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Novel monoanionic tripodal ligands: methylbis(1-methylimidazol-2-yl)(pyrazol-1-yl)borate (= $[MeB(Im^{N\text{-}Me})_2(Pz^R)]^-$). Synthesis and structural characterization of their nickel complexes and carboxylate shift from nickel to boron†

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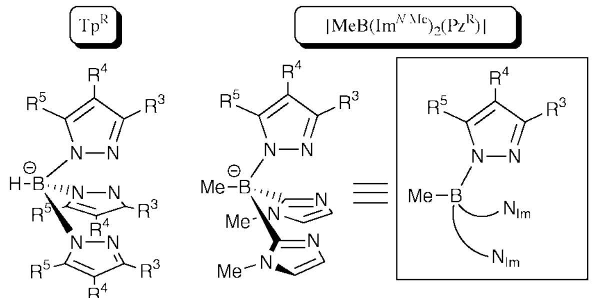
Novel monoanionic tripodal ligands, $[MeB(Im^{N\text{-}Me})_2(Pz^R)]^-$ (= methylbis(1-methylimidazol-2-yl)(pyrazol-1-yl)borate), are synthesized; their mode of coordination to a nickel center depends on the steric congestion around the boron centers.

A family of poly(pyrazol-1-yl)borate anions $[X_{4-n}B(Pz^R)_n]^-$ ($n = 2$–4; X = H, alkyl; Pz^RH = pyrazole where R denotes substituents on the pyrazole ring) has been widely adopted as supporting ligands for various inorganic and organometallic compounds because it is prepared by simple thermal dehydrogenation and the properties of its metal complexes (coordination environment and reactivity of metal centers, solubility in organic solvents, facility of crystallization, *etc.*) can be controlled by introduction of various substituent groups onto the pyrazolyl rings.[1] We have been investigating various transition metal complexes with hydrotris(pyrazolyl)borate ligands Tp^R (= $[HB(Pz^R)_3]^-$; see Chart 1) from bioinorganic and organometallic standpoints.[2] Recently, the need for a more sophisticated ligand system have grown in order to control the reactivity of the metal center by tuning the steric and electronic factors precisely, but no example of asymmetric tris(pyrazolyl)borates containing different pyrazolyl groups such as $[XB(Pz^{R^1})_2(Pz^{R^2})]^-$ and $[XB(Pz^{R^1})(Pz^{R^2})(Pz^{R^3})]^-$ ($R^1 \neq R^2 \neq R^3$) has been obtained so far.[3] Therefore, we have designed novel monoanionic borate compounds consisting of different nitrogen-donating groups, namely, methylbis(1-methylimidazol-2-yl)(pyrazol-1-yl)borate (= $[MeB(Im^{N\text{-}Me})_2(Pz^R)]^-$; **2**), which is formed by incorporation of a second functional group (= Pz^R) onto the methylbis(imidazol-2-yl)borane moiety (Chart 1).[4] Herein we report the metalation behavior of our brand-new ligands depending on the steric bulk of the pyrazolyl groups.‡



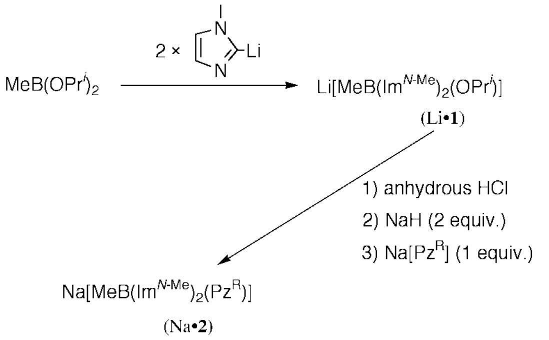
2a: R^3 = Ph, $R^4 = R^5$ = H

2b: R^3 = Me, $R^4 = R^5$ = H

2c: $R^3 = R^4 = R^5$ = Me

Chart 1

A bis(imidazolyl)borate compound, $[MeB(Im^{N\text{-}Me})_2(OPr^i)]^-$ (= methylbis(1-methylimidazol-2-yl)(isopropoxyl)borate; **1**), was prepared by treatment of methylbis(isopropoxyl)borane with 2 equiv. of 2-lithio-1-methylimidazole. In contrast to dihydrobis(pyrazolyl)borate $[H_2B(Pz^R)_2]^-$, **1** contains neither B–H nor B–N bonds which may be hydrolyzed under acidic conditions, and therefore the OPr^i moiety is expected to be readily replaced by another functional group. Treatment of the lithium salt of **1** with anhydrous HCl followed by reaction with sodium salts of substituted pyrazoles $Na\cdot Pz^R$ ($Pz^{Ph}H$ = 3-phenylpyrazole, $Pz^{Me}H$ = 3-methylpyrazole, $Pz^{Me_3}H$ = 3,4,5-trimethylpyrazole) yielded the corresponding sodium salts of the desired borate ligands, Na·**2** [Pz^{Ph} derivative (**2a**), Pz^{Me} derivative (**2b**) and Pz^{Me_3} derivative (**2c**)], as was confirmed by spectroscopy (NMR, FAB-MS) (Scheme 1).§



Scheme 1

In order to reveal the metal-chelating ability of **2**, metathesis of Na·**2** with NiX_2 (X = NO_3, OAc) was examined, but the composition and structure of the resulting Ni complexes were different depending on the type of incorporated pyrazole and X (Scheme 2). Reaction of THF solutions of the ligands of the 3-phenylpyrazolyl and 3-methylpyrazolyl derivatives, Na·**2a** and Na·**2b**, with a MeOH solution of 1 equiv. of $Ni(NO_3)_2\cdot 6H_2O$ and subsequent treatment with pyridine yielded the corresponding blue nitrato complexes, $Ni[\kappa^3\text{-}MeB(Im^{N\text{-}Me})_2(Pz^R)](\kappa^2\text{-}NO_3)(im^{Me})$ (im^{Me} = 1-methylimidazole;¶ **3a**: $Pz^R = Pz^{Ph}$; **3b**: $Pz^R = Pz^{Me}$), whose structures were confirmed by X-ray crystallography (top of Fig. 1).|| The overall molecular structures of **3a** and **3b** were almost identical except for the substituents on the pyrazolyl groups. The nickel centers have a six-coordinated octahedral geometry and the borate ligands (= **2a** and **2b**) coordinate to the Ni centers in facial κ^3-mode through two imidazolyl and one pyrazolyl nitrogen donor atoms. It is known that less hindered Tp^R ligands readily produce the coordinatively saturated 1:2 adducts, $Tp^R{}_2M$, which are usually inert with respect to subsequent replacement by

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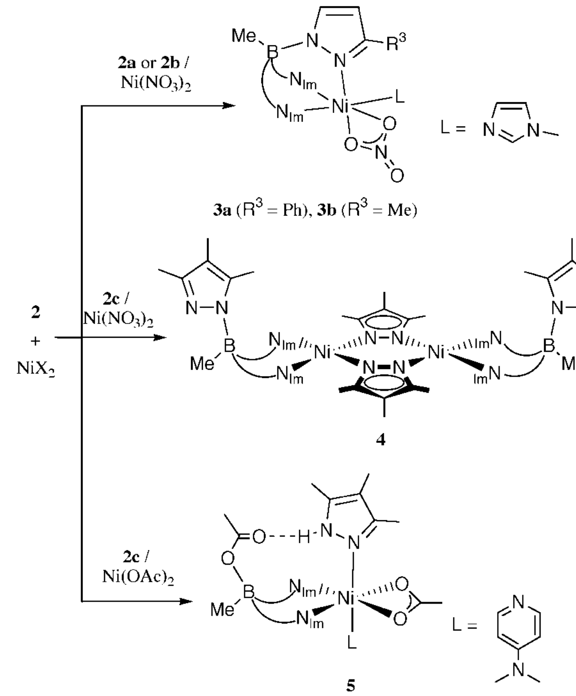
† Electronic supplementary information (ESI) available: molecular structures for **3a**·CH_2Cl_2, **3b**·CH_2Cl_2, **4**·$0.5C_8H_{18}\cdot H_2O$, **4**, **4**·$2H_2O$ and **5**. See http://www.rsc.org/suppdata/dt/a9/a908181j/



Scheme 2

other ligands.[1,5] In the case of the bis(imidazolyl)(pyrazolyl)borate ligand system, combination of the less-hindered imidazolyl and the 3-substituted pyrazolyl groups produce a sterically much less hindered environment of the metal center having only a single "picket fence". However, use of $Ni(NO_3)_2$ results in the formation of the 1 : 1 adduct with a κ^2-NO_3 ligand instead of 1 : 2 complexes, $Ni[MeB(Im^{N\text{-}Me})_2(Pz^R)]_2$.[6]

In contrast to **2a** and **2b**, the Pz^{Me_3} derivative (**2c**) resulted in κ^2-binding of the borate ligand due to steric congestion around the boron center. Reaction of a CH_2Cl_2 solution of Na·**2c** with a MeOH solution of $Ni(NO_3)_2·6H_2O$ in a manner similar to the preparation of **3** yielded a yellow complex **4**. In addition to its characteristic yellow color, a ^{1}H-NMR spectrum of **4** appeared in the normal diamagnetic region. These observations suggest that **4** contains low-spin (d^8, $S = 0$) nickel centers having four-coordinate square-planar geometry. Finally, X-ray analysis for single crystals of **4**, obtained by recrystallization from a CH_2Cl_2/octane solution, revealed its molecular structure, namely $\{Ni[\kappa^2\text{-}MeB(Im^{N\text{-}Me})_2(Pz^{Me_3})]\}_2(\mu\text{-}Pz^{Me_3})_2$ (middle of Fig. 1); **4** has a dimeric structure with pseudo C_{2v} symmetry involving structurally identical square-planar nickel centers bridged by two pyrazolate ligands resulting from partial decomposition of **2c**. The bis(imidazolyl)(pyrazolyl)borate ligand is coordinated to the nickel center in a κ^2-mode *via* two imidazolyl groups. The nitrogen atom of the remaining pyrazolyl group did not coordinate to the Ni center, but formation of a hydrogen-bonding interaction[7] with a H_2O molecule was observed as was evidenced by somewhat short N···O distances [2.97(1), 3.00(1) Å] and a characteristic broad IR band at 3413 cm^{-1}. We thus conclude that the κ^3-binding mode is unfavorable for **2c** due to steric repulsion between the 5-Me substituent on the Pz^{Me_3} moiety and the Me groups on the imidazolyl-nitrogen and boron atoms (Chart 2).

It is notable that reaction of **2c** with $Ni(OAc)_2·4H_2O$ instead of $Ni(NO_3)_2·6H_2O$ resulted in displacement of the 3,4,5-trimethylpyrazolyl group by acetate, and the resulting blue complex, $Ni[\kappa^2 N,N'\text{-}MeB(Im^{N\text{-}Me})_2(OAc)](\kappa^2\text{-}OAc)(Pz^{Me_3}H)(DMAP)$ (**5**; DMAP = 4-(dimethylamino)pyridine), was also characterized by X-ray crystallography as well as IR and mass spectroscopy (bottom of Fig. 1). The most striking aspect of **5** is that the acetate group originally attached to Ni has shifted to the B atom.[8] The acetoxy-borate component coordinates to the Ni center in a κ^2 mode through the two imidazolyl nitrogen donors. Moreover, the O32–N52 separation [O32···N52; 2.880(5) Å, νNH; 3296 cm^{-1}, νCO; 1660 cm^{-1}][9] suggests an intramolecular hydrogen bonding interaction between the carbonyl group of the B-binding acetate and the N–H moiety of 3,4,5-trimethylpyrazole, which results from the B–N bond hydrolysis of **2c** and serves as one of the two axial ligands of the octahedral Ni center. Remarkably, the pyrazolyl groups attached to the B atom in the above mentioned **3** and **4** were not displaced upon treatment with acetic acid. Therefore, the carboxylation of the borate component (*i.e.* formation of **5**) must be mediated by $Ni(OAc)_2$ during metalation; the driving force for this transformation may be the stability of the

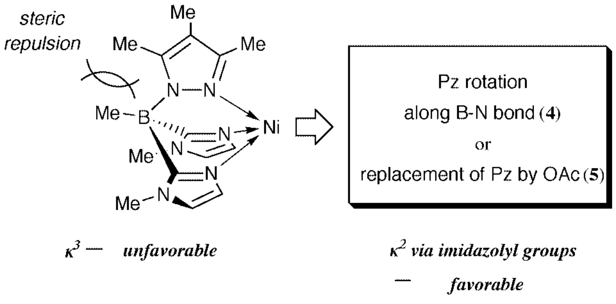


Chart 2

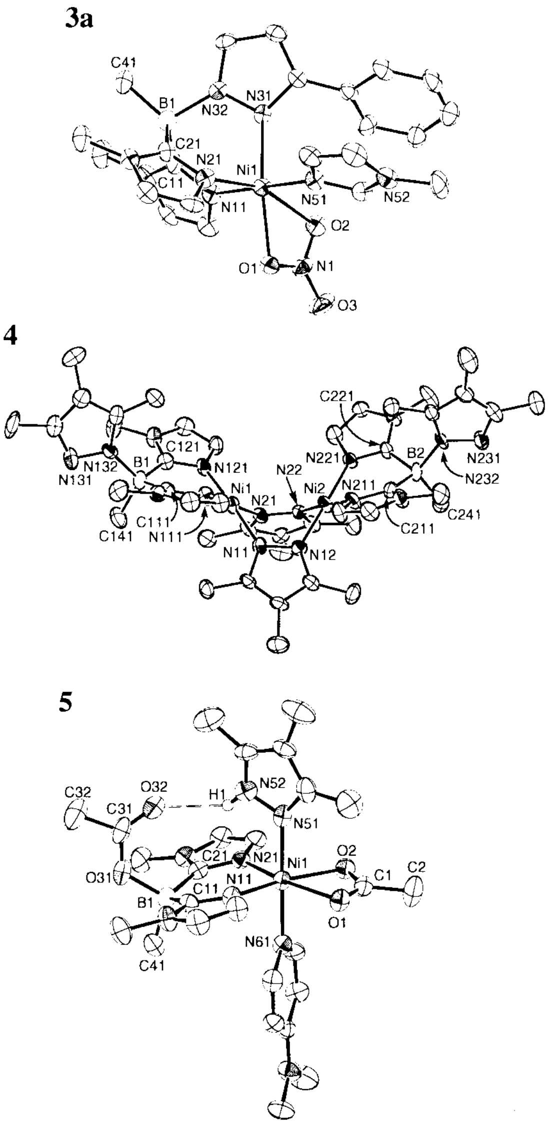


Fig. 1 Molecular structures of the Ni complexes **3a**, **4** and **5**. Top: $Ni[\kappa^3\text{-}MeB(Im^{N\text{-}Me})_2(Pz^{Ph})](\kappa^2\text{-}NO_3)(im^{Me})$ (**3a**, drawn at 30% probability level). Middle: $\{Ni[\kappa^2\text{-}MeB(Im^{N\text{-}Me})_2(Pz^{Me_3})]\}_2(\mu\text{-}Pz^{Me_3})_2$ (**4**; 30% probability). Bottom: $Ni[\kappa^2 N,N'\text{-}MeB(Im^{N\text{-}Me})_2(OAc)](\kappa^2\text{-}OAc)(Pz^{Me_3}H)(DMAP)$ (**5**, 50% probability). All hydrogen atoms except that attached to the nitrogen atom (N52) of the 3,4,5-trimethylpyrazole ligand in **5** and the solvates are omitted for clarity.

intramolecular hydrogen bonding interaction in **5**, but the mechanism of the carboxylate group shift from the Ni to B centers remains to be studied. Interestingly, the formation of **5** indicates a capacity for introducing various functional groups (Y^-) onto the B atom yielding $[MeB(Im^{N\text{-}Me})_2(Y)]^-$ and, moreover, the carboxylate functional group is expected to work as a substrate receptor *via* hydrogen bonding interactions.

In summary, a new family of tripodal metal supporting ligands, bis(imidazolyl)(pyrazolyl)borate $[MeB(Im^{N\text{-}Me})_2(Pz^R)]^-$ (**2**), and its Ni complexes are prepared and characterized successfully. The coordination mode (κ^3 *vs.* κ^2) of **2** depends on the steric congestion around the boron centers due to the substituent on the pyrazolyl functional groups. In addition, the replacement of the B-bonded 3,4,5-trimethylpyrazolyl group by acetate anion occurred during the metathesis of the Pz^{Me_3} derivative **2c** with $Ni(OAc)_2 \cdot 4H_2O$ in $MeOH/CH_2Cl_2$. Detailed investigations of the chemical properties of the obtained complexes **3**–**5**, application of **2** to other metal complexes, and development of novel ligands based on the bis(imidazolyl)borate motif are in progress and the results will be reported in due course.

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Notes and references

‡ Abbreviations used in this paper: Pz^R, 3,4,5-substituted pyrazol-1-yl anion; $[X_{4-n}B(Pz^R)_n]^-$, poly(pyrazol-1-yl)borate anion; Tp^R ($= [HB(Pz^R)_3]^-$), hydrotris((3,4,5-substituted)pyrazol-1-yl)borate; $Im^{N\text{-}Me}$, 1-methylimidazol-2-yl anion; $[MeB(Im^{N\text{-}Me})_2(Pz^R)]^-$, methylbis(1-methylimidazol-2-yl)((3,4,5-substituted)pyrazol-1-yl)borate; im^{Me}, 1-methylimidazole; DMAP, 4-(dimethylamino)pyridine.

§ For **2a** and **b**, a structural isomer of methylbis(imidazolyl)(pyrazolyl)borate carrying the 5-substituted pyrazolyl group was also formed as was evidenced from two sets of signals observed in ^{1}H-NMR. Unfortunately, separation of two isomers (*i.e.* 3- and 5-substituted pyrazolyl compounds) has not been successful yet. Details of the ligands synthesis will be reported as a full paper in the near future. Selected spectroscopic data. For **2a** (mixture of two isomers): FAB-MS (*m*/*z*): 333 ([**2a** + $2H^+$]$^+$). Calcd for $C_{18}H_{21}N_6B$ (H·**2a**): C, 65.08; H, 6.37; N, 25.30. Found: C, 65.17; H, 6.68; N, 25.25%. For **2b** (mixture): FAB-MS (*m*/*z*): 271 ([**2b** + $2H^+$]$^+$). Calcd for $C_{13}H_{19}N_6B$ (H·**2b**): C, 57.80; H, 7.09; N, 31.11. Found: C, 57.53; H, 7.15; N, 30.88%. For **2c**: ^{1}H-NMR ($CDCl_3$): δ 0.49 (br, 3H, B-*Me*). FAB-MS (*m*/*z*; anion): 297 ([**2c**]$^-$). Calcd for $C_{15}H_{23.4}O_{0.2}N_6B$ (H·**2c**·$0.2H_2O$): C, 59.70; H, 7.81; N, 27.85. Found: C, 60.04; H, 7.80; N, 27.56%. For **3a**: Calcd for $C_{23}H_{28}N_9O_3BCl_2Ni$ (**3a**·CH_2Cl_2): C, 44.99; H, 4.54; N, 20.99; Cl, 11.22. Found: C, 44.63; H, 4.56; N, 20.37; Cl, 11.46%. IR (KBr pellet, ν/cm^{-1}): 1455 (NO_3). FAB-MS (*m*/*z*): 389 ([Ni·**2a**]$^+$). For **3b**: Calcd for $C_{18}H_{26}N_9O_3BCl_2Ni$ (**3b**·CH_2Cl_2): C, 38.89; H, 4.53; N, 22.31; Cl, 12.76. Found: C, 39.33; H, 4.18; N, 22.31; Cl, 12.64%. IR (KBr pellet, ν/cm^{-1}): 1457 (NO_3). FAB-MS (*m*/*z*): 327 ([Ni·**2b**]$^+$). For **4**: Calcd for $C_{46}H_{77}N_{16}O_3B_2Ni_2$ (**4**·$0.5C_8H_{18} \cdot 3H_2O$): C, 53.68; H, 7.27; N, 21.12. Found: C, 53.06; H, 7.45; N, 21.52%. IR (KBr pellet, ν/cm^{-1}): 3413 (H_2O). ^{1}H-NMR ($CDCl_3$): δ 1.08 (s, 6H, B-*Me*). FAB-MS (*m*/*z*): 355 ([Ni·**2c**]$^+$). For **5**: Calcd for $C_{26}H_{40}N_8O_{4.5}BNi$ (**5**·$0.5H_2O$): C, 51.52; H, 6.76; N, 18.65. Found: C, 51.52; H, 6.65; N, 18.49%. IR (KBr pellet, ν/cm^{-1}): 3296 (NH), 1660 (C=O). FAB-MS (*m*/*z*): 306 ({Ni·[MeB($Im^{N\text{-}Me}$)$_2$(OAc)]}$^+$).

¶ The im^{Me} ligands of **3** might arise from a contaminated imidazole during the synthesis of **2** or/and partial decomposition of **2** during the metalation. Further purification of **2** and detailed investigation of the metalation processes are now underway.

‖ Crystal data. For **3a**·CH_2Cl_2: $C_{23}H_{28}N_9O_3BCl_2Ni$, $M = 618.95$, monoclinic, space group $P2_1/n$ (no. 14), $a = 11.262(2)$, $b = 20.712(7)$, $c = 12.232(2)$ Å, $\beta = 100.23(1)°$, $V = 2808(1)$ Å^3, $Z = 4$, $D_c = 1.46$ g cm^{-1}, μ(Mo-Kα) = 9.24 cm^{-1}, $R(Rw) = 7.82(7.45)\%$ (based on F) for 2921 ($I > 3\sigma(I)$) reflections with 371 parameters. For **3b**·CH_2Cl_2: $C_{18}H_{26}N_9O_3BCl_2Ni$, $M = 556.88$, orthorhombic, space group $P2_12_12_1$ (no. 19), $a = 14.813(3)$, $b = 21.240(9)$, $c = 7.9613(9)$ Å, $V = 2505(1)$ Å^3, $Z = 4$, $D_c = 1.48$ g cm^{-1}, μ(Mo-Kα) = 10.27 cm^{-1}, $R(Rw) = 5.89(5.52)\%$ (based on F) for 1932 ($I > 2.5\sigma(I)$) reflections with 310 parameters. For **4**·$0.5C_8H_{18} \cdot H_2O$: $C_{46}H_{73}N_{16}OB_2Ni_2$, $M = 1014.28$, triclinic, space group $P1$ (no. 2), $a = 15.82(2)$, $b = 16.671(5)$, $c = 12.221(2)$ Å, $\alpha = 104.22(2)$, $\beta = 97.27(4)$, $\gamma = 67.22(2)°$, $V = 2878(3)$ Å^3, $Z = 2$, $D_c = 1.17$ g cm^{-1}, μ(Mo-Kα) = 7.01 cm^{-1}, $R(Rw) = 7.91(7.32)\%$ (based on F) for 5155 ($I > 3\sigma(I)$) reflections with 601 parameters. For **5**: $C_{26}H_{39}N_8O_4BNi$, $M = 597.16$, monoclinic, space group $P2_1/n$ (no. 14), $a = 10.670(2)$, $b = 21.735(5)$, $c = 13.97(2)$ Å, $\beta = 110.14(4)°$, $V = 3041(4)$ Å^3, $Z = 4$, $D_c = 1.30$ g cm^{-1}, μ(Mo-Kα) = 6.82 cm^{-1}, $R(Rw) = 5.21(5.39)\%$ (based on F) for 3900 ($I > 3\sigma(I)$) reflections with 366 parameters. Molecular structure of **3b**·CH_2Cl_2 is provided as supplementary material. CCDC reference number 186/1748.

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