Structural Characterization and Electrochemical Properties of Nickel(II) Complexes Bearing Sterically Bulky Hydrotris(3-phenyl)- and Hydrotris(3-*tert*-butylpyrazol-1-yl)borato ligands.

Alycia K. Frampton, Kathryn Gartland[†], Nicholas Piro[†], W. Scott Kassel[†] and William G. Dougherty*

Department of Chemistry, Susquehanna University, Selinsgrove, PA 17870.

[†]Department of Chemistry, Villanova University, Villanova, PA 19085.

** Corresponding Author. Tel.: 5703724255*

*307A Natural Sciences Center
Susquehanna University
514 University Ave.
Selinsgrove, PA 17870*

E-mail address: doughertyw@susqu.edu

Abstract.

Two series of pseudo-tetrahedral nickel(II) complexes bearing the bulky hydrotris(3-phenyl)- or hydrotris(3-*tert*-butylpyrazol-1-yl)borato ligands, $\text{Tp}^{\text{Ph}}\text{NiL}$ and $\text{Tp}^{\text{tBu}}\text{NiL}$ respectively, have been synthesized and characterized with the intent of investigating the affects of substituent size on the redox properties of the nickel center ($\text{L} = \text{Cl}, \text{Br}, \text{I}, \text{NCS}, \text{NO}_3$). X-ray analysis reveals both Tp ligands bind in a κ^3 fashion with the R groups pointing out towards the metal producing a pocket in which the 4th ligand, L, resides. The Tp^{Ph} ligand results in a larger pocket and produces nickel complexes with distorted solid-state geometries, specifically bent $\text{B}\dots\text{Ni}\dots\text{L}$ angles, unlike the corresponding Tp^{tBu} complexes which show much less variation in structure. Cyclic voltammetry experiments indicate all complexes undergo a $\text{Ni}^{2+}/1+$ reduction at large negative potentials vs. ferrocene with varying levels of reversibility. The NCS complexes are the most reversible and the easiest to reduce with an average reduction potential of -1.51 V due to the slightly electron withdrawing nature of the thiocyanate ligand. The strong donor properties of the bidentate nitrate ligand result in complexes that are the most difficult to reduce at an average of -1.80 V. Overall, the $\text{Tp}^{\text{Ph}}\text{NiL}$ complexes are easier to reduce than their corresponding $\text{Tp}^{\text{tBu}}\text{NiL}$ complexes resulting from the weakened donor ability of the Tp^{Ph} ligand. While the two ligands do produce different structural motifs, the electrochemical trends are more in line with the electronic properties of the complexes than structural differences.

Keywords:

Trispyrazolylborate

Nickel Complexes

Crystal Structures

Electrochemistry

1. Introduction

The hydrotris(pyrazolyl)borate, Tp, ligand has been a valuable tool for synthetic chemists ever since its development by Trofimenko in the late 1960s [1]. The ability to modify the electronic and steric properties by substitution around the pyrazole rings has lead to widespread use of Tp ligands in the fields of inorganic, organometallic and bioinorganic chemistry [2]. Of particular interest are derivatives with large groups at the 3 or 5 positions that discourage formation of the coordinatively saturated $(\text{Tp}^{\text{R}})_2\text{M}$ sandwich complexes promoting monomeric metal complexes with available sites opposite the Tp^{R} ligand for additional ligand binding. Within the bulky Tp^{R} ligands, there is structural variation depending on the size and nature of the R group. Large aliphatic groups like *tert*-butyl produce “tetrahedral enforcer” ligands, which leave a small rigid pocket around the metal available for only one additional ligand [3-4]. However, planar aromatic groups such as phenyl, produce larger, more flexible pockets with greater diversity in overall structure and ligand identity [5]. Nickel complexes of the latter have been investigated for their

biomimetic chemistry [6-8] and the their promise as homogeneous catalysts for organic transformations [9-11]. However, the basic redox properties of the nickel center in these types of complexes have not been thoroughly studied. Specifically, do the structural properties imposed by the bulky pyrazolyl substituent affect the redox properties of the metal center?

In this work, we investigate the role of substituent nature on the redox properties of Tp nickel complexes by generating two series of molecules bearing the Tp^{tBu} and Tp^{Ph} ligands. The solid-state structures of the novel complexes are investigated using single crystal X-ray diffraction and the redox properties of the nickel center are monitored by cyclic voltammetry. The Tp^{Ph} ligand produces a series of complexes with far more structural diversity than the Tp^{tBu} ligand. However, the differences in redox potential are more closely aligned with the electronic differences between the two sets of molecules.

2. Experimental

2.1. Materials and general procedures

All solvents and chemicals (Aldrich Chemical Co.) were reagent grade and used as received unless otherwise indicated. Thallium hydrotris-(3-phenylpyrazol-1-yl)borate, $\text{Tl}[\text{Tp}^{\text{Ph}}]$, and sodium hydrotris-(3-t-butylpyrazol-1-yl)borate, $\text{Na}[\text{Tp}^{\text{tBu}}]$, were prepared from the melt method outlined previously for other bulky Tp ligands [5,12]. *Caution: Thallium salts are known to be toxic, extra care should be taken when handling these complexes.* FT-NMR spectra were recorded on a Varian Mercury 300 spectrometer and a JEOL Eclipse 400 spectrometer. ^1H NMR spectra were referenced to residual solvent peaks. IR spectra ($4000 - 400 \text{ cm}^{-1}$) were recorded on a Perkin Elmer Spectrum One equipped with a diamond ATR attachment or a Thermo Nicolet Nexus 870 FT-IR equipped with a diffuse reflectance accessory. UV-Visible spectroscopy was recorded on a Cary 50 Bio UV-Vis spectrometer. Elemental analysis was performed by Atlantic Microlab, Inc., Norcross GA. Xray data was collected on a Bruker-AXS Kappa diffractometer equipped with an APEX II CCD detector. Cyclic voltammetry experiments were conducted on a BAS 50W Electrochemical Analyzer and an EDAQ 466 Integrated Potentiostat System.

2.2. Experimental procedures

2.2.1. Metal complex syntheses

Synthesis of $\text{Tp}^{\text{Ph}}\text{NiCl}(\mathbf{1})$. To a yellow solution of $\text{NiCl}_2 \cdot 6 \text{ H}_2\text{O}$ (0.440g, 1.8 mmol) in 150 mL of a 50:50 MeOH:THF mixture was added $\text{Tl}[\text{Tp}^{\text{Ph}}]$ (1.00g, 1.5 mmol) resulting in immediate formation of a white precipitate. The solution was stirred for 1 hr. The solvent was removed under vacuum and 100 mL of methylene chloride was added to the residue. The solution was filtered through a Celite® plug on a medium frit and the filtrate was evaporated to dryness under vacuum yielding a purple, tacky solid. The solid was redissolved in 10 mL of diethyl ether and the solvent was removed under vacuum. The pink powder (0.580g, 71%) was collected on a medium frit, washed with hexanes, and dried under vacuum. ^1H -NMR (CDCl_3) δ

74.7 (br, *Pz*), δ 24.3 (br, *Pz*), δ 10.0 (br, *Ph*), δ 8.5 (s, *Ph*), δ 8.2 (s, *Ph*) 7.26 (CDCl₃), δ -11.3 (br, *BH*). UV-Vis in CH₂Cl₂: $\lambda_{\max}(\epsilon, \text{cm}^{-1}, \text{M}^{-1})$ 487(245), 543(70), 807(37), 941(77) nm. IR (cm⁻¹). 2500w (ν_{BH}), 1489m, 1469m, 1361m, 1187s, 1073m, 1051s, 790m, 755s, 726s, 694s, 676m. Anal. Calcd: C, 60.56; H, 4.14; N, 15.69. Found: C, 60.29; H, 4.08; N, 15.39.

Synthesis of Tp^{Ph}NiBr(2). To a warm orange solution of NiBr₂ (0.110g, 0.50 mmol) in 30 mL of a 50:50 MeOH:THF mixture was added Tl[Tp^{Ph}] (0.300g, 0.46 mmol) resulting in immediate formation of a white precipitate. The solution was stirred for 0.5 hr. The solvent was removed under vacuum and 30 mL of methylene chloride was added to the residue. The solution was filtered through a Celite® plug on a medium frit and the filtrate was evaporated to dryness under vacuum yielding a red, tacky solid. The solid was redissolved in 10 mL of diethyl ether and the solvent was removed under vacuum. The maroon powder (0.137g, 50%) was collected on a medium frit, washed with hexanes, and dried under vacuum. ¹H-NMR (CDCl₃) δ 74.2 (br, *Pz*), δ 25.6 (br, *Pz*), δ 8.8 (br, *Ph*), δ 7.8 (br, *Ph*), δ 7.26 (CDCl₃), δ -8.4 (br, *BH*). UV-Vis in CH₂Cl₂: $\lambda_{\max}(\epsilon, \text{cm}^{-1}, \text{M}^{-1})$ 500(395), 567(sh, 100), 822(58), 945(100) nm. IR (cm⁻¹). 2505w (ν_{BH}), 1493m, 1468m, 1373m, 1365m, 1189s, 1070m, 1052s, 795s, 756s, 729s, 699s, 675m. Anal. Calcd: C, 55.92; H, 3.82; N, 14.49. Found: C, 55.83; H, 3.74; N, 14.42.

Synthesis of Tp^{Ph}NiNO₃(3). To a pale blue solution of Ni(NO₃)₂ • 6 H₂O (0.052g, 0.18 mmol) in 30 mL of a 50:50 MeOH:THF mixture was added Tl[Tp^{Ph}] (0.100g, 0.15 mmol) resulting in immediate formation of a white precipitate. The solution was stirred for 0.5 hr. The solvent was removed under vacuum and 30 mL of methylene chloride was added to the residue. The solution was filtered through a Celite® plug on a medium frit and the filtrate was evaporated to dryness under vacuum yielding a green, tacky solid. The solid was redissolved in 10 mL of diethyl ether and the solvent was removed under vacuum. The green residue was dissolved in 2 mL of CHCl₃ and the green solution was layered with hexanes. After one day green crystals were present. The green crystals (0.021g, 24%) were isolated, washed with hexanes, and dried under vacuum. ¹H-NMR (CDCl₃) δ 67.1 (s, *Pz*), δ 29.4 (s, *Pz*), δ 8.6 (s, *Ph*), δ 8.1 (s, *Ph*), δ 7.3 (CDCl₃), δ 6.8 (br, *Ph*), δ -10.3 (br, *BH*). UV-Vis in CH₂Cl₂: $\lambda_{\max}(\epsilon, \text{cm}^{-1}, \text{M}^{-1})$ 309(sh, 570), 355(sh, 230), 421(110), 680(30) nm. IR (cm⁻¹). 2489w (ν_{BH}), 1533m, 1490m, 1466m, 1361m, 1249m, 1186s, 1072m, 1048s, 1012m, 792m, 758s, 720m, 696s. Anal. Calcd: C, 57.70; H, 3.94; N, 17.44. Found: C, 57.64; H, 3.83; N, 17.24.

Synthesis of Tp^{Ph}NiI(4). To a solution of NaI (0.055g, 0.37 mmol) in 10 mL of MeOH was added Tp^{Ph}NiCl (0.100g, 0.19 mmol) resulting in a green solution. The solution was stirred for 0.5 hr. The solvent was removed under vacuum and 10 mL of methylene chloride was added to the residue. The solution was filtered through a Celite® plug on a medium frit and the filtrate was evaporated to dryness under vacuum yielding a red, tacky solid. The solid was redissolved in 10 mL of diethyl ether and the solvent was removed under vacuum. The brown residue was dissolved in 10 mL of a 50:50 CH₂Cl₂/hexanes mixture and the dark-red solution

was layered with hexanes. After three days purple and colorless crystals were present. The dark purple crystals (0.060g, 51%) were isolated, washed with hexanes, and dried under vacuum. $^1\text{H-NMR}$ (CDCl_3) δ 72.5 (s, *Pz*), δ 28.0 (s, *Pz*), δ 8.8 (s, *Ph*), 7.26 (CDCl_3), δ 3.3 (br, *Ph*), δ -1.3 (br, *BH*). UV-Vis in CH_2Cl_2 : $\lambda_{\text{max}}(\epsilon, \text{cm}^{-1}, \text{M}^{-1})$ 324(1080), 389(1385), 431(1192), 519(873), 593(242), 854(100), 964(126) nm. IR (cm^{-1}). 2503w (ν_{BH}), 1492m, 1468m, 1373m, 1362m, 1187s, 1050s, 794m, 760s, 728m, 697s, 675m. Anal. Calcd: C, 51.73; H, 3.54; N, 13.41. Found: C, 52.00; H, 3.65; N, 13.51.

Synthesis of $\text{Tp}^{\text{tBu}}\text{NiBr}$ (5). To a yellow slurry of (8) (0.100g, 0.20 mmol) in 25 mL of MeOH was added NaBr (0.105g, 1.0 mmol) resulting in a purple solution. The solution was stirred for 30 min. The solvent was removed under vacuum and 25 mL of methylene chloride was added to the residue. The purple solution was filtered through a Celite® plug on a medium frit and the filtrate was evaporated to dryness under vacuum yielding a solid. The purple powder (0.076g, 73%) was collected on a medium frit, washed with hexanes, and dried under vacuum. $^1\text{H-NMR}$ (CDCl_3) δ 80.3 (br, *Pz*), δ 20.5 (br, *Pz*), δ 7.26 (CDCl_3), δ 0.4 (br, *tBu*), δ -7.5 (br, *BH*). UV-Vis in CH_2Cl_2 : $\lambda_{\text{max}}(\epsilon, \text{cm}^{-1}, \text{M}^{-1})$ 323(1300), 528(200), 828(12), nm. IR (cm^{-1}). 2530m (ν_{BH}), 1502s, 1366s, 1200s, 1063s, 787s, 737s. Anal. Calcd: C, 48.51; H, 6.59; N, 16.16. Found: C, 48.61; H, 6.73; N, 16.24.

Complexes 6 was synthesized by the same procedure described for 5 using the appropriate sodium salt.

Synthesis of $\text{Tp}^{\text{tBu}}\text{NiI}$ (6). Black powder, 75% Yield. $^1\text{H-NMR}$ (CDCl_3) δ 78.4 (br, *Pz*), δ 23.0 (br, *Pz*), δ 7.26 (CDCl_3), δ -2.2 (br, *tBu*). UV-Vis in CH_2Cl_2 : $\lambda_{\text{max}}(\epsilon, \text{cm}^{-1}, \text{M}^{-1})$ 377(800), 432(sh, 360), 550(160), 854(10) nm. IR (cm^{-1}). 2522m (ν_{BH}), 1502s, 1365s, 1334s, 1199s, 1063s, 786s, 736s. Anal. Calcd: C, 44.49; H, 6.04; N, 14.82. Found: C, 44.24; H, 5.99; N, 14.82.

2.2.2. Electrochemistry

All experiments were conducted in N_2 -degassed methylene chloride in a cell containing a glassy carbon working electrode, an Ag^+/Ag reference electrode and a Pt wire as the counter electrode with 0.1M [$n\text{Bu}_4\text{N}$][PF_6] as a supporting electrolyte. The analyte solution concentrations were ~ 3 mM and scan rates of 250 mV/s were employed. All potentials were referenced internally and reported against Fc/Fc^+ [13].

2.2.3 Xray Diffraction Studies

Single crystals were selected and mounted using Paratone or NVH immersion oil onto a glass fiber or a nylon fiber and cooled to the data collection temperature of 100(2) K with a stream of dry nitrogen gas, unless otherwise noted. Data were collected on a Brüker-AXS Kappa APEX II CCD diffractometer with 0.71073 Å Mo-K α radiation. Unit cell parameters were obtained from 60 data frames, 0.5° ϕ , from three different sections of the Ewald sphere and complete data collection strategies

were determined for each crystal using the APEX2 suite [14]. Each data set was treated with SADABS [15] absorption corrections based on redundant multi-scan data. The structures were solved by direct methods or intrinsic phasing and refined by least squares method on F^2 using the SHELXL [16] program package within APEX2. All non-hydrogen atoms were refined with anisotropic displacement parameters and all hydrogen atoms were treated as idealized contributions, unless otherwise noted. Selected crystallographic data and refinement details are displayed in **Table 1** and **Table 2**. Details regarding specific solution refinement for each compound are provided in the supporting information.

3. Results and Discussion

3.1.1. Synthesis of $Tp^{Ph}NiL$ complexes.

Synthesis of the phenyl-substituted nickel complexes was achieved through the metathesis of $Tl[Tp^{Ph}]$ with the appropriate nickel (II) salt in a THF/MeOH mixture in the case of the Cl, Br and I complexes or through the metathesis of isolated chloride complex with 2-fold excess sodium iodide salt in methanol for the I complex. This is a modification of the previously procedure reported by Trofimenko [5]. A 2-fold excess of the NaI gave the highest conversion to the desired complex as indicated by the 1H -NMR spectrum of the product. The pyrazolyl protons in these complexes are paramagnetically shifted downfield and sensitive to the identity of the L ligand. Recrystallization of the NO_3 and I complex from methylene chloride was required to achieve analytically pure samples of the desired molecules.

3.1.2. Synthesis of $Tp^{tBu}NiL$ complexes.

Similar to the corresponding $Tp^{Ph}NiL$ complexes, the t-butyl derivatives were synthesized through metathesis reactions with excess NaL in methanol. However, the chloride derivative is not an appropriate starting material in these complexes. The metathesis does not occur with this complex and we obtain the starting material in nearly quantitative yield. We found isolated $Tp^{tBu}NiNO_3$ [17] to be an appropriate starting material for the synthesis of $Tp^{tBu}NiBr$ when mixed with 5-fold excess of NaBr. Synthesis of $Tp^{tBu}NiI$ worked best with only 3 eq. of NaI leading to a cleaner isolated product. The isolated powder from these reactions required no further crystallization and gave clean 1H -NMR spectrum with no sign of starting material or decomposition products.

3.2 Structural Analysis

Molecular structures of all complexes were determined through single crystal X-ray diffraction studies. Although these ligands were first reported in the late 1980's, these particular nickel complexes have not been previously characterized by X-ray analysis. X-ray quality crystals were grown by vapor-diffusion of organic solvents such as diethylether, pentane or hexanes into solutions of the complexes in methylene chloride. Non-coordinating solvents are preferred because Tp^{Ph} metal complexes have been shown previously to bind solvent and form 5-coordinate solvate complexes [5,18]. Metal coordination number affects both the solution and

solid-state color in these systems. The desired 4-coordinate nickel complexes are red or purple in color while 5-coordinate complexes are green or yellow. We are interested in comparing solid-state structure with solution behavior so it is essential that the solid-state structures are as representative as possible of the actual solution structure. We have also obtained structures for $\text{Tp}^{\text{Ph}}\text{NiNCS}$ and $\text{Tp}^{\text{tBu}}\text{NiNCS}$ which have been previously synthesized but whose X-ray structures have not been reported [5].

3.2.1 $\text{Tp}^{\text{Ph}}\text{NiL}$ complexes

The solid-state structures of the four-coordinate halide complexes are isomorphous with a trigonal unit cell (**Figure 1**). The Tp^{Ph} ligand is face-capping the nickel center through the free nitrogen atoms of the three pyrazolyl rings and the L ligand occupying the 4th position of the pseudo-tetrahedron. The molecules lie on a 3-fold symmetry element running through the B...Ni...L vector making all three pyrazolyl rings equivalent. The phenyl substituents are arranged in a propeller-like motif creating a pocket that the L ligand occupies. There are slight differences in the bond distances and angles of the Tp^{Ph} substituent across the series but the molecules are virtually identical except for length of the Ni-L bond which increases, as expected, from 2.168(2) Å for the chloride derivative to 2.462(1) Å for the iodide complex.

The pocket created by the phenyl rings is large enough to allow movement of the L ligand within the pocket. The I complex has a second, low-symmetry monoclinic polymorph found along with the trigonal crystals in which the B...Ni...I angle is not linear. (**Figure 2**) The iodide ligand sits off-center in the pocket located closer to two of the three phenyl rings with a B...Ni...I angle of 162.1(1)° markedly different from the 180° angle in the trigonal polymorph. This type of distortion has been described previously for a $\text{Tp}^{\text{Me,Ph}}$ nickel thiolate complex with a similar pocket [8]. The two phenyl rings are splayed open and cradle the iodide ligand possibly stabilizing the distorted geometry through electrostatic interactions. However, the closest contacts between the iodide and the *ortho* carbons on the two phenyl rings is ~3.7 Å which is long for pi-type interactions.

The N-bound thiocyanate complex exhibits the same distortion with a B...Ni...N angle of 167.0(1)° bent towards two of the phenyl rings which again appear to cradle the ligand (**Figure 3**). The N-C-S bond vector overlaps closely with the $C_{\text{ortho}}-C_{\text{meta}}$ bond vector in both phenyl rings with a closest contact of ~ 3.3 Å which is in the range for possible pi-pi interactions. The NO_3 complex exhibits a symmetrical, bidentate nitrate ion with Ni-O distances of 2.077(1) and 2.092(1) Å (**Figure 4**). The nitrate ion is also shifted from the center of the pocket with a B...Ni...N angle of 164.7(1)° lying between two parallel phenyl rings.

The τ_4 parameter has been developed to approximate the 4-coordinate geometry of a metal center [19] It is a numerical value calculated from the two largest angles around the metal. The values range from 1.00 for perfect tetrahedral geometry to 0.00 for perfect square planar geometry. Calculated values for the $\text{Tp}^{\text{Ph}}\text{NiL}$ complexes are found in the bottom of **Table 3**. However, the bite angle of the face-

capping Tp^{R} ligands prohibits the molecules from ever reaching a true tetrahedral geometry. Thus, using the τ_4 parameter as the sole structural descriptor for these complexes is not sufficiently robust. The reduction of symmetry towards a distorted trigonal pyramid (C_{3v} symmetry) in these complexes occurs through an umbrella-opening distortion resulting from the compression of three of the four tetrahedral angles [20]. This best describes the three, high-symmetry $\text{Tp}^{\text{Ph}}\text{NiL}$ halide complexes. The thiocyanate and nitrate complex are further distorted trigonal pyramids resulting from a combination of off-axis (one small and two larger N-Ni-L angles) and sawhorse distortions (two small and one larger N-Ni-L angles). Although the nitrate ligand is bidentate, for the purposes of this discussion we treat this ligand as monodentate with the nitrogen atom bound to the metal. The low-symmetry iodide polymorph is best described as a distorted sawhorse under this classification.

Considering the nitrate complex is technically a 5-coordinate metal complex, use of the τ_5 parameter described by Addison for 5-coordinate complexes is also applicable [21]. The nitrate complex has a value of $\tau_5 = 0.41$ indicating a distorted square-pyramidal structure with one of the pyrazolyl nitrogen atoms occupying the apical position.

3.2.2 $\text{Tp}^{\text{tBu}}\text{NiL}$ complexes

The structures of the $\text{Tp}^{\text{tBu}}\text{NiL}$ compounds assume the standard three-nitrogen Tp coordination as in the Tp^{Ph} complexes with the three *tert*-butyl substituents pointing out towards metal creating a pocket for the L ligand to reside. (**Figure 5**) The bulky *tert*-butyl groups result in a smaller pocket for the L ligand to reside and disfavor the off-center distortions seen in the corresponding Tp^{Ph} complexes. The B...Ni...L angles of the compounds are all between $176 - 178^\circ$ and the previously crystallized Cl [22] and NO_3 [17] derivatives have angles of $176.1(4)$ and $167.7(2)$ respectively. The complexes can all be described as having distorted trigonal pyramidal geometry similar to the halide structures of Tp^{Ph} counterparts with the nitrate complex exhibiting an additional off-axis distortion. A τ_5 analysis of this nitrate complex results in a $\tau_5=0$, indicating a perfect tetragonal structure imposed by the mirror plane of the crystal system on which this molecule lies with the nickel atom raised slightly out of the basal plane. **Table 4** contains relevant structural parameters for these complexes.

3.2.3 Structural Comparison

Comparing across the two series, the Tp^{tBu} and Tp^{Ph} complexes have similar structural parameters with the same L ligand. Notable exceptions are with the larger bromide and iodide ligands where the larger *t*-butyl substituents in the Tp^{tBu} ligand cause a simultaneous lengthening of both the Ni-N_{avg} and the Ni-L bond lengths due to steric crowding. The τ_4 values for the Tp^{tBu} complexes show much less variation with only the NO_3 complex having a value $\neq 0.79$. Overall, the bulkier Tp^{tBu} ligand results in a series of complexes with less solid-state structural variation than the Tp^{Ph} ligand. ORTEP diagrams, complete

3.3 Electrochemistry

3.3.1 $Tp^{Ph}NiL$ complexes

The electrochemical properties of the complexes were investigated using cyclic voltammetry in the non-coordinating solvent methylene chloride. The complexes exhibit the same general voltammogram with a pseudo-reversible Ni^{2+}/Ni^{1+} reduction at a large negative potential versus the ferrocene reference. The amount of reversibility varies across the complexes with the NCS complex (**Figure 6, top**) having the largest back wave and the Br complex (**Figure 6, middle**) approaching complete irreversibility. The iodide complex has the most interesting voltammogram with a two reduction waves present and an oxidation wave positive of ferrocene. (**Figure 6, bottom**). We originally thought these discrepancies were the result of impurities, but the CV was recollected using crystalline sample and the result was the same. The oxidation wave is presumably iodide based as neither the ligand nor metal is oxidized in any other complex we studied. We assign the second, most negative reduction wave as further reduction of the metal center from Ni^{1+} to Ni^0 . The soft nature of the iodide ligand must stabilize the Ni^0 oxidation state in this specific complex, as this state is not accessible in any of the other complexes.

The reduction potentials of each complex loosely correlates with the donor-acceptor properties of the L ligand with the pi-donor NO_3 complex being hardest to reduce at -1.72 V and the slightly withdrawing NCS complex being the easiest to reduce at -1.49 V. This makes sense, as it should be harder to put an electron into a more electron-rich metal center. The halide series shows a strong correlation between halide size and reduction potential. The I complex is the easiest to reduce at -1.49 V for the Ni^{2+}/Ni^{1+} process and the chloride the hardest at -1.86 V. The large iodide ligand coupled with the steric bulk of the Tp^{tBu} ligand results in poor orbital overlap with the nickel center making the iodide a weaker donor in this system compared to the smaller chloride ligand.

3.3.2 $Tp^{tBu}NiL$ complexes

These complexes have similar electrochemical properties to the complexes described above; however, the peak broadening of the voltammograms is much larger in these complexes. This is the result of our inability to apply a reasonable internal resistance compensation for our non-aqueous cell using our current electrochemistry setup. While the peak broadening is less-than-ideal, the $E_{1/2}$ values for ferrocene were reproducible across multiple trials resulting in reduction potentials for our metal complexes that we can use in comparisons across the two series.

The complexes all show a Ni^{2+}/Ni^{1+} reduction at a large negative potential versus the ferrocene reference with varying levels of reversibility. The NCS complex is again the most reversible (**Figure 7, top**) with the NO_3 complex showing almost complete irreversibility (**Figure 7, middle**). The iodide complex (**Figure 7, bottom**) shows the same two-peak behavior as the corresponding Tp^{Ph} complex and we

propose the same explanation for this behavior as described above. Like the $\text{Tp}^{\text{Ph}}\text{NiI}$, there is an iodide-based oxidative wave present in the voltammogram but it is obscured by the ferrocene standard. Similarly, the reduction potentials for these complexes loosely correlate with the donating properties of L with the NCS complex at -1.53 V and the NO_3 complex at -1.92 V. The iodide complex, at -1.55 V, again has a more positive reduction potential for the $\text{Ni}^{2+}/\text{Ni}^{1+}$ couple when compared to the Cl or Br complex. **Table 5** contains the reduction potentials for both series of complexes.

3.3.3 Electrochemical Comparisons.

Both series of complexes have similar shaped voltammograms in methylene chloride. The lack of completely reversible spectra in all cases suggests the Ni^{+1} state is not stable in these systems. In both series, the NCS complex exhibits the most reversible spectrum suggesting the withdrawing nature of thiocyanate is stabilizing the electron-rich Ni^{1+} complex upon formation. The reduction potentials for the $\text{Tp}^{\text{Ph}}\text{NiL}$ complexes are all more negative than their $\text{Tp}^{\text{tBu}}\text{NiL}$ counterparts. The electron-withdrawing properties of the phenyl substituents make the Tp^{Ph} ligand a weaker donor than the Tp^{tBu} ligand easing reduction at the nickel center. Also, the shortening of the Ni-L bond distances in the Tp^{Ph} series, should increase donor properties of L compared to the corresponding Tp^{tBu} complex.

The halide complexes of the Tp^{tBu} ligand have significantly different reduction potentials following ligand size trends. However, the corresponding Tp^{Ph} complexes show much less variation in reduction potentials with the Br and Cl complexes exhibiting virtually identical reduction potentials. The availability of more distorted geometries in the Tp^{Ph} series may be tempering the orbital overlap trends seen in the more rigid Tp^{tBu} series. If the $\text{Ni}^{2+}/^{1+}$ transition can be stabilized by a geometrical distortion about the nickel center, then the Tp^{Ph} complexes with their large pocket should accommodate geometry changes better than the Tp^{tBu} complexes. However, without a complete molecular orbital calculation it is hard to predict if such a transition would benefit from a structural change.

4. Conclusions

We have synthesized two series of pseudo-tetrahedral nickel(II) complexes bearing bulky trispyrazolylborate ligands. The planar nature of the phenyl substituents on the Tp^{Ph} ligand produces a large pocket around the metal center and results in a more structurally diverse set of complexes. The complexes all exhibit a pseudo-reversible $\text{Ni}^{2+}/^{1+}$ reduction at large negative potentials versus ferrocene. The iodide complexes in each series undergo an additional $\text{Ni}^{1+}/\text{Ni}^0$ reduction stabilized by the soft nature of the iodide ligand. The redox potential trends are more consistent with the different electronic properties of the ligands involved. However, the larger binding pocket produced by the Tp^{Ph} ligand gives rise to accessible distorted geometries about the metal center thus influencing overall reduction potential trends. The combination of electronic and steric effects should be considered when

examining redox potentials of metal complexes bearing sterically demanding ligands.

Acknowledgements

We thank the Department of Chemistry at both Susquehanna University and Villanova University for financial support for this work. X-ray data was collected at Villanova University through support from the National Science Foundation (0521062).

References

- [1] Jesson, J. P.; Trofimenko, S.; Eaton, D. R.; *J. Am. Chem. Soc.* **1967**, *89*, 3148.
- [2] Trofimenko, S. *Scorpionates-The Coordination Chemistry of Polypyrazolylborate Ligands*; Imperial College Press: London, 1999.
- [3] Detrich, J. L.; Konecny, R.; Vetter, W. M.; Doren, D.; Rheingold, A. L.; Theopold, K. H. *J. Am. Chem. Soc.* **1996**, *118*, 1703.
- [4] Detrich, J. L.; Reinaud, O. M.; Rheingold, A. L.; Theopold, K. H. *J. Am. Chem. Soc.* **1995**, *117*, 11745.
- [5] Trofimanko, S.; Calabrese, J. C.; Thompson, J. S. *Inorg. Chem.* **1987**, *26* 1507.
Ciunik, Z.; Ruman, T.; Lukasiewicz, M.; Wolowiec, S. *J. Mol. Struct.* **2004**, *690*, 175.
- [6] Deb, T.; Jensen, M. P.; *Inorg. Chem.* **2015**, *54*, 87.
- [7] Deb, T.; Rohde, G. T.; Young Jr., V. G.; Jensen, M. P.; *Inorg. Chem.* **2012**, *51*, 7257.
- [8] Chattopadhyay, S.; Deb, T.; Ma, H.; Petersen, J. L.; Young Jr.; V. G.; Jensen, M. P.; *Inorg. Chem.* **2008**, *47*, 3384.
- [9] Abubekеров, M.; Gianetti, T. L.; Kunishita, A.; Arnold, J. *Dalton Trans.* **2013**, *42*, 10525.
- [10] Uehara, K.; Hikichi, S.; Akita, M. *J. Chem. Soc. Dalton Trans.* **2002**, 3529.
- [11] Kläui, W.; Turkowski, B.; Rheinwald, G.; Lang, H. *Eur. J. Inorg. Chem.* **2002**, *1*,

205.

- [12] Ciunik, Z.; Ruman, T.; Lukasiewicz, M.; Wolowiec, S. *J. Mol. Struct.* **2004**, *690*, 175.
- [13] Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877.
- [14] APEX II, v. 2009.3; Bruker AXS Inc.: Madison, WI, 2009.
- [15] SADABS, v. 2008/1; Bruker AXS Inc: Madison, WI, 2008.
- [16] Sheldrick, G. M.; SHELXTL, v. 2008; Bruker AXS Inc.:Madison, WI, 2008.
- [17] Han, R.; Parkin, G. *J. Am. Chem. Soc.* **1991**, *113*, 9707.
- [18] Siemer, C. J.; Meece, F. A.; Armstrong, W. H.; Eichhorn, D. M. *Polyhedron* **2001**, *20*, 2637.
- [19] Yang, L.; Powell, D. R.; Houser, R. P. *Dalton Trans.* **2007**, 955.
- [20] Cirera, J.; Alemany, P.; Alvarez, S. *Chem. Eur. J.* **2004**, *10*, 190.
- [21] Addison, A. W.; Rao, T. N.; Reedijk, J.; van Rijn, J.; Verschoor, G. C. *J. Chem. Soc. Dalton Trans.* **1984**, 1349.
- [22] Belderraín, T. R.; Paneque, M.; Carmona, E.; Gutiérrez-Puebla, E.; Monge, M. A.; Ruiz-Valero, C. *Inorg. Chem.* **2002**, *41*, 425.

Figure 1. Molecular structure of the high-symmetry polymorph of $\text{Tp}^{\text{Ph}}\text{NiI}$ at 30% probability displacement ellipsoids. This is a representative structure of the other halide complexes. Hydrogen atoms, except for the B-H, have been omitted for clarity.

Figure 2. Molecular structure of the low-symmetry polymorph of $\text{Tp}^{\text{Ph}}\text{NiI}$ at 30% probability displacement ellipsoids. Hydrogen atoms, except for the B-H, have been omitted for clarity.

Figure 3. Molecular structure of $\text{Tp}^{\text{Ph}}\text{NiNCS}$ at 30% probability displacement ellipsoids. Hydrogen atoms, except for the B-H, have been omitted for clarity.

Figure 4. Molecular structure of $\text{Tp}^{\text{Ph}}\text{NiNO}_3$ at 30% probability displacement ellipsoids. Hydrogen atoms, except for the B-H, have been omitted for clarity.

Figure 5. Molecular structure of $\text{Tp}^{\text{tBu}}\text{NiBr}$ at 30% probability displacement ellipsoids. This is a representative structure of the other $\text{Tp}^{\text{tBu}}\text{NiL}$. Hydrogen atoms, except for the B-H, have been omitted for clarity.

Figure 6. CVs of $\text{Tp}^{\text{Ph}}\text{NiNCS}$ (top), $\text{Tp}^{\text{Ph}}\text{NiBr}$ (middle) and $\text{Tp}^{\text{Ph}}\text{NiI}$ (bottom) in CH_2Cl_2 solutions 0.1 M in $[\text{nBu}_4\text{N}][\text{PF}_6]$ with a scan rate of 0.250 V/s. A glassy carbon working electrode, Ag^+/Ag reference electrode and a Pt wire counter electrode setup was used under inert conditions. The results were referenced internally to Fc/Fc^+ (*).

Figure 7. CVs of $\text{Tp}^{\text{tBu}}\text{NiNCS}$ (top), $\text{Tp}^{\text{tBu}}\text{NiNO}_3$ (middle) and $\text{Tp}^{\text{tBu}}\text{NiI}$ (bottom) in CH_2Cl_2 solutions 0.1 M in $[\text{nBu}_4\text{N}][\text{PF}_6]$ with a scan rate of 0.250 V/s. A glassy carbon working electrode, Ag^+/Ag reference electrode and a Pt wire counter electrode setup was used under inert conditions. The results were referenced internally to Fc/Fc^+ (*).

Table 1 Crystallographic details and refinement data for $\text{Tp}^{\text{Ph}}\text{NiL}$ complexes.

	$\text{Tp}^{\text{Ph}}\text{NiCl}$	$\text{Tp}^{\text{Ph}}\text{NiBr}$	$\text{Tp}^{\text{Ph}}\text{NiI}$	$\text{Tp}^{\text{Ph}}\text{NiI}$	$\text{Tp}^{\text{Ph}}\text{NiNCS}$	$\text{Tp}^{\text{Ph}}\text{NiNO}_3$
Molecular formula	$\text{C}_{27}\text{H}_{22}\text{BClN}_6\text{Ni}$	$\text{C}_{27}\text{H}_{22}\text{BBrN}_6\text{Ni}$	$\text{C}_{27}\text{H}_{22}\text{BIN}_6\text{Ni}$	$\text{C}_{27}\text{H}_{22}\text{BIN}_6\text{Ni}$	$\text{C}_{28}\text{H}_{22}\text{BN}_7\text{NiS}$	$\text{C}_{27}\text{H}_{22}\text{BN}_7\text{NiO}_3$
Formula mass	535.47	579.93	626.93	626.93	558.11	562.04
Crystal system	trigonal	trigonal	trigonal	monoclinic	monoclinic	monoclinic
Space group	$P-3$	$P-3$	$P-3$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a (Å)	11.371(3)	11.339(1)	11.371(1)	17.527(4)	9.409(1)	9.419(1)
b (Å)	11.371(3)	11.339(1)	11.371(1)	9.115(2)	20.194(1)	15.296(2)
c (Å)	11.266(3)	11.381(1)	11.692(1)	17.622(4)	13.546(1)	18.218(2)
α (°)	90	90	90	90	90	90
β (°)	90	90	90	114.38(1)	96.456(2)	101.709(3)
γ (°)	120	120	120	90	90	90
V (Å ³)	1261.5(5)	1267.1(1)	1309.3(2)	2564.0(5)	2557.4(2)	2570.2(5)
$Z(Z')$	18(0.33)	18(0.33)	18(0.33)	4(1)	4(1)	4(1)
T (K)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
D_c (g cm ⁻³)	1.410	1.520	1.590	1.624	1.450	1.452
θ Range (°)	1.81-33.09	1.79-33.28	1.74-36.46	2.54-33.18	1.82-36.03	2.27-33.23
GOF (F^2)	1.027	1.019	1.058	1.058	1.018	1.029
μ (mm ⁻¹)	0.903	2.370	1.947	1.989	0.873	0.799
R(F), $R_w(F)$	0.0282, 0.0768	0.0271, 0.0619	0.0316, 0.0757	0.0360, 0.0868	0.0505, 0.0967	0.0349, 0.0876

Quantity minimized = $R(wF^2) = \Sigma[w(F_0^2 - F_c^2)^2] / \Sigma[(wF_0^2)^2]^{0.5}$; $R = \Sigma\Delta / \Sigma(F_0)$,
 $\Delta = |(F_0 - F_c)|$, $w = 1/[\sigma^2(F_0^2) + (aP)^2 + bP]$, $P = [2F_c^2 + \text{Max}(F_0, 0)]/3$

Table 2 Crystallographic details and refinement data for Tp^{tBu}NiL complexes.

	Tp^{tBu}NiBr	Tp^{tBu}NiNCS	Tp^{tBu}NiI
Molecular formula	C ₂₁ H ₃₄ BBrN ₆ Ni	C ₂₂ H ₃₄ BN ₇ NiS	C ₂₁ H ₃₄ BIN ₆ Ni
Formula mass	519.97	498.14	566.96
Crystal System	orthorhombic	monoclinic	orthorhombic
Space group	<i>Pnma</i>	<i>P2₁/n</i>	<i>Pnma</i>
<i>a</i> (Å)	15.953(1)	9.505(1)	16.198(1)
<i>b</i> (Å)	15.591(1)	16.795(2)	15.537(1)
<i>c</i> (Å)	9.690(1)	16.368(2)	9.813(1)
α (°)	90	90	90
β (°)	90	95.455(4)	90
γ (°)	90	90	90
<i>V</i> (Å ³)	2410.2(2)	2601.2(4)	2469.6(2)
<i>Z</i> (<i>Z'</i>)	8(0.5)	4(1)	8(0.5)
<i>T</i> (K)	100(2)	100(2)	100(2)
<i>D_c</i> (g cm ⁻³)	1.433	1.272	1.525
θ Range (°)	2.46-33.14	1.74-34.34	2.43-32.03
GOF (<i>F</i> ²)	1.024	1.039	1.046
μ (mm ⁻¹)	2.482	0.849	2.055
<i>R</i> (<i>F</i>), <i>R_w</i> (<i>F</i>)	0.0254, 0.0605	0.0287, 0.0741	0.0324, 0.0811

Quantity minimized = $R(wF^2) = \Sigma[w(F_0^2 - F_c^2)^2] / \Sigma[(wF_0^2)^2]^{0.5}$; $R = \Sigma\Delta / \Sigma(F_0)$,
 $\Delta = |(F_0 - F_c)|$, $w = 1/[\sigma^2(F_0^2) + (aP)^2 + bP]$, $P = [2F_c^2 + \text{Max}(F_0, 0)]/3$

Table 3. Selected bond distances and angles for the Tp^{Ph}NiL complexes.

L ⁻	Cl	Br	I _{linear}	I _{bent}	NO ₃	NCS
B-N _{avg} (Å)	1.547(2)	1.539(2)	1.539(2)	1.544(3)	1.546(2)	1.542(2)
Ni-N _{avg} (Å)	2.011(2)	2.000(2)	2.001(2)	2.006(2)	2.016(2)	1.995(2)
Ni-L (Å)	2.168(2)	2.289(1)	2.462(1)	2.495(1)	2.085(2)	1.903(2)
B...Ni...L (°)	180 ^a	180 ^a	180 ^a	162.1(1)	164.7(1) ^b	167.0(1)
τ_4	0.80	0.80	0.80	0.73	0.70	0.74

^a Symmetry imposed

^b Calculated from the nitrogen of the nitrate ligand

Table 4. Selected bond distances and angles for the $\text{Tp}^{\text{tBu}}\text{NiL}$ complexes.

L^-	Cl	Br	I	NO_3	NCS
B-N_{avg} (Å)	1.543(7)	1.534(2)	1.535(3)	1.534(3)	1.540(2)
Ni-N_{avg} (Å)	2.021(4)	2.021(2)	2.042(2)	2.044(2)	1.994(1)
Ni-L (Å)	2.172(2)	2.349(1)	2.521(1)	2.094(2)	1.913(1)
$\text{B}\dots\text{Ni}\dots\text{L}$ ($^\circ$)	176.1(4)	177.3(1)	176.5(1)	167.7(2) ^a	177.0(1)
τ_4	0.79	0.79	0.79	0.73	0.79

^a Calculated from the nitrogen of the nitrate ligand**Table 5.** Reduction potentials for $\text{Ni}^{2+/1+}$ reduction of $\text{Tp}^{\text{R}}\text{NiL}$ complexes. All values are reported against a Fc/Fc^+ internal reference.

L^-	Cl	Br	E_{red} (V) I^{a}	NCS	NO_3
R = Ph	-1.61	-1.64	-1.49, -1.65	-1.49	-1.72
R = tBu	-1.86	-1.72	-1.55, -1.89	-1.53	-1.92

^a second value is $\text{Ni}^{1+/0}$ reduction present in voltammogram

Figures
Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figures 6 and 7

A series of nickel (II) complexes bearing sterically bulky Tp^{R} (R= *tert*-butyl or phenyl) ligands were synthesized and structurally characterized. The redox properties of the nickel center were investigated and results indicate that the redox trends fall more in line with the electronic properties of the complexes than the structural differences.