Development of a novel scorpionate ligand with 6-methylpyridine and comparison of structural and electronic properties of nickel(II) complexes with related tris(azolyl)borates

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A novel anionic tridentate borate ligand with 6-methlpyridyl donor, Tpy^{Me}, has been synthesized. Comparison of molecular structures and reactivities of nickel(II)-bromido complexes with tris(azolyl)borate ligands composed of pyridyl, pyrazolyl, or oxazolinyl donors indicates the characteristic steric demanding nature and strong electron donating ability of Tpy^{Me}.

Anionic facially-capping tris(azolyl)borate so-called as scorpionate ligands,[1] $[BL_3X]^-$ (L = nitrogen atom donor such as pyrazole,[1,2] oxazoline,[3-6] pyridine,[7-13] imidazole[14]; X = H, phenyl, alkyl, alkoxide, *etc*.), have been extensively utilized to various coordination compounds.[1] In general, the tris(azolyl)borate ligands produce a relatively stable metal-ligand fragment due to electrostatic interaction as well as the chelating effect. Tris(pyrazolyl)borates (= Tp^R) are authentic of these types of ligands, and the coordination environment and reactivity of the resulting metal complexes can be controlled by the introduction of various substituent groups onto the pyrazolyl rings.[1] However, the B-N bond of Tp^R has ionic bonding characteristics and low resistance to hydrolysis. Therefore, Tp^R analogues composed of the stable B-C linkages have been developed by utilization of oxazoline (= To^R)[3] and pyridine (= Tpy^R)[7] instead of pyrazole. Because pyridyl donors show both σ-electron-donating and π-electron-accepting nature, they have potential applications in a wide range of coordination compounds related to catalytic and bioinorganic chemistry.[15, 16] In fact, high performance of vanadium(V) complex catalysts with phenyltris(2-pyridyl)borate $[PhB(Py^H)_3]^-$ (= Tpy^H) toward alkene polymerization has been reported.[11]

The pyridyl-based tridentate borate ligands reported to date are Tpy^H and its substituted aryl derivatives which consist of an unsubstituted pyridine.[7-11] Because of the small steric hindrance of the unsubstituted pyridine donors to the metal center, it is readily to form homoleptic complexes of divalent metal ions.[7-10] The resulting six-coordinate octahedral complexes seem to be inert to forming reactive species during catalytic process. Very recently, 4-*tert*-butylphenyltris(6-trifluoromethyl-2-pyridyl)borate, $[PhB(Py^{CF3})_3]^-$ (= Tpy^{CF3}), has been reported.[12, 13] In the ethylene complexes of Cu(I), Ag(I) and Au(I) with this fluorinated ligand, Tpy^{CF3} coordinates to the metal center with κ^2 but not κ^3 fashion.[12] Tpy^{CF3} also coordinates with κ^2 fashion in the carbonyl complexes of Cu(I) and Ag(I), whereas the related 3-trifluoromethylpyrazolyl ligand, $[PhB(Pz^{CF3})_3]^-$, coordinates to the copper(I) center with κ^3 fashion in the carbonyl complex.[13] Therefore we have designed a moderately hindered tris(pyridyl)borate ligand, namely phenyltris(6-methyl-2-pyridyl)borate, $[PhB(Py^{Me})_3]^-$ (= Tpy^{Me}; **1**), in which an electron-donating methyl group is introduced at the 6-position of the pyridyl group to construct bowl-shaped cavity surrounding the metal center for preventing the formation of a homoleptic inert complex. In this study, we have established a synthetic procedure of **1** successfully. In addition, nickel(II) complexes have been synthesized using the brand-new ligand **1**, and their molecular structures have been characterized and catalytic activities have been evaluated.

The reported tris(2-pyridyl)borates are synthesized by the reaction of the corresponding dibromophenylborane and Grignard reagent of pyridine (i.e. 2-pyridylmagnesium chloride-THF complex).[7, 8, 11-13] The similar procedure could be applicable for the synthesis of **1** (Scheme 1). The reaction of dichlorophenylborane with three equiv. of a LiCl adduct of Grignard reagent of 6-methylpyridine (= $Py^{Me}MgCl{\bullet}LiCl$) yielded a proton adduct of **1** (H-**1**), of which the molecular structure was confirmed by NMR analyses and X-ray crystallography (Fig. S5). Overall structural and spectroscopic properties of H-**1** were close to those of the proton adduct of 4-*tert*-butylphenyltris(2-pyridyl)borate, which is the first reported tris(pyridyl)borate compound.[7] An intramolecular hydrogen bonding was formed between the proton attached to one pyridyl nitrogen and another pyridyl nitrogen atom. An ^{11}B NMR signal was observed at −12.14 ppm. Notably, a proton adduct of phenytris(4,4-

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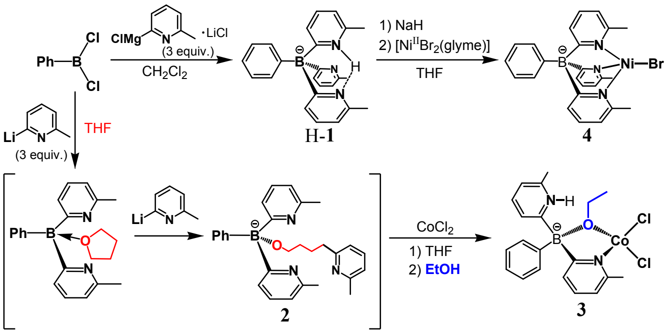
Electronic Supplementary Information (ESI) available: Experimental details, IR, NMR, electrospray ionization (ESI)-MS and UV-vis spectra, crystal structures, time course of catalytic reactions. See DOI: 10.1039/x0xx00000x dimethyl-2-oxazolynyl)borate (To^M) exhibited an ^{11}B NMR signal at –17.82 pm.[3] The downfield shift of the ^{11}B NMR signal of **1** indicates the lower electron density of the boron atom center of **1** than that of To^M. Although both **1** and To^M have the same phenyltris(azolyl)borate scaffold, the electronic property of the boron center depended on the attached azoles (6-methyl-2-pyridyl vs 4,4-dimethyl-2-oxazolynyl).

The reaction of 2-lithio-4,4-dimethyloxazoline with phenyldichloroborane yields To^M through phenylbis(4,4-dimethyl-2-oxazolinyl)borane intermediate and following nucleophilic addition of oxazolynyl anion to the boron center of the intermediate.[4] Notably, 2-lithio-6-methylpyridine (= LiPy^{Me}) is more stable than a lithiated form of the unsubstituted pyridine, and neutral ligands [E(6-methyl-2-pyridyl)$_3$], where E denotes bridgehead groups such as Si-Ph, As, Sb and Bi, can be synthesized using LiPy^{Me} in high yields.[17] Also, a related anionic ethyltris(6-methyl-2-pyridyl)aluminate, [EtAl(Py^{Me})$_3$]$^-$, has been synthesized by reaction of EtAlCl$_2$ with three equiv. of LiPy^{Me}.[18] Therefore, we attempted to synthesize **1** using LiPy^{Me} instead of Grignard's reagent (Scheme 1). Mass spectrometric analysis of the product (= **2**) obtained from the reaction of dichlorophenylborane with three equiv. of LiPy^{Me} in tetrahydrofuran (= THF)/*n*-hexane showed molecular ion peaks consistent with the composition of **1** + C_4H_8O. A ^{1}H NMR spectrum of **2** exhibited the signals of two sets of pyridyl groups in a different chemical environment with the peak integration ratio of 2 : 1. Also, peaks attributed to CH$_2$ groups other than the methyl groups attached on the pyridyl rings were detected. Although crystallographic structural analysis of **2** has not been met with success so far, single crystal X-ray structure analysis of a cobalt(II) complex **3** obtained from the reaction of **2** with Co^{II}Cl$_2$ was successfully carried out. The chelating ligand scaffold of **3** is composed of two pyridyl groups binding to boron, and the ethoxide ion derived from ethanol used in the synthesis of **3** bridged the boron and cobalt(II) centers (**Fig. 1**). Therefore, compound **2** attributed to the composition of **1** + C_4H_8O was identified as an alkoxide-borate [PhB(OC$_4$H$_8$-Py^{Me})(Py^{Me})$_2$]$^-$, involving a ring-opened THF moiety. This is presumably due to high Lewis acidity of the boron atom in the phenylbis(6-methyl-2-pyridyl)borane intermediate. As mentioned above, the electron density of the boron center in H-**1** is lower than that of H-To^M. Therefore, in the case of phenylbis(2-oxazolinyl)borane, which is produced as a precursor of To^M, the oxazolinyl anion is directly added to the boron center without the reaction being inhibited by THF. On the other hand, in the case of phenylbis(2-pyridyl)borane intermediate, the coordination and activation of THF on the highly Lewis acidic boron center occurred.



Scheme 1 Synthesis of **1** - **4**.

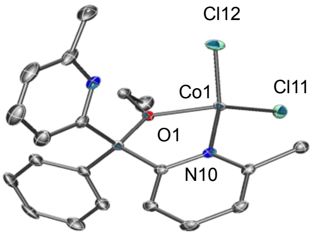


Fig. 1 Molecular structure of **3**. Thermal ellipsoids are set at 30% probability. Hydrogen atoms are omitted for clarity.

As reported previously, To^M can also function as a neutral bidentate ligand by protonation of the nitrogen donor.[5] Therefore, H-**1** was treated by sodium hydride prior to reacting with a transition metal compound. *In situ* generated sodium complex of **1** reacted with [NiBr$_2$(1,2-dimethoxyethane)] in THF to give a purple compound. The molecular structure of the resulting purple complex, [Ni^{II}Br(Tpy^{Me})] (**4**), was successfully determined by single crystal X-ray analysis as shown in **Fig. 2**. Unique properties of Tpy^{Me} were revealed by comparison of the molecular structures of the pseudo-tetrahedral nickel(II)-bromide complexes with Tpy^{Me} (**4**), To^M (**5**), and Tp* (**6**) (Fig. S10 and Table S4).[2] Solid angle analysis[19] of **4** – **6** revealed that the percentage of the sphere shielded with respect to the nickel center and the equivalent cone angle of the tridentate ligands were Tpy^{Me} (**4**; 65.36 %, 215.78 deg) > To^M (**5**; 63.74 %, 211.91 deg) > Tp* (**6**; 60.18 %, 203.48 deg). These values indicate that Tpy^{Me} is the most sterically demanding one in the tris(azolyl)borates containing multiple methyl groups which surround the metal center of the resulting complex. Such steric characteristics of the ligands arise from the difference in the ring structure of the azoles. In the case of To^M and Tp*, the methyl groups attached on the five-membered oxazolynyl and pyrazolyl rings are oriented outward from the metal center. In contrast, three methyl group attached to the 6-position of the pyridyl groups of Tpy^{Me} are positioned approximately parallel to the Ni-Br bond. The multiple methyl substituents of these ligands formed the bowl-shaped cavity surrounding the metal center. The order of the depths of the cavity is Tpy^{Me} > Tp* > To^M as was revealed by the distance between the bromine atoms and the least square planes defined by the carbon atoms of the nickel-surrounding methyl groups of each complex (1.419 Å for **4**, 2.251 Å for **5**, 1.769 and 1.774 Å for **6**).[6] The dihedral angles between the planes of adjacent azole rings are 101.3, 124.4, and 134.1 deg in **4**, and 103.3, 126.5, and 130.1 deg in **5** (the oxazoline rings are planar to within 0.090 Å), respectively, while those angles between the planes of adjacent pyrazole rings of **6** are close to 120 deg as expected for ideal C_{3v} symmetry (116.8, 116.8 and 126.5 deg in molecule 1 and 119.7, 119.7 and 120.5 deg in molecule 2, respectively). Variation of Ni–N_{azole} lengths and Br–Ni–N_{azole} angles in **4** and **5** also indicates the large structural distortion of the nickel center from the ideal tetrahedral geometry. Such structural distortion might arise from the steric repulsion between each methyl substituent. The order of Ni–Br lengths was **4** (2.3631(3) Å) > **5** (2.3178(3) Å) > **6** (2.2928(13) Å, 2.2887(13) Å), and that might correlate with the extent of electron-donating ability of the tris(azolyl)borates. In other words, the ligand with the highest electron-donating capacity is Tpy^{Me}, which coordinates to nickel, pushing the bromide ligand out and elongating the Ni–Br bond.

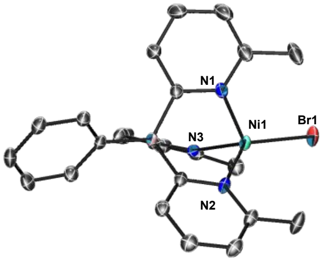


Fig. 2 Molecular structure of **4**. Thermal ellipsoids are set at 30% probability. Hydrogen atoms are omitted for clarity.

A cyclic voltammogram of **4** was also compared with those of **5** and **6**. The reduction potential of **4** was the highest among the compared complexes (Fig. S11). The π-acceptable nature of the pyridyl donors of Tpy^{Me} affects to stabilize the reduced state of the nickel center. Noteworthy, only **4** exhibited a pseudo-reversible Ni(II)/Ni(I) redox wave. Such electrochemical characteristics seem to be correlated with the structural rigidity of **4**. The tetrahedrally-distorted coordination geometry of the nickel center supported by Tpy^{Me} might be kept even in the $3d^9$ Ni(I) state. On the other hand, the structural flexibility of the nickel centers supported by To^M and Tp* lead to the irreversible redox CV waves of **5** and **6**.

Spectroscopic analyses of the solutions of **4** also suggest that the geometry of its nickel center has highly distorted four-coordinate geometry as predicted from the solid-state structure described above. A ^{1}H NMR spectrum of **4** exhibited paramagnetically shifted peaks (Fig. S12). A detailed spectral analysis has been performed for the nickel(II) halide complexes of Tp*, including complex **6**.[2] The bands appearing in the visible region are attributed to d-d transitions in the C_{3v} symmetric four-coordinated nickel(II) center; the bands around 500 nm are assigned as the spin-arrowed transition from the lowest d-orbital to the highest d_{xz} and d_{yz} orbitals on the z axis coinciding with the C_{3v} axis. Strong σ-donation from the nitrogen donors of Tp* leads to rise in the energy level of d_{z^2}, $d_{xz,}$ and d_{yz}. In a series of the Ni-Br complexes **4** – **6**, the order of the energy of the highest d-d transitions was **4** > **5** > **6** (**Fig. 3**), and that might correlate with the strength of the σ-donation from the tris(azolyl)borate. Conversely, the energy of the bands around 800 nm are in the order **6** > **5** > **4**. DFT and TD-DFT calculation of **4** suggests that the lower energy d-d bands are attributed to the transition from not only the nickel d_{z^2} (contributing bonding with Br ligand) but also the nickel-Tpy^{Me} bonding orbitals to the singly occupied orbitals composed of d_{xz} and d_{yz} (Figs. S14-S16 and Table S6). These trends in the lower energy d-d transitions are interpreted to be due to the dominant interaction between nickel and the tris(azolyl)borate ligands.

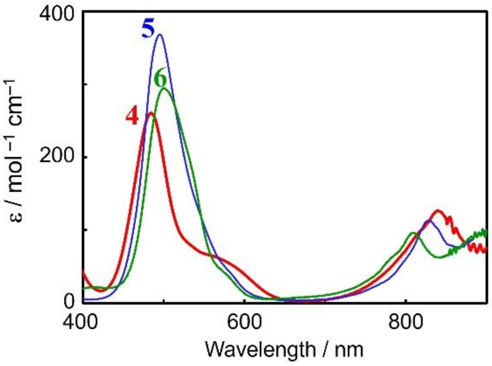


Fig. 3 Electronic spectra of CH_2Cl_2 solutions of **4** – **6** at ambient temperature.

The chemical property of Tpy^{Me} was assessed by the comparison of the activity of the Ni–Br complexes **4** – **6** toward cyclohexane oxidation with *meta*-chloroperbenzoic acid (*m*CPBA).[20] As proposed by Qiu and Hartwig, *m*CPBA is activated by nickel complexes through coordination to the nickel center and following O–O bond cleavage. The hydroxylation of cyclohexane proceeded through radical chain reaction initiated by aroyloxyl radical generated from *m*CPBA.[21] In addition, Itoh and co-workers revealed some nickel-based oxidants such as nickel–oxyl species contribute the alkane oxidation.[22] We have reported that the nickel(II)-acylperoxido adduct is stabilized by the incorporation of electron-withdrawing groups on the pyrazolyl rings of Tp^R ligands.[23] Therefore, fast ligand exchanging from bromide to *m*CPBA on the nickel and the following electron back donation from nickel to the peroxide moiety of the bound *m*CPBA promotes the O–O homolysis and accelerate the alkane oxidation reaction. The order of the cyclohexane oxidation rate was **4** > **5** > **6** (**Fig. 4**). Among the three complexes compared, complex **4** has the longest Ni–Br bond length, and as predicted, the ligand exchange reaction between the bromide and *m*CPBA will occur most rapidly in complex **4**. Also, as indicated by the longest Ni-Br bond length, Tpy^{Me} has the highest electron-donating capacity among the three ligands compared, and therefore, the formed *m*CPBA adduct from **4** is expected to be the most likely to cause O–O bond cleavage.

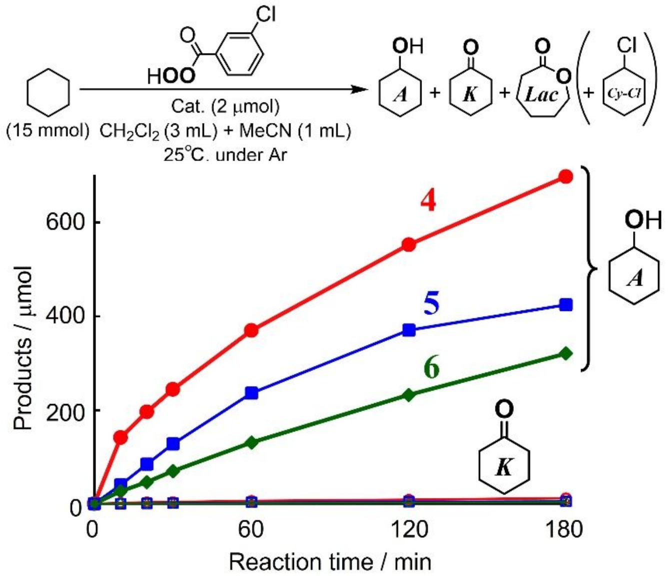


Fig. 4 Time course of cyclohexane oxidation with *m*CPBA mediated by **4** – **6**.

A nickel(II)-chlorido complex **7** with Tpy^{Me} ligand exhibited a slower cyclohexane oxidation reaction rate than that of the bromido complex **4** (Fig. S18 and Table S7). This indicates that the ligand exchange rate between the halogen ligand and *m*CPBA is a dominant factor in the oxidation reaction rate. Single crystal X-ray diffraction analysis of **7** revealed that the Ni–Cl bond length was shorter than the Ni–Br bond length in **4** (Fig. S17 and Table S5). Therefore, the chloride ligand in **7** is deeply buried in the hollow formed by the methyl group at the 6-position of the pyridine ring, which is considered to be sterically protected to prevent the ligand exchange with *m*CPBA.

In conclusion, the desired Tpy^{Me} ligand can be obtained by the reaction of phenyldichloroborane and the Grignard reagent of 6-methylpyridyl precursor in the absence of tetrahydrofuran. Reaction of phenyldichloroborane and 2-lithio-6-methylpyridine causes unusual THF activation due to high Lewis acidity of the bis(6-methyl-2-pyridyl)phenylborane intermediate. Comparison of molecular structures of nickel(II)-bromido complexes with tris(azolyl)borate ligands indicates the higher steric demanding nature of Tpy^{Me}. The nickel(II)-bromido complex with Tpy^{Me} activates *m*CPBA to promote alkane oxidation, and its reaction rate and alcohol selectivity were higher than those of the analogous complexes with the similar borate ligands composed of pyrazole or oxazoline donors.

Conflicts of interest

There are no conflicts to declare.

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