



Nickel(II)-methyl complexes adopting unusual seesaw geometries†

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We report four-coordinate nickel(II)-methyl complexes of tris-carbene borate ligands which adopt rare seesaw geometries. Experimental and computational results suggest the structural distortion from threefold symmetry results from a combination of electronic stabilization of the singlet state, strong field donors, and constrained angles from the chelating ligand.

Nickel-alkyl complexes have been invoked as important intermediates in a host of chemical transformations including the production of acetic acid and cross-coupling reactions.^{1–6} In all reported examples of crystallographically characterized Ni(II)-methyl complexes, a diamagnetic, square planar geometry is observed and many attempts to synthesize such species in other, four-coordinate geometries have proven unsuccessful frequently leading to reduction or other degradation.^{7–11} Despite this, catalytically active Ni(II)-alkyl species may likely exhibit or transition through different coordination geometries.^{12–14} For example, other synthetic Ni(II) complexes can be found in tetrahedral geometries in addition to the more common square planar geometries. While a square planar geometry is favored due to electronic stabilization of the d⁸ Ni(II) ion, a tetrahedral geometry may be favored with suitably bulky or chelating ligands.¹⁵

An alternative geometry for four-coordinate metal centers that has rarely been observed is a seesaw geometry. In fact, only a handful of examples of Ni(II) complexes in this geometry have been reported.^{13,16–18} In these cases, steric bulk is used to enforce the desired geometry. For example, the first of these reported by Bröring and co-workers utilized a tripyrranato ligand which positions methyl substituents within the square plane, forcing halide ligands above this plane.^{19–21} Other examples include those by Gossage and Baruah where homoleptic complexes of Ni(II) were synthesized with bulky propan-2-ylidene and

oxazoline substituents that prevent planarization of the Ni(II) coordination environment.^{14,22} Another recent example of a seesaw geometry at a Ni(II) center involves a diisopropylpyrazole-substituted carbazole ligand to enforce steric crowding of the square plane.¹³ Finally, an example of a ligand-constrained geometry around a Ni(II) center can be seen in a complex bound to a triphosphacyclododecane ligand.²³ This ligand binds in a facial manner with strongly donating trialkylphosphines which are proposed to enforce a low-spin state at nickel. Due to the constrained ligand environment, the coordination geometry distorts to accommodate the low-spin state but cannot fully isomerize to a square planar geometry. These examples demonstrate the lengths required to enforce this geometry at a d⁸ Ni(II) center.

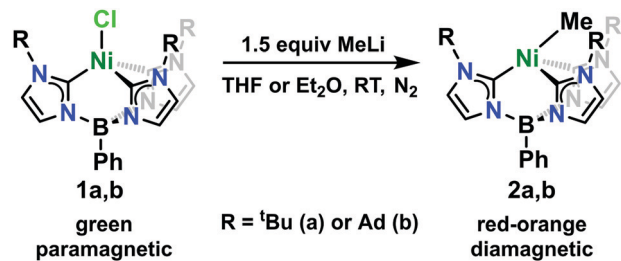
We have been interested in exploring the chemistry of late transition metals supported by chelating and strongly donating tris-N-heterocyclic carbene (NHC) borate scaffolds.^{24,25} These ligand scaffolds typically enforce a pseudo-tetrahedral geometry, but also favor low-spin states due to the strong donor properties of the carbene ligands. These factors suggest that Ni(II) complexes supported by this ligand would have geometric frustration between an electronically preferred square planar geometry and a chelate-enforced pseudo-tetrahedral geometry. We therefore rationalized that Ni(II) complexes of this ligand with suitably strong ligand fields might display unusual geometries and electronic structures.^{26–28} Here we report the isolation and characterization of two Ni(II)-methyl complexes supported by a strongly donating tris-carbene borate ligand which display unusual seesaw geometries.

The Ni(II)-chloride complexes were first synthesized by initial deprotonation of the proligand, [PhB(RImH)₃][OTf]₂ (where R = ^tBu or Ad), with *in situ* generated lithium diisopropylamide (LDA) followed by metalation with tetraethylammonium tetrachloronickelate ([Et₄N]₂[NiCl₄]) to yield PhB(^tBuIm)₃NiCl and PhB(AdIm)₃NiCl (**1a** and **1b**) in low but synthetically viable yields (see ESI†). The title complexes, PhB(^tBuIm)₃NiMe and PhB(AdIm)₃NiMe (**2a** and **2b**), were synthesized by treatment of the Ni(II)-chloride complexes **1a** and **1b** with a solution of methyllithium following a similar reported procedure for related

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Scheme 1 Synthesis of complexes **2a** and **2b**.

complexes of cobalt (Scheme 1).²⁹ Complexes **2a** and **2b** can be isolated as red, microcrystalline solids in good yield. These complexes are thermally unstable at room temperature, but pure solids can be stored at -35°C for weeks to months without noticeable decomposition. Despite their intense, red-orange color in solution, complexes **2a** and **2b** display no distinct absorption features by UV-vis spectroscopy with only trailing absorbances from the UV region of the spectra into the visible region. Contrary to the parent Ni(II)-chloride complexes **1a** and **1b**, both complexes **2a** and **2b** are diamagnetic. However, ^1H NMR spectra of both the Cl and Me complexes in C_6D_6 indicate C_3 -symmetric geometries in solution at room temperature (see ESI†).

We then turned to single-crystal X-ray diffraction (SXRD) measurements to probe the structures of these Ni complexes in the solid-state. As expected from their threefold symmetric NMR spectra, complexes **1a** and **1b** are pseudo-tetrahedral in the solid-state and have a C_3 -axis with a B–Ni–Cl angle of $177.92(6)^\circ$ and $178.8(2)^\circ$, respectively (see ESI†). In contrast, while the room temperature ^1H NMR spectra of the methyl complexes **2a** and **2b** are consistent with a C_3 -symmetric structure, an unusual seesaw coordination geometry at the Ni(II) centers is observed in their solid-state structures (Fig. 1). The metrical parameters of the Ni centers in complexes **2a** and **2b** are consistent with a seesaw geometry around the Ni(II) center composed of three carbon donors from the tris-carbene borate ligand and a fourth from the bound methyl group. The Ni–methyl carbon atom distances are nearly identical between the two complexes at $1.965(2)$ and $1.959(2)$ Å, respectively. Additionally, there is no evidence of agostic interactions between the Me hydrogen atoms and the Ni(II) center. The two widest C–Ni–C angles which describe the seesaw geometry are $177.19(8)^\circ$ and $121.49(8)^\circ$ for **2a** and $177.80(7)^\circ$ and $121.25(7)^\circ$ for **2b**. Using both of these angles, a geometry index parameter τ_4 can be calculated to describe the coordination environment of the Ni(II) center between square planar ($\tau_4 = 0$) or tetrahedral ($\tau_4 = 1$).^{30,31} For both **2a** and **2b**, the τ_4 parameter is calculated to be 0.43, indicating a nearly perfect mono-vacant, trigonal bipyramidal or seesaw geometry around the Ni(II) center. These are the first such cases to be crystallographically characterized.†

With the disparity between solid-state and solution structural data, we sought to better understand the dynamics of complexes **2a** and **2b** in solution. Variable temperature ^1H NMR experiments were conducted in d_8 -toluene to determine an isomerization barrier, ΔG^\ddagger (Fig. 2).^{32,33} In these complexes, the barrier being measured represents the energy to reorient

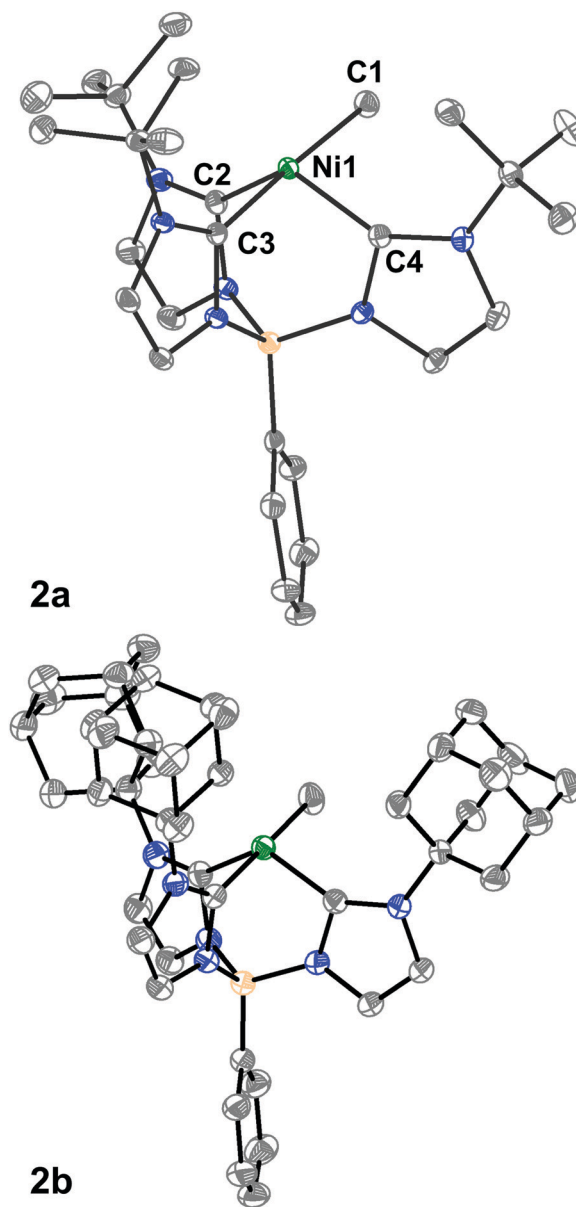


Fig. 1 SXRD structures of **2a** and **2b**. Ellipsoids are shown at 50% and H atoms are omitted for clarity. Ni is shown in green, N in blue, B in tan, and C in gray. Atom labels for **2b** are the same as those depicted for **2a**. Selected bond lengths (Å) and angles ($^\circ$) and geometric parameters for **2a**: Ni1–C1 = $1.965(2)$, Ni1–C2 = $1.895(2)$, Ni1–C3 = $1.922(2)$, Ni1–C4 = $1.887(2)$, C1–Ni1–C3 = $177.19(8)$, C2–Ni1–C4 = $121.49(8)$, $\tau_4 = 0.43$. For **2b**: Ni1–C1 = $1.959(2)$, Ni1–C2 = $1.886(2)$, Ni1–C3 = $1.912(2)$, Ni1–C4 = $1.884(2)$, C1–Ni1–C3 = $177.79(7)$, C2–Ni1–C4 = $121.25(7)$, $\tau_4 = 0.43$.

the methyl substituent from between one pair of NHC groups to between a different pair through either an effective lever mechanism or *via* B–Ni–Me linearization to a C_3 -symmetric isomer (see below).³⁴ For an NHC resonance of **2a** (labeled with an asterisk in Fig. 2), a coalescence temperature of 215 K was determined and from the value of $\Delta\nu$, the peak-to-peak splitting in Hz of the fully resolved asymmetric structure, a barrier to isomerization was calculated to be $10.4 \pm 0.5 \text{ kcal mol}^{-1}$. In the case of **2b** with the larger adamantyl groups, we anticipated a

