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Structural, Spectroscopic, and Electrochemical Properties of a Series of High-Spin Thiolatonickel(II) Complexes

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A series of high-spin thiolatonickel(II) complexes, [PhTt^{tBu}]Ni(SR) (PhTt^{tBu} = phenyltris((*tert*-butylthio)methyl)borate; **2**, R = triphenylmethyl; **3**, R = pentafluorophenyl; **4**, R = phenyl), were synthesized via the reaction of [PhTt^{tBu}]-Ni(NO_3) (**1**) with thiols (RSH) in the presence of triethylamine. The [PhTt^{tBu}]Ni(SR) products were isolated and characterized by various physicochemical measurements including X-ray diffraction analyses. These thiolatonickel(II) complexes have a distorted trigonal pyramidal geometry with somewhat different τ values: 0.80 and 0.90 for two crystalline phases of **2**, 0.74 for **3**, and 0.69 for **4**, where τ is a normalized measure of pyramidalization (τ = 0 for tetrahedron, τ = 1 for trigonal pyramid). The electronic absorption spectra display characteristic sulfur-to-nickel(II) charge transfer (CT) bands at 532 nm (7500 M^{-1} cm^{-1}) for **2**, 510 nm (4800 M^{-1} cm^{-1}) for **3**, and 569 nm (4100 M^{-1} cm^{-1}) for **4**. The cyclic voltammograms show a quasi-reversible redox couple at $E_{1/2}$ = –1.11 V for **2**, and reversible redox couples at $E_{1/2}$ = –1.03 V for **3** and $E_{1/2}$ = –1.17 V for **4** (vs Fc^+/Fc). Correlation between the τ value and the CT intensity was observed: the strong CT intensity results from the high τ value, which provides for strong orbital overlap (**2** > **3** > **4**). Additionally, the CT transition energy correlates with the reduction potential: both the CT transition energy and potential decrease in the order **3** > **2** > **4**, consistent with the influence of decreasing electron withdrawing abilities, R = pentafluorophenyl > triphenylmethyl > phenyl. The three thiolatonickel complexes exhibit dramatically different thermal stabilities. Complex **4** is the least stable, undergoing decomposition to [κ^2-PhBt^{tBu}SPh]Ni(η^2-CH_2SBu^t) (**5**) via net exchange of Ni–SPh and B–CH_2SBu^t groups.

Introduction

The chemistry of transition metal−thiolate complexes is of fundamental importance in biology.[1,2] A number of metalloprotein active sites feature metal−thiolate linkages as key elements seminal to their structure and function. While thiolates exhibit a propensity to bridge between and among metal sites, protein site isolation[2] allows for a number of mononuclear metal thiolates, with the blue copper proteins archetypal. Indeed, the unusual bonding characteristic of the Cu^{2+}−thiolate, i.e., high covalency, is responsible for the unique spectroscopic features of the sites and for providing an efficient pathway for electron transfer.[3] In a different context, the axial thiolate ligand in cytochrome P450 engenders an electronic structure that favors an oxoiron(IV) intermediate capable of hydroxylation reactions.[4] More recent discoveries include nickel metalloproteins with diverse functions including superoxide processing (superoxide dismutase),[5] hydrogen oxidation (hydrogenases),[6] reductive methane generation (methyl coenzyme M reductase),[7] and acetate synthesis (acetyl coenzyme A synthase).[8] Our understanding of the fundamental role(s) of nickel−thiolate linkages, particularly in high-spin states, in these contexts is only beginning to emerge.[8b]

Preparative chemistry has played a central role in advancing understanding. Kitajima and co-workers synthesized the first Cu^{2+}−thiolate complexes outside of a protein matrix,

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by employing thiolates less prone to oxidation. [Tp^{iPr2}]Cu(SCPh$_3$) and [Tp^{iPr2}]Cu(SC$_6$F$_5$) successfully replicate certain structural and spectroscopic features of the blue copper active sites.[9] More recently, Tolman and co-workers prepared a β-diketiminate supported Cu^{2+} model featuring both thiolate and thioether donors.[10] The complex displays perturbed spectral features in accord with its distorted geometry.

Given the longstanding interest in thiolato−nickel chemistry,[11] it is perhaps surprising that only recently have high-spin, four-coordinate complexes possessing a single thiolate donor been reported. Fujisawa and co-workers described the complex [Tp^{iPr2}]Ni(SC$_6$F$_5$) as a member of a series of isostructural transition metal complexes.[12] Note that the C$_6$F$_5$ substituent is the same as that utilized by Kitajima and Tolman due to its reluctance to undergo oxidation. Peters' laboratory characterized a related complex supported by his PhBP$_3$ tripod, [PhBP$_3$]Ni(SC$_6$H$_4$*p*-Bu^t).[13] It is of interest that these room-temperature stable complexes provide the opportunity to evaluate a single nickel−thiolate interaction in high-spin complexes.

Our current efforts toward the investigation of thiolato−nickel complexes have yielded a series of high-spin complexes, [PhTt^{tBu}]Ni(SR) (R = CPh$_3$ for **2**, C$_6$F$_5$ for **3**, and Ph for **4**), where [PhTt^{tBu}] is phenyltris((*tert*-butylthio)methyl)borate, by the reaction of [PhTt^{tBu}]Ni(NO$_3$) (**1**) with thiols (RSH) and triethylamine. Specifically, we have evaluated the effect of the thiolate substituents on the structural, spectroscopic, and electrochemical properties and thermal stability of the complexes. Further motivation for these studies stem from our prior efforts to install strong σ-donor ligands, e.g., alkyl, aryl, and hydride, into the [PhTt^{tBu}]Ni fragment, strategies that generally led to reductive B−C degradation[14] without evidence for intermediates. Herein, we have characterized one such intermediate, **4**, and its rearranged product, [κ^2-PhBt^{tBu}SPh]Ni(η^2-CH$_2$SBu^t) (**5**).

Experimental Section

Synthesis. [PhTt^{tBu}]Tl was synthesized according to the literature method.[15] [PhTt^{tBu}]Ni(NO$_3$) was first prepared by Schebler.[16] Other reagents were purchased commercially and used without further purification. The syntheses of the thiolato−nickel(II) complexes were all carried out either in an Ar glovebox or under N$_2$ using standard Schlenk techniques. Elemental analyses were performed at Desert Analytics, Inc., Tucson, AZ.

Physical Measurements. UV−vis spectra were measured with a HP 8453 diode array spectrometer. ^{1}H NMR spectra were recorded on a 400 MHz Bruker DRX spectrometer. Chemical shifts (δ) were referenced to the residual proton peak in the deuterated solvent. Solid-state magnetic moments were determined using a Johnson Matthey magnetic susceptibility balance calibrated with mercury(II) tetrathiocyanatocobaltate(II).

Cyclic voltammetry (CV) experiments were performed on a BAS 50W electrochemical analyzer in tetrahydrofuran (THF) containing 0.1 M electrolyte (Bu$_4$NPF$_6$) and 3 mM sample. The cell was housed in an Ar-filled Vacuum Atmospheres glovebox. A carbon working electrode was polished with an alumina (0.06 μm) paste and then rinsed with THF before use. The counter electrode was a Pt wire. The Ag/Ag$^+$ couple was used as a reference electrode, and the potentials were determined using the ferrocenium/ferrocene (Fc$^+$/Fc) couple as an internal reference

[PhTt^{tBu}]Ni(NO$_3$) (1). [PhTt^{tBu}]Tl (1.20 g, 2 mmol) was added to a THF solution (100 mL) of Ni(NO$_3$)$_2$·6H$_2$O (0.58 g, 2 mmol). The resulting solution was stirred for 3 h, affording a green solution and a white precipitate. The reaction mixture was dried over Na$_2$SO$_4$ and filtered through Celite. The solvent was removed under vacuum yielding **1** as a green solid, which was recrystallized from pentane to afford crystals suitable for X-ray analysis. Crystalline yield: 0.74 g (71%). ^{1}H NMR (C$_6$D$_6$, 400 MHz): δ 17.4 (br, (CH$_3$)$_3$C), 8.4 (br, (*o*-C$_6$H$_5$)B), 7.6 (t, (*p*-C$_6$H$_5$)B), 7.4 (br, (*m*-C$_6$H$_5$)B). UV−vis (λ_{max} (nm) (ϵ (M^{-1} cm^{-1})) in toluene): 355 (2900), 403 (2000), 695 (100), 866 (54). μ_{eff} = 3.28 μ_B. Anal. Calcd for C$_{21}$H$_{38}$BNO$_3$S$_3$Ni: C, 48.67; H, 7.39; N, 2.70. Found: C, 48.53; H, 7.24; N, 2.86.

[PhTt^{tBu}]Ni(SCPh$_3$) (2). A mixture of **1** (0.052 g, 0.1 mmol) and Ph$_3$CSH (0.028 g, 0.1 mmol) was dissolved in 5 mL of acetone. To this yellow-green solution was added triethylamine (14 μL, 0.1 mmol), producing a dark violet solution. The resulting solution was left for a few days at −25 °C, giving **2** as dark red crystals suitable for X-ray analysis. Crystalline yield: 0.027 g (37%). ^{1}H NMR (C$_6$D$_6$, 400 MHz): δ 30.2 (br, (*o*-C$_6$H$_5$)C), 16.9 (br, (CH$_3$)$_3$C), 8.6 (br, (*o*-C$_6$H$_5$)B + (*p*-C$_6$H$_5$)C), 8.1 (br, (*p*-C$_6$H$_5$)B + (*m*-C$_6$H$_5$)C), 7.6 (br, (*m*-C$_6$H$_5$)B). UV−vis (λ_{max} (nm) (ϵ (M^{-1} cm^{-1})) in toluene): 391 (2900), 532 (7500), 855 (400). μ_{eff} = 3.06 μ_B. Anal. Calcd for C$_{40}$H$_{53}$BS$_4$Ni: C, 65.67; H, 7.30. Found: C, 65.43; H, 7.54.

[PhTt^{tBu}]Ni(SC$_6$F$_5$) (3). C$_6$F$_5$SH (20 μL, 0.1 mmol) was added to a pentane solution of **1** (0.052 g, 0.1 mmol). To this light red solution was added triethylamine (14 μL, 0.1 mmol), producing a dark violet solution. The resulting solution was left for a few days at −25 °C, giving **3** as dark red crystals suitable for X-ray analysis. Crystalline yield: 0.035 g (53%). ^{1}H NMR (C$_6$D$_6$, 400 MHz): δ 18.7 (br, (CH$_3$)$_3$C), 9.2 (br, (*o*-C$_6$H$_5$)B), 7.7 (br, (*p*-C$_6$H$_5$)B), 7.6 (br, (*m*-C$_6$H$_5$)B). UV−vis (λ_{max} (nm) (ϵ (M^{-1} cm^{-1})) in toluene): 390 (3200), 510 (4800), 820 (350). μ_{eff} = 3.30 μ_B. Anal. Calcd for C$_{27}$H$_{38}$BF$_5$S$_4$Ni: C, 49.48; H, 5.84. Found: C, 49.75; H, 6.10.

[PhTt^{tBu}]Ni(SPh) (4). PhSH (11 μL, 0.1 mmol) was added to a pentane solution of **1** (0.052 g, 0.1 mmol) at −40 °C. To this yellow-green solution was added triethylamine (14 μL, 0.1 mmol), producing a dark purple solution. The resulting solution was left for a few days at −25 °C, giving **4** as dark red crystals suitable for X-ray analysis. Crystalline yield: 0.031 g (55%). ^{1}H NMR (C$_6$D$_6$, 400 MHz): δ 32.2 (br, (*m*-C$_6$H$_5$)S), 17.0 (br, (CH$_3$)$_3$C), 8.9 (br, (*o*-C$_6$H$_5$)B), 7.6 (br, (*p*-C$_6$H$_5$)B), 7.6 (br, (*m*-C$_6$H$_5$)B), −39.0 (br,

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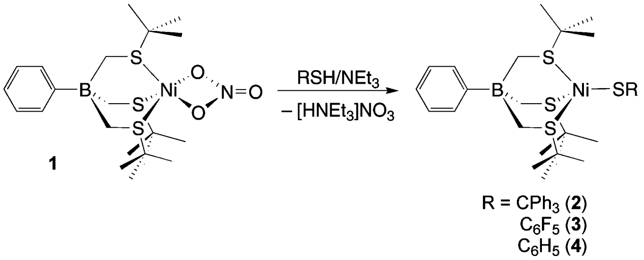
Table 1. Crystallographic Data for Complexes **1**−**5**

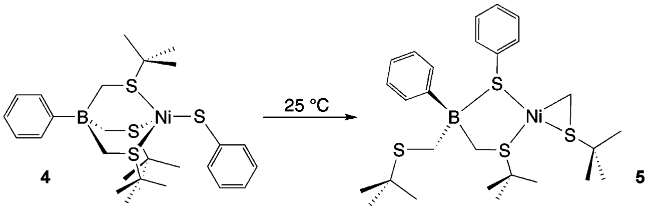
	1	**2*β***	**3**	**4**	**5**
formula	$C_{21}H_{38}BNNiO_3S_3$	$C_{40}H_{53}BNiS_4$	$C_{27}H_{38}BF_5NiS_4$	$C_{27}H_{43}B\ NiS_4$	$C_{27}H_{43}BNiS_4$
fw	518.22	731.58	655.33	565.37	565.37
cryst syst	triclinic	monoclinic	monoclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1$	$P2_1/n$	$P\bar{1}$	$P2_1/n$
a, Å	10.134(4)	9.593(6)	13.093(4)	9.724(4)	10.858(6)
b, Å	11.592(4)	14.124(7)	14.447(5)	11.597(5)	19.215(9)
c, Å	12.326(5)	14.545(8)	16.340(5)	13.026(6)	14.368(8)
α, deg	91.425(4)	90	90	88.138(15)	90
β, deg	111.515(4)	99.73(1)	100.908(5)	87.704(15)	90.151(10)
γ, deg	104.426(4)	90	90	86.385(15)	90
V, Å^3	1293.8(8)	1942.4(18)	3034.9(17)	1464.1(11)	2998(3)
Z	2	2	4	2	4
T, K	120	120	120	120	120
D_{calcd}, g/cm^{-1}	1.330	1.251	1.434	1.282	1.253
2θ range, deg	1.83 - 28.22	2.02 - 25.00	1.83 - 28.21	1.57 - 28.33	1.77- 28.12
μ (Mo Kα), mm^{-1}	1.013	0.741	0.962	0.962	0.940
R1, wR2	0.0255, 0.0676	0.0459, 0.1149	0.0338, 0.0839	0.0489, 0.0952	0.0554, 0.1387

[a] Quantity minimized $= R(wF^2) = \sum[w(F_o^2 - F_c^2)^2]/\sum[(wF_o^2)^2]^{1/2}$; $R - \sum\Delta/\sum(F_o)$, $\Delta = |(F_c - F_o)|$.

Scheme 1



Scheme 2



(o-C_6H_5)S), −45.7 (br, (p-C_6H_5)S). UV−vis (λ_{max} (nm) (ϵ (M^{-1} cm^{-1})) in toluene): 381 (2500), 429 (2500), 569 (4100), 825 (390). $\mu_{eff} = 3.34\ \mu_B$. Anal. Calcd for $C_{27}H_{43}BS_4Ni$: C, 57.36; H, 7.67. Found: C, 57.13; H, 7.49.

[PhBt^{tBu}SPh]Ni(η^2-CH_2SBu^t) (5). Complex **4** (0.057 g, 0.1 mmol) was dissolved in 15 mL of pentane at room temperature giving a dark purple solution, which was stirred for several hours affording a brown solution. The resulting solution was left for a few days at −25 °C, giving **5** as brown crystals suitable for X-ray analysis. Crystalline yield: 0.026 g (45%). ^{1}H NMR (C_6D_6, 400 MHz): δ 7.91 (d, (o-C_6H_5)B), 7.74 (d, (o-C_6H_5)S), 7.38 (t, (m-C_6H_5)B), 7.24 (t, (p-C_6H_5)B), 6.98 (m, (m-C_6H_5)S + (p-C_6H_5)S), 2.57 (d, BCH_2), 2.45 (s, BCH_2), 2.33 (d, BCH_2), 1.69 (d, $NiCH_2$), 1.52 (d, $NiCH_2$), 1.34 (s, $(CH_3)_3$), 1.28 (s, $(CH_3)_3$), 0.98 (s, $(CH_3)_3$). Anal. Calcd for $C_{27}H_{43}BS_4Ni$: C, 57.36; H, 7.67. Found: C, 56.92; H, 7.63.

X-ray Crystallography. Crystals were selected, mounted with viscous oil on glass fibers, and flash-cooled to the data collection temperature. Unit cell parameters (Table 1) were obtained from 60 data frames, 0.3° ω, from three different sections of the Ewald sphere. Two different crystalline phases of **2** (**α** and ***β***) were obtained and characterized. The systematic absences in the diffraction data were consistent for the space groups $P2_1$ and $P2_1/m$ for **2α** and uniquely consistent for $P2_1/n$ for **3** and **5**. No symmetry higher than triclinic was observed for **1** and **4**. Solution in the space group $P\bar{1}$ for **1** and **4** and $P2_1$ for **2α** yielded chemically reasonable and computationally stable results of refinement. Samples of **2α** deposited from solution as weakly diffracting crystals with diffraction maxima of 45° in 2θ. Crystallographic results for **2α** are contained in the Supporting Information. Samples of **2*β***, grown under similar conditions, afforded superior quality diffraction data. One of the thioether arms (C5−S1−C11−C12−C13−C14) in the structure of **2*β*** is disordered in two positions with refined site occupancy of 60/40. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions. Structure factors are contained in the SHELXTL 6.12 program library (Sheldrick, G., Bruker-AXS, 2001). The CIFs are available from the Cambridge Crystallographic Data Center under the depositary numbers CCDC 659304−659309.

Results and Discussion

Synthesis of High-Spin Thiolatonickel Complexes. Synthetic procedures for a series of thiolato−nickel(II) complexes are summarized in Scheme 1. The starting material, [PhTt^{tBu}]Ni(NO_3) (**1**), was prepared via the metathetical reaction of [PhTt^{tBu}]Tl and $Ni(NO_3)_2{\cdot}6H_2O$ in THF. The resulting yellow-green solid is stable to air and moisture and freely soluble in a range of solvents, including pentane and chlorinated hydrocarbons. The reaction of **1** with 1 equiv each of Ph_3CSH and triethylamine in acetone at room temperature caused a color change to dark violet. From the reaction mixture, [PhTt^{tBu}]Ni($SCPh_3$) (**2**) was isolated at a temperature below −25 °C.

[PhTt^{tBu}]Ni(SC_6F_5) (**3**) was obtained by a method similar to that for **2** with the corresponding thiol, C_6F_5SH, in pentane.

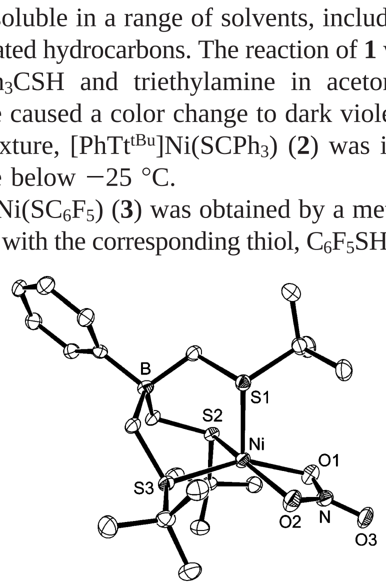
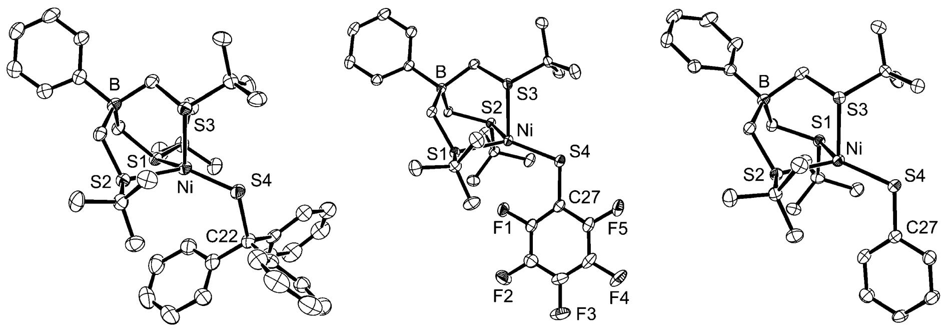


Figure 1. Thermal ellipsoid plot of [PhTt^{tBu}]Ni(NO_3) (**1**) at the 50% probability level. Hydrogen atoms are omitted for clarity.



(a) (b) (c)

Figure 2. Thermal ellipsoid plots of (a) [PhTt^{tBu}]Ni(SCPh$_3$) (**2*β***), (b) [PhTt^{tBu}]Ni(SC$_6$F$_5$) (**3**), and (c) [PhTt^{tBu}]Ni(SPh) (**4**) at the 50% probability level. One of the two positionally disordered thioether fragments for **2*β*** is shown with the other contributing form contained in the Supporting Information. Hydrogen atoms are omitted for clarity.

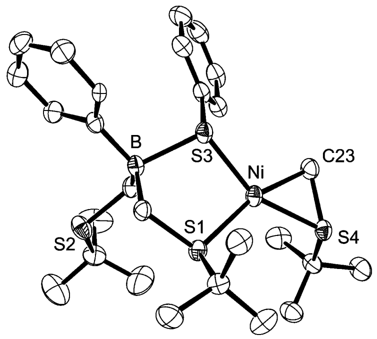


Figure 3. Thermal ellipsoid plot of [[κ^2-PhBt^{tBu}SPh]Ni(η^2-CH$_2$SBu^t) (**5**) at the 50% probability level. Hydrogen atoms are omitted for clarity.

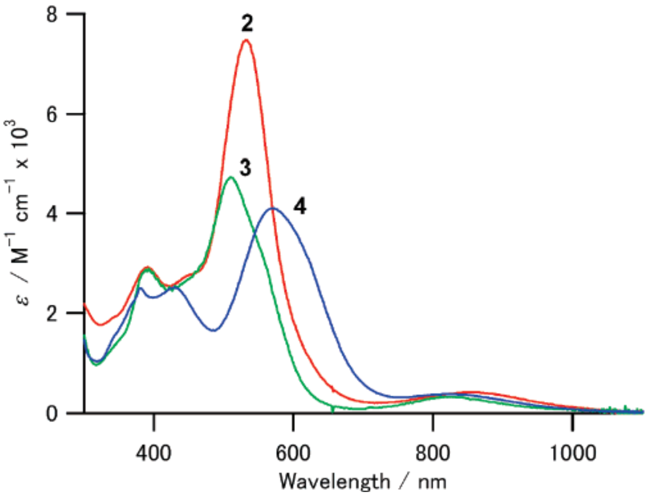


Figure 4. Electronic absorption spectra of **2**−**4** in toluene at room temperature.

However, [PhTt^{tBu}]Ni(SPh) (**4**) could not be obtained under similar experimental conditions, due to its thermal instability, vide infra. Similar instability was noted for certain thiolatocopper(II) complexes of [Tp^{iPr2}] due to an internal redox reaction.[9b] Complex **4** was obtained successfully by the low-temperature reaction of **1** with 1 equiv each of PhSH and triethylamine, which led to a dark purple species at temperatures below −40 °C. The thermal decomposition of **4** at room temperature cleanly gave a nickel alkylation product, [κ^2-PhBt^{tBu}SPh]Ni(η^2-CH$_2$SBu^t) (**5**), via net exchange of Ni−SPh and B−CH$_2$SBu^t groups, as shown in Scheme 2.

Structural Description. Complexes **1**−**5** were characterized successfully by X-ray diffraction analyses. The molecular structures of **1**−**5** are depicted in Figures 1−3, with selected bond distances and angles contained in Table 2. Complex **1** has a five-coordinate nickel(II) with a monoanionic face-capping [PhTt^{tBu}] and a symmetrically coordinated bidentate nitrate, comparable to that observed for [Tp^{tBu}]Ni(NO$_3$).[17] The nickel geometry is best described as square-pyramidal with two oxygens from the nitrate occupying the basal plane.

Two different crystalline phases of **2** (**α** and ***β***) were analyzed by single-crystal X-ray diffraction. Results from the higher quality crystal, **2*β***, are contained in the paper with the data from the weaker diffracting crystal phase, **2α**,[18] contained in the Supporting Information. Complex **2** possesses a four-coordinate nickel(II) ion consisting of three thioether sulfurs (S1 and S2 are in the equatorial positions, whereas S3 is axial) from [PhTt^{tBu}] and the thiolate sulfur from triphenylmethylthiolate. A normalized measure of pyramidalization τ is used to describe the distortion of tetrahedral coordination along a pseudo-C_3 axis ($\tau = 0$ for tetrahedron, $\tau = 1$ for trigonal pyramid with flat base).[19] The pyramidalization of **2** ($\tau = 0.90$) indicates the nickel stereochemistry is quite distorted away from tetrahedral and, thus, is better described as trigonal-pyramidal. The Ni−S$_{thiolate}$ bond distance of 2.1668(15) Å is in the range of those for thiolato−transition metal complexes (2.07−2.39 Å).[12,20] The Ni−S4−C22 angle of 116.54(13)° is comparable to that in [Tp^{iPr2}]Cu(SCPh$_3$) (124°).[9c]

The coordination geometry of **3** is best described as trigonal-pyramidal with a τ value of 0.74, which is smaller than that of **2**. The nickel(II) ligation is composed of three thioether sulfurs from [PhTt^{tBu}] and the thiolate sulfur from the pentafluorophenylthiolate. The Ni−S$_{thiolate}$ bond distance

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(18) Complex **2α** crystallized in the space group $P2_1/n$ with the following unit cell parameters: $a = 9.397(4)$ Å, $b = 16.170(7)$ Å, $c = 25.002(9)$ Å, $b = 90.272(14)°$, $V = 3799(3)$ Å^3, and $Z = 4$.

(19) The parameter τ is defined as $\tau = [\Sigma(\angle L_{basal}-M-L_{basal}) - \Sigma(\angle L_{basal}-M-L_{axial})]/90$ in: Vela, J.; Stoian, S.; Flaschenriem, C. J.; Münck, E.; Holland, P. L. *J. Am. Chem. Soc.* **2004**, *126*, 4522−4523.

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Table 2. Selected Bond Distances (Å) and Angles (deg) for **1**, **2*β***, **3**, **4**, and **5**

1			2*β*	3	4	5
Ni−S1	2.3003(6)	Ni−S1	2.3596(19)	2.2847(7)	2.2848(12)	2.2288(11)
Ni−S2	2.3213(7)	Ni−S2	2.3232(13)	2.2910(7)	2.2948(12)	
Ni−S3	2.3185(7)	Ni−S3	2.3409(14)	2.3289(8)	2.2991(13)	2.1571(12)
Ni−O1	2.0873(11)	Ni−S4	2.1668(15)	2.2355(9)	2.1868(12)	2.1408(14)
Ni−O2	2.0907(12)	Ni−C23				1.914(3)
S1−Ni−O1	109.17(4)	S1−Ni−S2	82.69(5)	96.49(3)	94.89(4)	
S1−Ni−O2	102.11(4)	S1−Ni−S3	105.72(6)	93.25(2)	92.91(3)	92.45(5)
S1−Ni−S2	94.98(3)	S1−Ni−S4	138.18(6)	130.29(2)	129.94(4)	113.44(5)
S1−Ni−S3	94.86(3)	S2−Ni−S3	91.22(5)	89.96(2)	94.47(3)	
S2−Ni−O1	96.49(4)	S2−Ni−S4	128.98(4)	128.52(2)	129.00(4)	
S2−Ni−O2	155.82(3)	S3−Ni−S4	100.57(5)	105.13(2)	104.49(4)	
S2−Ni−S3	93.93(3)	S4−C23−Ni				71.55(13)
S3−Ni−O1	152.76(3)	C23−Ni−S3				103.90(11)
S3−Ni−O2	101.45(4)	C23−Ni−S4				50.43(11)
O1−Ni−O2	61.85(5)	C23−S4−Ni				58.01(10)

Table 3. Electronic Absorption Spectral Data for Thiolatonickel(II) and -copper(II) Complexes

	$\lambda_{\max}$ (nm) (ϵ ($\mathrm{M^{-1}\,cm^{-1}}$))	ref
nickel complexes		
2	532 (7500)	this work
3	510 (4800)	this work
4	569 (4100)	this work
$[\mathrm{Tp}^{\mathrm{iPr2}}]\mathrm{Ni(SC_6F_5)}$	434 (3100)	12, 20
copper complexes		
$[\mathrm{Tp}^{\mathrm{iPr2}}]\mathrm{Cu(SCPh_3)}$	625 (6600)	9b, 9d
$[\mathrm{Tp}^{\mathrm{iPr2}}]\mathrm{Cu(SC_6F_5)}$	665 (5960)	9b, 12, 20

of 2.2355(9) Å is comparable to that found in $[\mathrm{Tp}^{\mathrm{iPr2}}]\mathrm{Ni(SC_6F_5)}$ (2.259 Å) and longer than that of **2** (2.1668(15) Å).[9b] The Ni−S4−C27 angle of 110.48(7)° is smaller than that in **2** (116.54(13)°).

Complex **4** has a coordination geometry similar to those of **2** and **3**, albeit with the smallest τ value of the series at 0.69. The $\mathrm{Ni{-}S_{thiolate}}$ bond distance of 2.1868(12) Å is slightly longer than that of **2** (2.1668(15) Å) and shorter than that of **3** (2.2355(9) Å). The Ni−S4−C27 angle of 111.62(11)° is only slightly larger than that of **3** (110.48(7)°).

Complex **5** possesses a square-planar stereochemistry in which one of the side arms of the $[\mathrm{PhTt}^{\mathrm{tBu}}]$ ligand has been transferred entirely to the nickel yielding the three-membered thianickelacycle ring. The phenylthiolate group bridges the nickel and boron resulting in a five-membered chelate ring. The Ni−C23 (1.914(3) Å) and Ni−S4 (2.1408(14) Å) bond distances are comparable to those found in $[\kappa^2\text{-}\mathrm{PhTt}^{\mathrm{tBu}}]\mathrm{Ni}(\eta^2\text{-}\mathrm{CH_2SBu^t})$ (1.939 and 2.256 Å, respectively).[14]

Spectroscopic Characterization of 2−4. The electronic absorption spectra of **2**−**4** were measured in toluene (300−1100 nm) at room temperature, Figure 4. Spectroscopic properties of **2**−**4** are qualitatively similar to those of analogous thiolatocopper(II) complexes supported by the $[\mathrm{Tp}^{\mathrm{iPr2}}]$ ligand as summarized in Table 3. The spectrum of **2** shows an intense band at 532 nm (ϵ = 7500 $\mathrm{M^{-1}\,cm^{-1}}$), which is at higher energy compared to $[\mathrm{Tp}^{\mathrm{iPr2}}]\mathrm{Cu(SCPh_3)}$ ($\lambda_{\max}$ = 625 nm, ϵ = 6600 $\mathrm{M^{-1}\,cm^{-1}}$).[9b] The absorption band of $[\mathrm{Tp}^{\mathrm{iPr2}}]\mathrm{Cu(SCPh_3)}$ has previously been assigned to the $\mathrm{S_{thiolate}} \rightarrow \mathrm{Cu(II)}$ charge-transfer (CT) transition arising from the relatively high covalency of the $\mathrm{Cu{-}S_{thiolate}}$ bond.[9d]

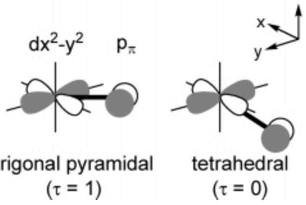

Figure 5. Orientation of π orbitals involved in the CT transition at limiting values of τ.[19]

The spectrum of **3** exhibits an intense band at 510 nm (ϵ = 4800 $\mathrm{M^{-1}\,cm^{-1}}$), at lower energy than that of $[\mathrm{Tp}^{\mathrm{iPr2}}]\mathrm{Ni(SC_6F_5)}$ ($\lambda_{\max}$ = 434 nm, ϵ = 3100 $\mathrm{M^{-1}\,cm^{-1}}$).[12] Such an intense band has been assigned to the $\mathrm{S_{thiolate}}\ p_\pi \rightarrow \mathrm{Ni(II)}\ d_{x^2-y^2}$ CT transition on the basis of theoretical calculations.[21] The lower CT transition energy of **3** is due to the thioether donors of $[\mathrm{PhTt}^{\mathrm{tBu}}]$. The thioether sulfur p orbitals mix with the $\mathrm{Ni{-}S_{thiolate}}$ bonding orbitals such that the energy of the CT is reduced. A similar situation has been described for the O → Ni CT bands in the bis-μ-oxo complexes, $[(\mathrm{PhTt}^{\mathrm{tBu}})\mathrm{Ni}]_2(\mu\text{-O})_2$.[22] Nonetheless, the CT transition energies for the thiolato−nickel complexes of **2** and **3** having $[\mathrm{PhTt}^{\mathrm{tBu}}]$ are higher than those of the corresponding thiolato−copper complexes of $[\mathrm{Tp}^{\mathrm{iPr2}}]\mathrm{Cu(SCPh_3)}$ and $[\mathrm{Tp}^{\mathrm{iPr2}}]\mathrm{Cu(SC_6F_5)}$ having $[\mathrm{Tp}^{\mathrm{iPr}}]$,[9b] because the d orbital energy of nickel(II) is much higher than that of copper(II).

The spectrum of **4** shows an intense band at 569 nm (ϵ = 4100 $\mathrm{M^{-1}\,cm^{-1}}$), which is at lower energy than those of **2** and **3**. Thus, the trend in CT transition energies in thiolatonickel complexes is **3** > **2** > **4**. CT transition energies of thiolatonickel complexes having relatively strong electron withdrawing groups are higher than those having relatively weak electron withdrawing groups. This may be ascribed to a decrease in the sulfur p_π orbital energy due to the orbital stabilization provided by electron withdrawing groups.

The geometry of the thiolatonickel complexes, as reflected in the τ values, plays an important role in determining the intensity of the $\mathrm{S_{thiolate}}\ p_\pi \rightarrow \mathrm{Ni(II)}\ d_{x^2-y^2}$ CT transition. The trend in the CT intensities, **2** > **3** > **4**, Figure 4, parallels that found in the τ values, (**2** (0.90) > **3** (0.74) > **4** (0.69)). The complex with the largest τ value displays the most

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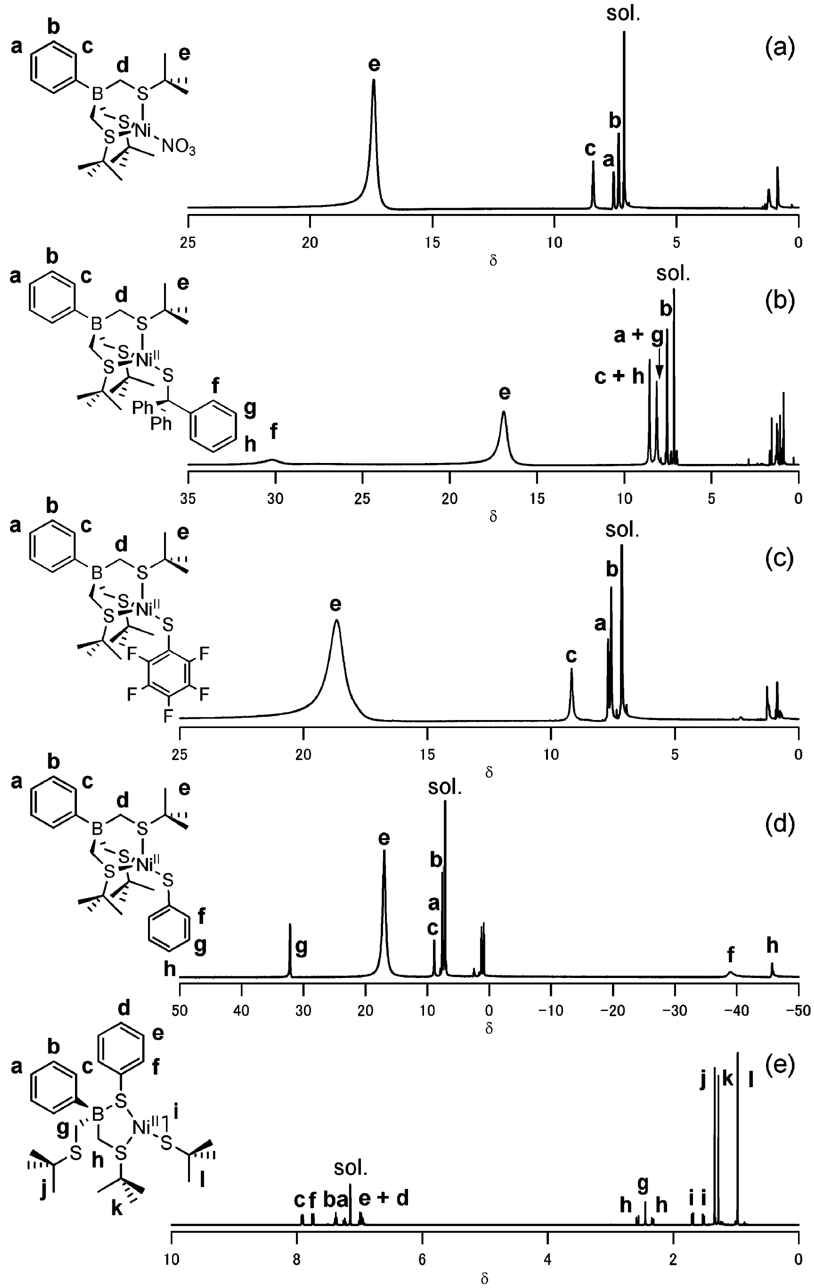

Figure 6. ^{1}H NMR spectra of (a) **1**, (b) **2**, (c) **3**, (d) **4**, and (e) **5** in benzene-d_6 at room temperature.

intense CT transition. The explanation is depicted pictorially in Figure 5. The S_{thiolate} p_π orientation parallel to the $d_{x^2-y^2}$ plane provides for significant orbital overlap. Thus, the high τ value, along with the high CT intensity, is indicative of a high degree of Ni−S π covalency. In addition, the relatively large difference in CT intensity of **2** when compared with **3** and **4** can be attributed to the aryl groups of the latter complexes which provide a means for delocalizing the thiolate electron density.

Magnetic Properties. The room-temperature effective magnetic moments are 3.06 μ_B for **2**, 3.30 μ_B for **3**, and 3.34 μ_B for **4**, values consistent with an $S = 1$ ground state. These values are similar to those reported for Ni(II)-substituted azurin (3.2 μ_B) and a synthetic model complex (3.30 μ_B, $[\text{Tp}^{\text{iPr}}]\text{Ni}(\text{SC}_6\text{F}_5)$).[20,23] In general, the effective magnetic moment of an idealized tetrahedral Ni(II) complex should be ~4.2 μ_B at room temperature, but distortions reduce the value into the range from 4.0 to 3.0 μ_B.[24] These results show good agreement with the coordination geometries of **2**−**4** discussed in the structural description, vide supra.

The ^{1}H NMR spectra of complexes **1**−**5** are displayed in Figure 6. The spectrum of **1** shows a relatively broad peak at $\delta = 17.40$ and three resonances in the range $\delta = 8.42$−7.37 with an intensity ratio of 27:5, which are assignable to the chemical shifts of *tert*-butyl and phenyl protons, respectively. The chemical shift for the methylene protons was not detected presumably due to broadening beyond detection by

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the paramagnetic center. These features are similar to those of 3-fold symmetric nickel(II) and cobalt(II) complexes having [PhTt^{tBu}] ligation, e.g., [PhTt^{tBu}]NiCl.[15] A single set of the *tert*-butyl protons observed also indicates that **1** has 3-fold rotational symmetry in solution.

The chemical shifts of the protons of [PhTt^{tBu}] in **2**−**4** are very similar to those of **1**. The chemical shifts of phenyl protons of the coordinated thiolates in **2** and **4** exhibit significant upfield and downfield shifts. For **2**, the signal at $\delta = 30.17$ is assigned to the *o*-protons, which are closest to the paramagnetic center, on the basis of integration of two protons and line broadening, the latter attributed to a spin delocalization pathway. The *p*- and *m*-protons are assigned to the peaks at $\delta = 8.55$ and 8.14, respectively.

For **4**, there is one downfield feature at $\delta = 32.16$ and two upfield-shifted peaks at $\delta = -38.97$ and −45.70. A similar chemical shift pattern has been observed in [Fe(TPA)(SPh)]$^+$ ($\delta = 22.6$ for *m*-H, −19.5 for *o*-H, and −26.0 for *p*-H).[20a] These patterns are characteristic of spin polarization pathway, which results in an alternating pattern of parallel and antiparallel spins on adjacent nuclei along chemical bonds, affording alternating downfield- and upfield-shifted peaks, respectively.[25] Thus, the chemical shifts of phenylthiolate protons in **4** are assigned as $\delta = 32.16$ for *m*-H, −38.97 for *o*-H, and −45.70 for *p*-H.

The spectrum of **5** exhibits sharp resonances in the $\delta = 0-10$ region, in support of its diamagnetic ground state. The analysis of the 2-D ^{1}H NMR COSY spectrum permits for assignment of the chemical shifts of two phenyl groups in the range $\delta = 7.91-6.98$ (Figure S6 of the Supporting Information). The singlet at $\delta = 2.45$ is assigned to methylene protons of the uncoordinated thioether group of [PhBt^{tBu}SPh], whereas the four doublets at $\delta = 2.57$, 2.33, 1.69, and 1.52 are assigned to diastereotopic methylene protons of the coordinated thioether side arm of [PhBt^{tBu}-SPh] and η^2-CH_2SBu^t, respectively. The three distinct *tert*-butyl group protons resonate at $\delta = 1.34$, 1.28, and 0.98.

Cyclic Voltammetry of 2−4. The cyclic voltammograms (CV) of the thiolatonickel(II) complexes in THF exhibit a quasi-reversible redox couple at $E_{1/2} = -1.11$ V for **2**, and reversible redox couples at $E_{1/2} = -1.03$ V for **3** and $E_{1/2} = -1.17$ V for **4** (vs Fc$^+$/Fc), as shown in Figure 7 with data collected in Table 4. The redox couples correspond to the one-electron reduction of the Ni(II) state to the Ni(I) state. Peters' [PhBP$_3$]Ni(SC$_6$H$_4$*p*-Bu^t) displays a reversible wave at the same potential as **2** indicating that the tris(phosphino)borate and tris(thioether)borate stabilize the lower oxidation states to similar extents.[13] The data show that the presence of the electron withdrawing group on the thiolato group causes a positive shift of $E_{1/2}$ (Ni(II)/Ni(I)) values (**3** > **2** > **4**), consistent with the expected effect of increasing electron withdrawing abilities pentafluorophenyl > triphenylmethyl > phenyl. Such a positive shift is in line with the general trend that the electron withdrawing group differentially stabilizes the nickel(II) oxidation state. A similar trend is observed for the CT transition energies, vide supra.

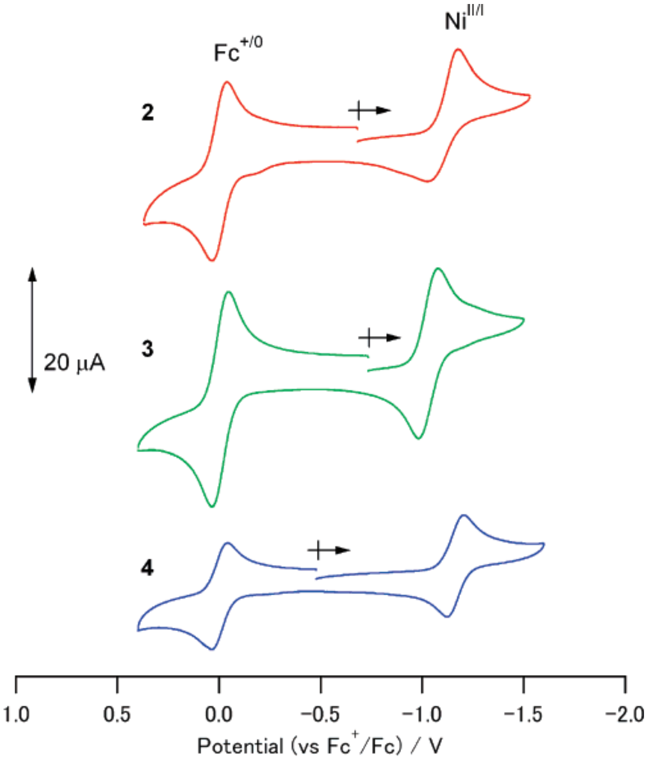

Figure 7. Cyclic voltammograms of **2**−**4** in THF (1 mM) containing 0.1 M *n*-Bu$_4$NPF$_6$ at room temperature (working electrode, glassy carbon; counter electrode, Pt; reference electrode, Ag/Ag$^+$; scan rate, 100 mV).

Table 4. Electrochemical Data for the Reduction of Thiolatonickel(II) Complexes **2**−**4** in THF at Room Temperature at Scan Rate = 0.1 V

complex	$E_{1/2}$(II/I) (ΔE) vs Fc$^+$/Fc (V)
2	−1.11 (∼0.15)
3	−1.03 (0.10)
4	−1.17 (0.09)

Thermal Decomposition of 4. The thiolatonickel(II) complexes exhibit dramatically different thermal stabilities with the order decreasing **3** > **2** > **4**. Complex **4** readily decomposes to **5** within several hours at room temperature via net exchange of Ni−SPh and B−CH_2SBu^t groups. X-ray diffraction analysis and ^{1}H NMR spectral studies show that **5** consists of a η^2-CH_2SBu^t ligand and a SPh functionalized borate ligand, which is coordinated to the nickel in a κ^2 fashion. One plausible mechanism for the formation of **5** from **4** under consideration is intramolecular nucleophilic substitution (S$_N$2) of a methylene group at boron by SPh. The resulting three-membered thianickelacycle ring favors square-planar geometry to give **5**. Previously, we have noted that a related thianickelacycle is a thermodynamic sink when handling [PhTt^{tBu}]NiCl under reducing conditions in the absence of suitable nickel(I) traps.[14] To the best of our knowledge, incorporation of a thiolato group into a borate ligand is not precedented.[14] Somewhat similar rearrangements involving hydridotris(pyrazolyl)borate ligands and Zr−CH$_2$-Ph [26] and Sm−CCPh [27] moieties have been reported. Com-

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pared to the pentafluorophenylthiolato group in **3**, the phenylthiolato group in **4** is more nucleophilic, consistent with different thermal stabilities of the thiolatonickel complexes (**3** > **4**). We consider Ni−SPh bond homolysis, i.e., a radical mechanism, unlikely because addition of CO, an established trap of the nickel(I) fragment, $[\mathrm{PhTt^{tBu}}]\mathrm{Ni}$, to solutions of **4** does not impact the course of decomposition. The unexpected formation of **5** suggests that other interesting insertion chemistry leading to modified ligands may be possible in this system, a topic for future investigation. Complex **2** decomposes over a period of days in solution, leading to the disulfido dimer, $[(\mathrm{PhTt^{tBu}})\mathrm{Ni}]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}\mathrm{S_2})$, the subject of a separate report. Complex **3** decomposes only at elevated temperatures, to an intractable product.

Conclusions

A series of the thiolatonickel(II) complexes, **2**−**4**, were successfully isolated and characterized by various physicochemical methods including X-ray crystallographic analysis. The relationship between structural factors (τ value) and spectroscopic properties (CT intensity) shows the strong CT transition intensity is derived from the high τ value, which reflects enhanced orbital overlap (**2** > **3** > **4**). The presence of the electron withdrawing group on the thiolato group makes the thiolatonickel(II) complexes easy to reduce in the order **3** > **2** > **4**, which is in line with the $\mathrm{S_{thiolate}}\ \mathrm{p}_\pi \rightarrow \mathrm{Ni(II)}\ \mathrm{d}_{x^2-y^2}$ CT transition energy. Thermal decomposition of **4** exhibits unusual nickel alkylation. Incorporation of SPh to the borato ligand of $[\mathrm{PhTt^{tBu}}]$ and activation of one of methylene groups of $[\mathrm{PhTt^{tBu}}]$ yield **5**.

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Supporting Information Available: Thermal ellipsoid plots including complete atom labeling and X-ray crystallographic details (CIF files) for **1**−**5** and a COSY NMR spectrum of **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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