylbis(2-methyl-1-imidazolyl)borate, Li[MeB(Im<sup>N-Me</sup>)<sub>2</sub>(OPr<sup>i</sup>)] (Li[**1**]) (Scheme 1), as was confirmed by spectroscopy. FAB-MS analysis showed an anion peak at *m/z* = 247 attributed to [1]<sup>-</sup>. A <sup>1</sup>H NMR spectrum was consistent with the formulation of **1**.

In contrast to dihydrobis(pyrazolyl)borate Bp<sup>R</sup> (= [H<sub>2</sub>B(Pz<sup>R</sup>)<sub>2</sub>]<sup>-</sup>), compound **1** contains neither a B–H nor a B–N bond which may be hydrolysed under acidic condition, and therefore the OPr<sup>i</sup> moiety is expected readily to be replaced by another functional group. In fact, treatment of Li[**1**] with anhydrous HCl yielded dihydrogen chloromethylbis(1-methyl-2-imidazolyl)borate chloride {H<sub>2</sub>[ClMeB(Im<sup>N-Me</sup>)<sub>2</sub>]}Cl (= {H<sub>2</sub>[**2**]}Cl), which can be alternatively formulated as a HCl adduct of

**Table 1** Structural parameters (bond lengths in Å, angles in °) of B-atom connecting imidazole rings

	{H <sub>2</sub> [2]}Cl X, M = Cl, H		H[3] N, H		Ni[4] <sub>2</sub> C, Ni		(Im <sup>R<sub>4</sub></sup> )BH <sub>3</sub> (ref. 11)	Li[Et <sub>3</sub> B(Im <sup>Me<sub>3</sub></sup> )] (ref. 12)
	ring 1	ring 2	ring 1	ring 2	ring 1	ring 2		
N1–C1	1.345(7)	1.360(7)	1.354(4)	1.330(4)	1.347(3)	1.347(3)	1.352(2)	1.337(4)
C1–N2	1.349(6)	1.346(7)	1.343(4)	1.376(4)	1.363(3)	1.361(3)	1.352(2)	1.373(4)
N2–C3	1.371(8)	1.378(6)	1.390(4)	1.364(4)	1.372(3)	1.376(3)	1.393(2)	1.389(5)
C3–C2	1.343(8)	1.330(8)	1.311(5)	1.336(5)	1.339(4)	1.328(4)	1.350(2)	1.346(5)
C2–N1	1.373(7)	1.366(7)	1.387(4)	1.387(4)	1.375(3)	1.379(3)	1.393(2)	1.388(5)
B–C1	1.615(8)	1.597(8)	1.635(4)	1.623(4)	1.635(3)	1.633(4)	1.603(3)	1.645(5)
B–C41		1.667(9)		1.629(4)		1.625(4)		
B–X31		1.887(6)		1.558(4)		1.631(3)		
N1–M	1.14(6)	0.93(7)	1.03(3)	1.78(4)	1.886(2)	1.896(2)		
	(H11)	(H21)						
N1–C1–N2	104.5(4)	105.3(4)	105.7(3)	108.4(3)	106.5(2)	106.6(2)	104.7(1)	107.4(3)
C1–N2–C3	110.5(5)	110.3(5)	109.9(3)	108.7(3)	109.6(2)	109.4(2)	111.2(1)	109.3(3)
N2–C3–C2	107.6(5)	106.7(4)	107.2(3)	106.1(3)	106.7(2)	106.7(2)	106.5(1)	105.7(3)
C3–C2–N1	105.7(5)	108.1(5)	107.9(3)	110.3(3)	108.6(2)	108.9(2)	106.5(1)	109.4(3)
C2–N1–C1	111.7(4)	109.6(5)	109.3(3)	106.4(3)	108.7(2)	108.3(2)	111.1(1)	108.2(3)
C1–B1–C41	108.7(4)	113.1(5)	109.5(2)	111.4(2)	110.1(2)	108.0(2)		
C1–B1–X31	110.1(4)	104.5(3)	107.7(2)	108.5(2)	109.5(2)	111.4(2)		
C11–B1–C21		110.5(5)		107.7(2)		103.9(2)		
C41–B1–X31		109.8(4)		111.8(3)		113.4(2)		
N11–M–N21		—		139(2)		88.48(8), 91.52(8)		

protonated **2** (=H[2]·HCl), and its molecular structure was revealed by X-ray crystallography. The molecular structure of {H<sub>2</sub>[2]}Cl is presented in Fig. 1 and structural parameters of the [MeB(Im<sup>N-Me</sup>)<sub>2</sub>(X)]<sup>-</sup> moiety in {H<sub>2</sub>[2]}Cl, H[3] and Ni[4]<sub>2</sub> (see below) are summarized in Table 1. The chlorine atom attached to the boron center was assigned on the basis of the longest bond length from the B atom, clearly distinct from the remaining B–C lengths, as well as its relatively high electron density on a Fourier map. Remarkably, both the imidazolyl groups were protonated which resulted in formation of hydrogen bonding interaction with the chloride anion (H11···Cl51, 1.98(6); N11···Cl51, 3.073(5); H21'···Cl51, 2.26(7); N21'···Cl51, 3.103(6) Å; H11···Cl51···H21', 100(3)°) giving a dimeric cyclic structure. Similar hydrogen bonding interaction between H<sup>+</sup> attached on the pyrazolyl N atoms and Cl<sup>-</sup> was observed upon treatment of Tp<sup>Bu</sup>Tl with HCl.<sup>6</sup>

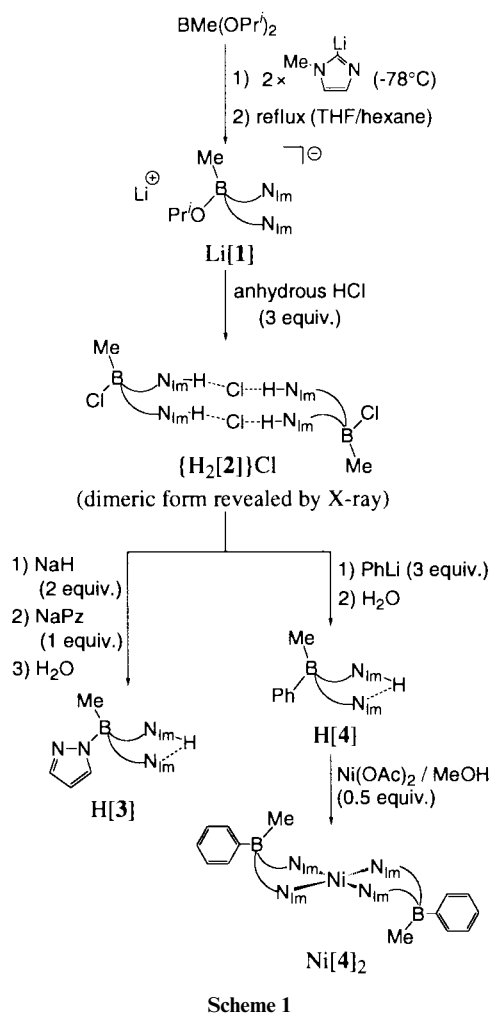
## 2. Nucleophilic substitution of the chloride in compound **2**

We examined the reaction of compound **2** with nucleophilic reagents such as sodium pyrazolate (=NaPz) and phenyllithium (=PhLi) in order to introduce a different functional group onto the boron center of the methylbis(imidazolyl)borane moiety. It should be noted that direct substitution of the OPr<sup>t</sup> group in **1** by pyrazolyl and alkyl groups failed. In contrast, the selective replacement of Cl in **2** by another functional group X giving the corresponding borate compounds [MeB(Im<sup>N-Me</sup>)<sub>2</sub>(X)]<sup>-</sup> was successful, and this behavior clearly demonstrated the utility of **2** for construction of novel metal-supporting “scorpionate” ligands consisting of different functional groups.

Neutralization of {H<sub>2</sub>[2]}Cl by 2 equivalents of NaH followed by reaction with 1 equivalent of NaPz and hydrolytic

work up yielded hydrogen methylbis(1-methyl-2-imidazolyl)-(pyrazolyl)borate, H[MeB(Im<sup>N-Me</sup>)<sub>2</sub>(Pz)] (H[3]). Both <sup>1</sup>H and <sup>13</sup>C NMR spectra contained signals arising from a pyrazolyl group. In addition, a single <sup>11</sup>B resonance at δ -10.6 was at higher field compared to those observed for Li[1] (δ -6.0) and {H<sub>2</sub>[2]}Cl (δ -7.3). These observations evidently indicated the incorporation of the pyrazolyl group onto the B. In addition, a D<sub>2</sub>O-exchangeable signal observed at δ 14.2 in its <sup>1</sup>H NMR indicated protonation of the compound. Finally, its molecular structure was revealed by X-ray crystallography (Fig. 2, Table 1). In contrast to the above mentioned {H<sub>2</sub>[2]}Cl which formed intermolecular hydrogen bonding, an intramolecular hydrogen bond between H11 and the non-protonated N atom (=N21) was formed. Owing to this interaction, the two imidazolyl rings were located almost coplanar. A similar intramolecular hydrogen bond has been observed in hydrogen dimethylbis(2-pyridyl)borate.<sup>7</sup>

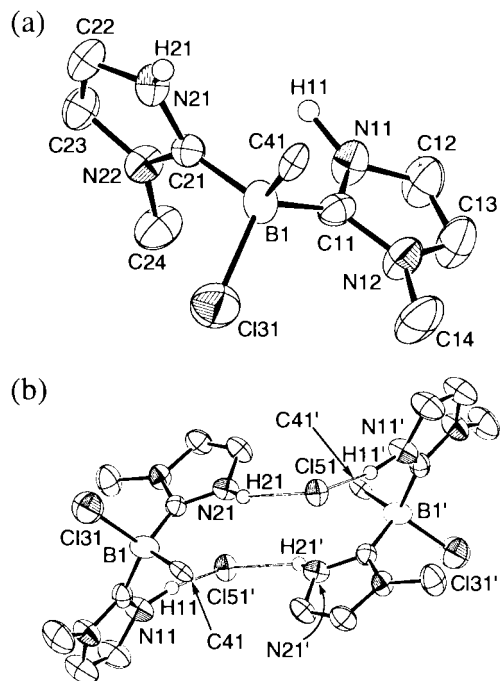
Introduction of another hydrocarbyl group onto the B was achieved by treatment of {H<sub>2</sub>[2]}Cl with 3 equivalents of phenyllithium. The resulting hydrogen methylbis(1-methyl-2-imidazolyl)phenylborate, H[MePhB(Im<sup>N-Me</sup>)<sub>2</sub>] (H[4]), was characterized by NMR spectroscopy. As found for H[3], a broad signal assigned as the imidazolium N–H proton was observed at δ 14.3. A single peak of in the <sup>11</sup>B NMR was observed at δ -17.4. In <sup>13</sup>C NMR, the B-bound carbon atoms of the phenyl and imidazolyl groups were observed as broad signals at δ 153.1 and 169.5, respectively, due to the quadrupole moment of the boron atom. Although our attempts to obtain single crystals of H[4] failed, its nickel complex, Ni[κ<sup>2</sup>-MePhB(Im<sup>N-Me</sup>)<sub>2</sub>] (Ni[4]<sub>2</sub>), was successfully characterized as shown in Fig. 3. The nickel center sat on a crystallographical symmetric center and was surrounded by the imidazolyl-nitrogen atoms in a square-planar arrangement. A six-membered Ni–N–C–B–C–N ring adopted a boat conformation. In summary, the overall



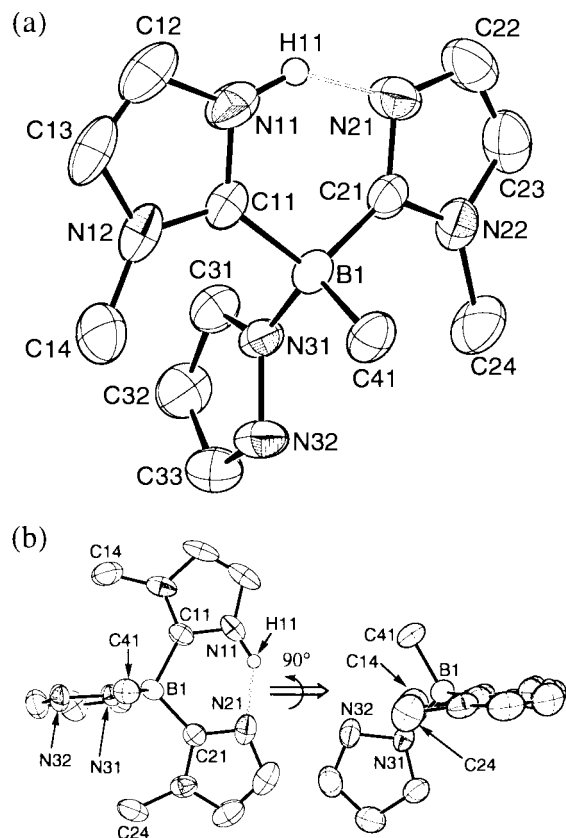
molecular structure of Ni[4]<sub>2</sub> was quite similar to those of nickel complexes with bis(1-pyrazolyl)borates ( $=[R'_2B(Pz^R)_2]^-$ )<sup>8</sup> and dimethylbis(2-pyridyl)borate ( $=[Me_2B(py)_2]^-$ )<sup>7</sup> ligands.

### 3. Structural comparison of [MeB(Im<sup>N-Me</sup>)<sub>2</sub>(X)] moieties

We succeeded in structural determination of cationic, neutral and anionic compounds containing the common [MeB(Im<sup>N-Me</sup>)<sub>2</sub>(X)] fragment. In each compound, the geometry of the boron center was a sp<sup>3</sup>-hybridized tetrahedron. However, bond lengths surrounding the B are clearly different (Table 1) and may depend on the formal charge of the molecules. The diprotonated form of **2** ( $=\{H_2[2]\}^+$ ) has relatively short B–C<sub>imidazolyl</sub> and opposite long B–C<sub>Me</sub> bond lengths compared to those found in the neutral H[3] and the mono-anionic **4** in its nickel complex ( $=Ni[4]_2$ ). In addition, the B–Cl bond length (1.887(6) Å) was somewhat longer than that found for 4,4,8,8-tetrachloro-1,5-dimethylimidazole (1.846(4) Å).<sup>9</sup> This might arise from delocalization of the positive charge over the imidazole ring giving the resonance structures **II** and **III** shown in Scheme 2; interaction between the negatively charged B atom and positively charged imidazole rings became strong, and that resulted in pushing out of the remaining methyl and chloride groups. In fact, the structures of the imidazole rings evidently indicate the delocalization of the positive charge (Table 1). The N1–C1–N2 linkages in the protonated imidazole rings of {H<sub>2</sub>[2]}<sup>+</sup> (rings 1 and 2) and H[3] (ring 1) show different characteristics to those in the non-protonated imidazolyl groups of H[3] and Ni[4]<sub>2</sub>; the C1–N2 bond lengths of the protonated imidazoles (1.343–1.349 Å) are shorter than those of the non-protonated imidazoles (1.360–1.377 Å) and the N1–C1–N2 angles in the protonated imidazoles have decreased when compared to those of the imidazolyl groups. In typical

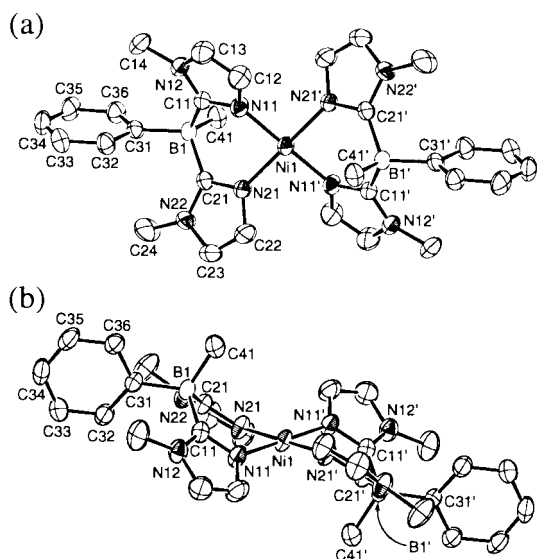


**Fig. 1** An ORTEP<sup>5</sup> drawing of  $\{H_2[ClMeB(Im^{N-Me})_2]\}Cl \cdot C_6H_5Me$  ( $\{H_2[2]\}Cl \cdot C_6H_5Me$ ) drawn at 50% probability level. All hydrogen atoms except those attached on the nitrogen atoms of the imidazolyl groups and the toluene molecule are omitted for clarity. (a) Cation part of the molecule (*i.e.*  $\{H_2[2]\}^+$ ). (b) Dimerized structure of  $\{H_2[2]\}Cl$  via intermolecular hydrogen bonding interaction.

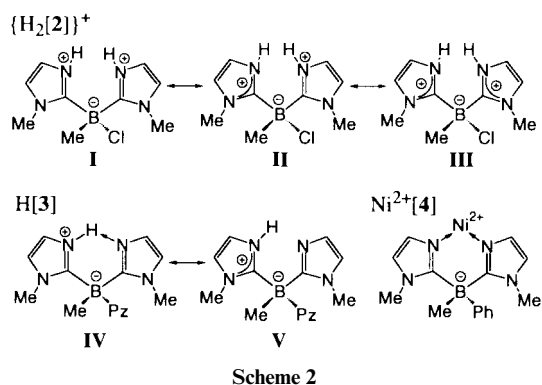


**Fig. 2** Molecular structure of  $H[MeB(Im^{N-Me})_2(Pz)]$  (H[3]) (drawn at 50% probability level). All hydrogen atoms except H11, attached on the nitrogen atom of one of the two imidazolyl groups, are omitted for clarity. (a) Perspective view. (b) Side views.

imidazole compounds, bond alternation (*i.e.* short C1–N1 and long C1–N2) is observed and N1–C1–N2 bond angles are in the range of 107–109°. On the other hand, C1 to N1 and N2



**Fig. 3** An ORTEP diagram of  $\text{Ni}[\kappa^2\text{-MePhB}(\text{Im}^{N\text{-Me}})_2]$  ( $\text{Ni}[4]_2$ ) (50% probability level; all hydrogen atoms are omitted). (a) Perspective view. (b)  $90^\circ$  rotated view of (a).



**Scheme 2**

distances are 1.352(2) Å and the  $\text{Ni}-\text{C}1-\text{N}2$  angle is  $104.7(1)^\circ$  in the tetra-alkylated imidazole–borane adduct,  $(\text{Im}^{\text{R}_2})\text{BH}_3$ , in which the positive charge may be delocalized on the imidazole ring arising from ylide character as found for  $N,N'$ -dialkyl-imidazol-2-ylidene. Moreover, its B–C bond length (1.603(3) Å) is very close to those found for  $\{\text{H}_2[2]\}^+$ .<sup>11</sup>

In contrast, the B–C<sub>imidazolyl</sub> bond lengths found for  $\text{H}[3]$  and  $\text{Ni}[4]_2$  were comparable to that found for a monoimidazolylborate compound, lithium triethyl(1,4,5-trimethyl-2-imidazolyl)borate  $[\text{Et}_3\text{B}(\text{Im}^{\text{Me}})]^-$  (1.645(5) Å).<sup>12</sup> Especially, the structure of ring 1 of  $\text{H}[3]$  indicates positive charge delocalization onto the imidazole ring and that may imply a contribution of the resonance structure **V** shown in Scheme 2. However, the strong intramolecular interaction between the rings 1 and 2 (see above) results in stabilization of the resonance structure **IV**.

## Conclusion

In this study, a series of alkylborate compounds  $[\text{MeB}(\text{Im}^{N\text{-Me}})_2(\text{X})]^-$  ( $\text{X} = \text{OPr}^i$  **1**,  $\text{Cl}$  **2**,  $\text{Pz}$  **3** or  $\text{Ph}$  **4**) is synthesized. The chlorobis(imidazolyl)methylborate **2** obtained by treatment of **1** with  $\text{HCl}$  is versatile, because it can be transformed to the pyrazolyl and phenyl derivatives **3** and **4**, respectively, *via* nucleophilic substitution of  $\text{Cl}$ . X-Ray crystallography of  $\{\text{H}_2[2]\}\text{Cl}$ ,  $\text{H}[3]$  and  $\text{Ni}[4]_2$  reveals the functions of the imidazole group as proton acceptor and metal-binding site as found for poly(pyrazolyl)borates. Protonation of the imidazolyl groups results in delocalization of the positive charge over the imidazole ring and strong interaction with the negatively charged B, and such an electronic effect as well as interaction *via*

inter- and intra-molecular hydrogen bonds result in stabilization of the protonated form. Formation of the nickel complex with **4** clearly indicates the chelation ability of the bis(imidazolyl)borate framework. Detailed investigation for the metallation behavior of our brand-new “scorpionate” ligand systems like **3**, and development of novel ligands based on the bis(imidazolyl)borate motif, is in progress and the results will be reported in due course. Metallation behavior of  $\text{Pz}^{\text{Ph}}$ ,  $\text{Pz}^{\text{Me}}$  and  $\text{Pz}^{\text{Me}_3}$  derivatives of bis(imidazolyl)methyl(pyrazolyl)borates (*i.e.* analogues of **3**) has been reported recently as a communication.<sup>13</sup>

## Experimental

### Instrumentation

The IR measurements were carried out as KBr pellets using JASCO FT/IR-5300 and FT/IR-550 spectrometers, NMR spectra at room temperature on JEOL GX-270 ( $^1\text{H}$ , 270;  $^{13}\text{C}$ , 67.8;  $^{11}\text{B}$ , 86.6 MHz), EX-400 ( $^{13}\text{C}$ , 100 MHz) and Bruker AC-200 ( $^1\text{H}$ , 200 MHz) spectrometers. Chemical shifts are reported in ppm downfield from internal  $\text{SiMe}_4$  (when  $\text{CDCl}_3$ ) or sodium 4,4-dimethyl-4-silapentane-1-sulfonate, DSS ( $\text{D}_2\text{O}$ ), for  $^1\text{H}$  and  $^{13}\text{C}$ , and external  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  for  $^{11}\text{B}$  spectra. Fast atom bombardment mass spectra (FAB-MS) and UV-vis spectra were recorded on a JEOL JMS-700 mass spectrometer and a Shimadzu UV-260 spectrometer, respectively.

### Materials and methods

All experiments were performed under Ar using a standard Schlenk technique. All solvents used were purified by the literature methods.<sup>14</sup> The compound  $\text{B}(\text{OPr}^i)_3$  was dried over Na followed by distillation under Ar. 1-Methylimidazole was dried over  $\text{CaH}_2$  and distilled under reduced pressure. A diethyl ether solution of anhydrous  $\text{HCl}$  was prepared by reaction of  $\text{NaCl}$  with concentrated  $\text{H}_2\text{SO}_4$ . The concentration of the resulting solution was determined by titration. Other reagents of the highest grade commercially available were used without further purification. The compound  $\text{MeB}(\text{OPr}^i)_2$  was prepared according to the literature procedure.<sup>4</sup>

### Synthesis and characterization of the compounds

**$\text{Li}[\text{MeB}(\text{Im}^{N\text{-Me}})_2(\text{OPr}^i)]$  (**Li[1]**).** A 1.5 M hexane solution of *n*-butyllithium (150 mL; 225 mmol) was slowly added to a THF solution (300 mL) of 1-methylimidazole (238 mmol) at  $-78^\circ\text{C}$ . The resulting mixture was allowed to warm gradually to ambient temperature, and stirring was continued for 12 h. A THF solution (30 mL) of  $\text{MeB}(\text{OPr}^i)_2$  (16.45g; 86 mmol; 114 mmol) was added dropwise to the mixture chilled to  $-78^\circ\text{C}$ . The resulting mixture was allowed to warm gradually to room temperature and stirred overnight. After refluxing the mixture for 4 h, volatiles were removed by evaporation. The resulting pale yellow solid was washed with water and  $\text{Et}_2\text{O}$ , and then the resulting white powder of **Li[1]** was dried under vacuum (21.94 g; 76% yield based on  $\text{MeB}(\text{OPr}^i)_2$ ). Calc. for  $\text{C}_{12}\text{H}_{20}\text{BLiN}_4\text{O}$  (**Li[1]**): C, 56.73; H, 7.83; N, 22.05. Found: C, 56.72; H, 7.88; N, 21.86%. IR (KBr,  $\text{cm}^{-1}$ ): 3109w, 2961vs ( $\nu_{\text{CH}}$ ), 2929vs ( $\nu_{\text{CH}}$ ), 2017w (br), 1562w, 1453s, 1399m, 1375m, 1361m, 1281vs ( $\nu_{\text{BC}}$ ), 1165s, 1139vs, 1128vs, 1010vs, 972vs, 955s, 931s, 831w, 765m, 731vs, 717s, 652m, 567w and 496s.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz):  $\delta$  0.08 (br, 3H, MeB), 0.81 (d, 12H,  $\text{Me}_2\text{CH}$ ,  $J = 6.1$ ), 3.13 (sept, 2H,  $\text{Me}_2\text{CH}$ ,  $J = 6.1$ ), 3.91 (s, 6H,  $\text{MeN}_{\text{im}}$ ), 6.82 (d, 2H,  $J = 1.4$ , 4- or 5- $\text{H}_{\text{im}}$ ) and 6.98 (d, 2H,  $J = 1.4$  Hz, 4- or 5- $\text{H}_{\text{im}}$ ).  $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ ):  $\delta$   $-6.0$ . FAB-MS (anion,  $m/z$ ): 247 (**[1]**<sup>-</sup>).

**$\{\text{H}_2[\text{ClMeB}(\text{Im}^{N\text{-Me}})_2]\text{Cl}$  ( $\{\text{H}_2[2]\}\text{Cl}$ ).** An ether solution of anhydrous  $\text{HCl}$  (1.0M, 47 mL) was added to a stirred suspension of **Li[1]** (3.01g, 11.9 mmol) in 90 mL of  $\text{CH}_2\text{Cl}_2$  and 70 mL

**Table 2** Crystallographic data of {H<sub>2</sub>[2]}Cl·C<sub>6</sub>H<sub>5</sub>Me, H[3] and Ni[4]<sub>2</sub>

	{H <sub>2</sub> [2]}Cl·C <sub>6</sub> H <sub>5</sub> Me	H[3]	Ni[4] <sub>2</sub>
Formula	C <sub>16</sub> H <sub>23</sub> BCl <sub>2</sub> N <sub>4</sub>	C <sub>12</sub> H <sub>17</sub> BN <sub>6</sub>	C <sub>30</sub> H <sub>36</sub> B <sub>2</sub> N <sub>8</sub> Ni
Formula weight	353.10	256.12	588.99
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i> (no. 14)	<i>P</i> 2 <sub>1</sub> (no. 4) <sup>a</sup>	<i>P</i> 1̄ (no. 2)
<i>a</i> /Å	8.428(2)	7.747(3)	9.0873(7)
<i>b</i> /Å	13.572(9)	10.905(2)	9.876(1)
<i>c</i> /Å	16.795(3)	8.445(2)	9.0289(8)
<i>a</i> /°			111.731(7)
<i>β</i> /°	101.75(1)	108.59(2)	100.971(7)
<i>γ</i> /°			89.276(8)
<i>V</i> /Å <sup>3</sup>	1880(1)	676.2(4)	737.5(1)
<i>Z</i>	4	2	1
<i>D</i> (calc.)/g cm <sup>-3</sup>	1.247	1.258	1.326
<i>μ</i> (Mo-Kα)/cm <sup>-1</sup>	3.48	0.81	6.93
No. measured reflections	3711	1750	3590
No. observed reflections ( <i>I</i> > 3.00σ( <i>I</i> ))	2059	1453	2371
No. parameters refined	217	178	260
<i>R</i> (%) (based on <i>F</i> )	8.86	4.47	3.62
<i>R</i> <sub>w</sub> (%)	7.91	4.38	2.78

<sup>a</sup> Attempts to find any additional symmetry failed.

of MeCN. After stirring for 5 h, the resulting suspension was concentrated by evaporation and then Et<sub>2</sub>O was added. Storage of this solution at -30 °C overnight afforded a white solid of {H<sub>2</sub>[2]}Cl, which was collected by filtration and then dried under vacuum (2.904 g; 11.3 mmol; 95% yield). For further transformation (e.g. 2 to 3 and 4) {H<sub>2</sub>[2]}Cl can be used as obtained (without further purification). A single crystal suitable for X-ray analysis was obtained from toluene–MeCN solution at -30 °C. Calc. for C<sub>9</sub>H<sub>15</sub>BCl<sub>2</sub>N<sub>4</sub> ({H<sub>2</sub>[2]}Cl): C, 41.42; H, 5.79; Cl, 27.17; N, 21.47. Found: C, 41.09; H, 5.87; Cl, 26.98; N, 21.53%. IR (KBr, cm<sup>-1</sup>): 3392vs, 3142vs, 3048vs (ν<sub>CH</sub>), 2965s (ν<sub>CH</sub>), 2843s (ν<sub>CH</sub>), 2741m, 1636m, 1587m, 1477s, 1416s, 1370s, 1315m, 1291s (ν<sub>BC</sub>), 1263s, 1180s, 1111s, 1011m, 967m, 916m, 867s, 799m, 765s, 704m, 627w, 579w, 505w and 469w. <sup>1</sup>H NMR (D<sub>2</sub>O, 270 MHz): δ 0.31 (br, 3H, MeB), 3.50 (s, 6H, MeN<sub>Im</sub>), 7.26 (d, 2H, *J* = 2.0, 4- or 5-H<sub>Im</sub>) and 7.29 (d, 2H, *J* = 2.0 Hz, 4- or 5-H<sub>Im</sub>). <sup>13</sup>C-{<sup>1</sup>H} NMR (D<sub>2</sub>O, 100 MHz): δ 7.1 (br, MeB), 37.6 (q, *J*<sub>CH</sub> = 144.6, MeN<sub>Im</sub>), 120.9 (dd, *J*<sub>CH</sub> = 198.6, <sup>2</sup>*J*<sub>CH</sub> = 11.0, 4-C<sub>Im</sub>), 127.1 (ddq, *J*<sub>CH</sub> = 198.6, <sup>2</sup>*J*<sub>CH</sub> = 11.0, <sup>3</sup>*J*<sub>CH</sub> = 3.7 Hz, 5-C<sub>Im</sub>) and 161.8 (br, 2-C<sub>Im</sub>). <sup>11</sup>B NMR (D<sub>2</sub>O): δ -7.3.

**H[MeB(Im<sup>N-Me</sup>)<sub>2</sub>(Pz)] (H[3]).** A THF solution (20 mL) of pyrazole (=HPz; 292 mg; 4.29 mmol) was added dropwise to a THF suspension (20 mL) of NaH (294 mg; 12.3 mmol) at 0 °C. The resulting mixture was stirred at 0 °C, until H<sub>2</sub> evolution ceased. Then the mixture was allowed to warm gradually to room temperature and stirred for 10 h. The resulting THF suspension of sodium pyrazolate was added to a THF suspension (40 mL; 0 °C) of {H<sub>2</sub>[2]}Cl, which was obtained from Li[1] (1.027 g; 4.04 mmol) according to the above method. The mixture was allowed to warm gradually to room temperature with stirring, and then refluxed for 4 h. After removal of volatiles by evaporation, the resulting residue was washed with water and pentane. An analytically and spectroscopically pure white solid of compound 3 was obtained by vacuum drying (542 mg; 2.12 mmol; 48% yield). Calc. for C<sub>12</sub>H<sub>17</sub>BN<sub>6</sub> (H[3]): C, 56.28; H, 6.69; N, 32.81. Found: C, 55.62; H, 6.53; N, 32.62%. IR (KBr, cm<sup>-1</sup>): 3154vs, 3082s (ν<sub>CH</sub>), 2941vs (ν<sub>CH</sub>), 1741w, 1654w, 1567vs, 1497m, 1466s, 1446m, 1413m, 1385s, 1365s, 1307s (ν<sub>BC</sub>), 1285s (ν<sub>BC</sub>), 1276s, 1265vs, 1206s, 1187s, 1160m, 1125s, 1104s, 1089vs, 1052s, 1025s, 1004m, 973s, 914s, 884s, 859m, 828w, 779s, 767vs, 737s, 717vs, 664m, 634m and 472w. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 270 MHz): δ 0.46 (br, 3H, MeB), 3.09 (s, 6H, MeN<sub>Im</sub>), 6.23 (dd, 1H, *J* = 1.7, *J* = 2.19, 4-H<sub>Pz</sub>), 6.73 (d, 2H, *J* = 2.0, 4- or 5-H<sub>Im</sub>), 7.00 (d, 2H, *J* = 2.0, 4- or 5-H<sub>Im</sub>), 7.54 (d, 2H, *J* = 2.19, 5-H<sub>Pz</sub>), 7.60 (d, 2H, *J* = 1.7 Hz, 3-H<sub>Pz</sub>) and 14.20 (br, 1H, HN<sub>Im</sub>). <sup>13</sup>C-{<sup>1</sup>H}

NMR (CDCl<sub>3</sub>, 67.8 MHz): δ 5.1 (br, MeB), 33.4 (q, *J*<sub>CH</sub> = 140.1, MeN<sub>Im</sub>), 104.2 (dt, *J*<sub>CH</sub> = 172.3, <sup>2</sup>*J*<sub>CH</sub> = 11.4, 4-C<sub>Pz</sub>), 120.2 (dd, *J*<sub>CH</sub> = 191.0, <sup>2</sup>*J*<sub>CH</sub> = 11.4, 4-C<sub>Im</sub>), 121.6 (ddq, *J*<sub>CH</sub> = 190.0, <sup>2</sup>*J*<sub>CH</sub> = 14.5, <sup>3</sup>*J*<sub>CH</sub> = 3.1, 5-C<sub>Im</sub>), 132.8 (dt, *J*<sub>CH</sub> = 180.6, <sup>2</sup>*J*<sub>CH</sub> = 5.2, 3-C<sub>Pz</sub>), 140.2 (dd, *J*<sub>CH</sub> = 181.7, <sup>2</sup>*J*<sub>CH</sub> = 7.3 Hz, 5-C<sub>Pz</sub>) and 164.8 (br, 2-C<sub>Im</sub>). <sup>11</sup>B NMR (CDCl<sub>3</sub>): δ -10.6.

**H[MePhB(Im<sup>N-Me</sup>)<sub>2</sub>] (H[4]).** A suspension of *in situ* generated {H<sub>2</sub>[2]}Cl (obtained from 6.01 mmol of Li[1]) in Et<sub>2</sub>O (20 mL) and toluene (20 mL) was chilled to -78 °C. An Et<sub>2</sub>O solution of PhLi (1.36 M; 20 mL) was then added dropwise. The resulting mixture was allowed to warm gradually to ambient temperature, and stirring was continued for 10 h. After refluxing the mixture for 4 h the volatile materials were evaporated. The resulting crude product was washed with water (30 mL × 3) and pentane (20 mL × 2), and then dried under vacuum. Spectroscopically pure H[4] was obtained as a pale brown powder (1.09 g; 4.09 mmol; 68% yield). Calc. for C<sub>15</sub>H<sub>19</sub>BN<sub>4</sub> (H[4]): C, 67.69; H, 7.20; N, 21.05. Found: C, 67.46; H, 7.17; N, 20.87%. IR (KBr, cm<sup>-1</sup>): 3413vs (ν<sub>NH</sub>), 3134s, 3056s (ν<sub>CH</sub>), 2926vs (ν<sub>CH</sub>), 1618w, 1562m, 1460s, 1429s, 1411m, 1358m, 1305m, 1285s (ν<sub>BC</sub>), 1250s, 1123s, 1086m, 1023m, 939vs, 911m, 826w, 776w, 739vs, 716vs, 683m, 598w, 486w, 454w, 437w and 420w. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 270 MHz): δ 0.30 (br, 3H, MeB), 3.23 (s, 6H, MeN<sub>Im</sub>), 6.67 (d, 2H, *J* = 1.5, 4- or 5-H<sub>Im</sub>), 6.98 (d, 2H, *J* = 1.5 Hz, 4- or 5-H<sub>Im</sub>), 7.04–7.25 (m, 5H, Ph) and 14.33 (br, 1H, HN<sub>Im</sub>). <sup>13</sup>C-{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz): δ 3.4 (br, MeB), 34.4 (q, *J*<sub>CH</sub> = 138.1, MeN<sub>Im</sub>), 119.5 (dd, *J*<sub>CH</sub> = 190.0, <sup>2</sup>*J*<sub>CH</sub> = 10.4, 4-C<sub>Im</sub>), 121.0 (ddq, *J*<sub>CH</sub> = 190.0, <sup>2</sup>*J*<sub>CH</sub> = 13.5, <sup>3</sup>*J*<sub>CH</sub> = 3.1, 5-C<sub>Im</sub>), 124.3 (dt, *J*<sub>CH</sub> = 158.8, <sup>2</sup>*J*<sub>CH</sub> = 6.2, *m*-C<sub>Ph</sub>), 127.1 (dd, *J*<sub>CH</sub> = 155.7, <sup>2</sup>*J*<sub>CH</sub> = 6.2, *o*-C<sub>Ph</sub>), 133.6 (dt, *J*<sub>CH</sub> = 154.7, <sup>2</sup>*J*<sub>CH</sub> = 7.3 Hz, *p*-C<sub>Ph</sub>), 153.1 (br, C<sub>Ph</sub>B) and 169.5 (br, 2-C<sub>Im</sub>). <sup>11</sup>B NMR (CDCl<sub>3</sub>): δ -17.4.

**Ni[MePhB(Im<sup>N-Me</sup>)<sub>2</sub>]<sub>2</sub> (Ni[4]<sub>2</sub>).** A CH<sub>2</sub>Cl<sub>2</sub> solution (25 mL) of H[4] (333 mg; 1.25 mmol) was added dropwise to a MeOH solution (10 mL) of Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O (151 mg; 0.61 mmol). The reaction mixture was stirred for 1 h, and then solvents were evaporated. The product was extracted with CH<sub>2</sub>Cl<sub>2</sub> to remove inorganic salts. Evaporation of the CH<sub>2</sub>Cl<sub>2</sub> solution followed by recrystallization from MeCN–CH<sub>2</sub>Cl<sub>2</sub> at -30 °C afforded a yellow crystalline solid of Ni[4]<sub>2</sub> (82 mg; 0.14 mmol; 23% yield). Calc. for C<sub>30</sub>H<sub>37</sub>B<sub>2</sub>N<sub>8</sub>NiO<sub>0.5</sub> (Ni[4]<sub>2</sub>·0.5H<sub>2</sub>O): C, 60.26; H, 6.24; N, 18.74. Found: C, 60.26; H, 6.29; N, 18.77%. IR (KBr, cm<sup>-1</sup>): 3135m, 3062m (ν<sub>CH</sub>), 3031m (ν<sub>CH</sub>), 2997m (ν<sub>CH</sub>), 2962s (ν<sub>CH</sub>), 2930m (ν<sub>CH</sub>), 1589w, 1546m, 1482m, 1453s, 1400s, 1290s (ν<sub>BC</sub>), 1262vs, 1164s, 1095vs, 1018vs, 940s, 899m, 866m, 800vs, 740s,

661s, 584m, 532m and 406s. UV-vis ( $\text{CH}_2\text{Cl}_2$ ,  $\lambda/\text{nm}$ , r.t., ( $\epsilon/\text{M}^{-1}\text{cm}^{-1}$ ): 645 (7) and 445 (53).

### X-Ray data collections and structural determinations

Conditions (solvent, temperature; under Ar unless otherwise stated) for crystallization were as follows:  $\{\text{H}_2[2]\}\text{Cl}\cdot\text{C}_6\text{H}_5\text{Me}$  (MeCN–toluene, r.t.), H[3] (water– $\text{Et}_2\text{O}$ , r.t., air),  $\text{Ni}[4]_2$  (MeCN– $\text{CH}_2\text{Cl}_2$ ,  $-30^\circ\text{C}$ ). The crystals were mounted on glass fibers.

Diffraction measurements of compounds H[3] and  $\text{Ni}[4]_2$  were made on a Rigaku AFC-7R automated four-circle diffractometer. A molybdenum X-ray source equipped with a graphite monochromator (Mo-K $\alpha$ ,  $\lambda = 0.71069 \text{ \AA}$ ) was used. Data collections were carried out at room temperature ( $23^\circ\text{C}$ ). Diffraction measurement of  $\{\text{H}_2[2]\}\text{Cl}\cdot\text{C}_6\text{H}_5\text{Me}$  was made on a Rigaku RAXIS IV imaging plate area detector with Mo-K $\alpha$  radiation. Data collection was carried out at  $-60^\circ\text{C}$ . The data processing was performed on an IRIS Indy computer.

Crystallographic data and the results of refinements are summarized in Table 2. Structure analysis was performed on an IRIS O2 computer by using the TEXSAN<sup>15</sup> program. The structures were solved by direct methods (SIR 92).<sup>16</sup> Subsequent difference Fourier synthesis (DIRDIF)<sup>17</sup> easily located all the non-hydrogen atoms, which were refined anisotropically. Neutral scattering factors were obtained from the standard source.<sup>18</sup> Hydrogen atoms of  $\{\text{H}_2[2]\}\text{Cl}$  and H[3] attached to the nitrogen atoms of the imidazolyl groups were found on the Fourier difference map and refined isotropically. The remaining hydrogen atoms were located at the calculated positions and not refined ( $d(\text{C}-\text{H}) = 0.95 \text{ \AA}$  with  $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{iso}}(\text{C})$ ). Positions of all hydrogen atoms of  $\text{Ni}[4]_2$  were determined by Fourier difference synthesis and refined isotropically.

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### References

- 1 S. Trofimenko, *Scorpionates – The Co-ordination Chemistry of Polypyrazolylborate Ligands*, Imperial College Press, London, 1999; S. Trofimenko, *Chem. Rev.*, 1993, **93**, 943; N. Kitajima and W. B. Tolman, *Prog. Inorg. Chem.*, 1995, **43**, 419.
- 2 Co–OOR: S. Hikichi, H. Komatsuzaki, M. Akita and Y. Moro-oka, *J. Am. Chem. Soc.*, 1998, **120**, 4699. Co, Ni–oxo: S. Hikichi,

- M. Yoshizawa, Y. Sasakura, M. Akita and Y. Moro-oka, *J. Am. Chem. Soc.*, 1998, **120**, 10567; S. Hikichi, M. Yoshizawa, Y. Sasakura, H. Komatsuzaki, M. Akita and Y. Moro-oka, *Chem. Lett.*, 1999, 979; S. Hikichi, M. Akita and Y. Moro-oka, *Coord. Chem. Rev.*, 2000, in the press. V–O<sub>2</sub>: M. Kosugi, S. Hikichi, M. Akita and Y. Moro-oka, *J. Chem. Soc., Dalton Trans.*, 1999, 1369. Fe–OOR: T. Ogihara, S. Hikichi, M. Akita, T. Uchida, T. Kitagawa and Y. Moro-oka, *Inorg. Chim. Acta*, 2000, **297**, 162. Fe, Co, Ni–alkyl: N. Shirasawa, M. Akita, S. Hikichi and Y. Moro-oka, *Chem. Commun.*, 1999, 417. Pd–OOH: M. Akita, T. Miyaji, S. Hikichi and Y. Moro-oka, *Chem. Lett.*, 1999, 813. Rh–olefin: K. Ohta, M. Hashimoto, Y. Takahashi, S. Hikichi, M. Akita and Y. Moro-oka, *Organometallics*, 1999, **18**, 3234. Rh–O<sub>2</sub> and –OOH: Y. Takahashi, M. Hashimoto, S. Hikichi, M. Akita and Y. Moro-oka, *Angew. Chem., Int. Ed.*, 1999, **38**, 3074. Ru–dpppe: Y. Takahashi, S. Hikichi, M. Akita and Y. Moro-oka, *Organometallics*, 1999, **18**, 2571. Ru–O<sub>2</sub>: Y. Takahashi, S. Hikichi, M. Akita and Y. Moro-oka, *Chem. Commun.*, 1999, 1491.
- 3 H. C. Brown, M. Srebnik and T. E. Cole, *Organometallics*, 1986, **5**, 2300.
- 4 U. E. Bucher, T. F. Fässler, M. Hunziker, R. Nesper, H. Rügger and L. M. Venanzi, *Gazz. Chim. Ital.*, 1995, **125**, 181.
- 5 C. K. Johnson, ORTEP II, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.
- 6 A. Looney, G. Parkin and A. L. Rheingold, *Inorg. Chem.*, 1991, **30**, 3099.
- 7 T. G. Hodgkins and D. R. Powell, *Inorg. Chem.*, 1996, **35**, 2140.
- 8 S. Trofimenko, *J. Am. Chem. Soc.*, 1967, **89**, 6288; H. M. Echols and D. Dennis, *Acta Crystallogr., Sect. B*, 1974, **30**, 2173; H. M. Echols and D. Dennis, *Acta Crystallogr., Sect. B*, 1976, **32**, 1267; F. A. Cotton and C. A. Murillo, *Inorg. Chim. Acta*, 1976, **17**, 121; D. A. Clemente and M. Cingi-Biagini, *Inorg. Chem.*, 1987, **26**, 2350; H. Kokusen, Y. Sohrin, M. Matsui, Y. Hata and H. Hasegawa, *J. Chem. Soc., Dalton Trans.*, 1996, 195.
- 9 I. I. Padilla-Martinez, F. J. Martinez-Martinez, A. López-Sandoval, K. I. Girón-Castillo, M. A. Brito and R. Contreras, *Eur. J. Inorg. Chem.*, 1998, 1547.
- 10 See for example; G. Bruno, F. Nicoló, F. Foti, G. Grassi, F. Risitano and G. de Munno, *Acta Crystallogr., Sect. C*, 1994, **50**, 428.
- 11 N. Kuhn, G. Henkel, T. Kratz, J. Kreutzberg, R. Boese and A. H. Maulitz, *Chem. Ber.*, 1993, **126**, 2041.
- 12 A. Wacker, H. Pritzkow and W. Siebert, *Eur. J. Inorg. Chem.*, 1998, 843.
- 13 K. Fujita, S. Hikichi, M. Akita and Y. Moro-oka, *J. Chem. Soc., Dalton Trans.*, 2000, 117.
- 14 D. D. Perrin, W. L. Armarego and D. R. Perrin, *Purification of Laboratory Chemicals*, 2nd edn., Pergamon, New York, 1980.
- 15 TEXSAN, Structure Analysis Package, Molecular Structure Corporation, Houston, TX, 1985.
- 16 SIR 92, A. Altomare, M. C. Burla, M. Camalli, M. Cascarano, C. Giacovazzo, A. Guagliardi and G. Polidori, *J. Appl. Crystallogr.*, 1994, **27**, 435.
- 17 DIRDIF, 92, P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, S. Garcia-Granda, R. O. Gould, J. M. M. Smith and C. Smykalla, The DIRDIF program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, 1992.
- 18 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1975, vol. 4.