Coupled C-H Bond Heterolysis and Tautomerism in a Nickel Macrocyclic Complex with a Thiolate Ligand

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Interest in the chemistry of Ni thiolate complexes has been stimulated by the discovery of Ni sites in the enzymes hydrogenase (H_2ase)[1] and carbon monoxide dehydrogenase[2] that are involved in the catalysis of key biological redox reactions and feature cysteine thiolate ligation of the Ni center.[3] Results from X-ray absorption spectroscopic studies of the Ni site in *Thiocapsa roseopersicina* H_2ase suggest that the Ni in an active form of this enzyme is bound to five non-hydrogen ligands including 2 ± 1 S-donor ligands.[4] Attempts to prepare a novel five-coordinate pyramidal thiolate complex of Ni(II) using the tetraaza macrocyclic ligand TIM[5] led to the discovery of a novel intramolecular deprotonation of the macrocycle that is dependent on the presence of a thiolate ligand (Scheme I). This reaction leads to the formation of a new macrocyclic complex of Ni(II) (**2**) that contains a β-diiminate moiety and two chiral centers, opens new routes for the functionalization of TIM, and may provide insight into a possible role for the Ni thiolate ligands in the heterolytic cleavage of H_2 by H_2ase.[6] We report here the synthesis of Ni(TIM) arylthiolate complexes, the structure of [Ni(TIM)S-*p*-C_6H_5Cl]PF_6, the structure of a racemic mixture of the reaction product, [Ni(L)]PF_6, and evidence that favors a unimolecular, nondissociative reaction mechanism.

[Ni(TIM)]($ZnCl_4$), prepared by a minor modification of a published procedure,[7] was used to prepare [Ni(TIM)]$(PF_6)_2$ by dissolution of the complex in H_2O followed by precipitation of the dication with NH_4PF_6. Because solutions of the thiolate complexes are O_2 sensitive, all solvents used in their synthesis and characterization were distilled under N_2 before use, and solutions of the complexes were handled under N_2 using standard Schlenk techniques. [Ni(TIM)SPh]PF_6 was prepared by the addition of 5.0 mL of a 0.15 M MeOH solution of NaSPh (0.77 mmol) to a filtered solution of [Ni(TIM)]$(PF_6)_2$ (0.50 g, 0.8 mmol) in 35 mL of MeOH. The resulting dark blue solution was cooled at −20 °C overnight. The black product that precipitated was collected on a frit, washed with EtOH and with Et_2O, and dried for several minutes under vacuum (yield = 0.23 g, 50%).[8] This diamagnetic complex reacts to form **2** even in the solid state.[9] The solid was stored under N_2 at −20 °C. Samples of [Ni(TIM)S-*p*-C_6H_4R]PF_6 (R = Cl, NO_2) were obtained in an analogous manner.

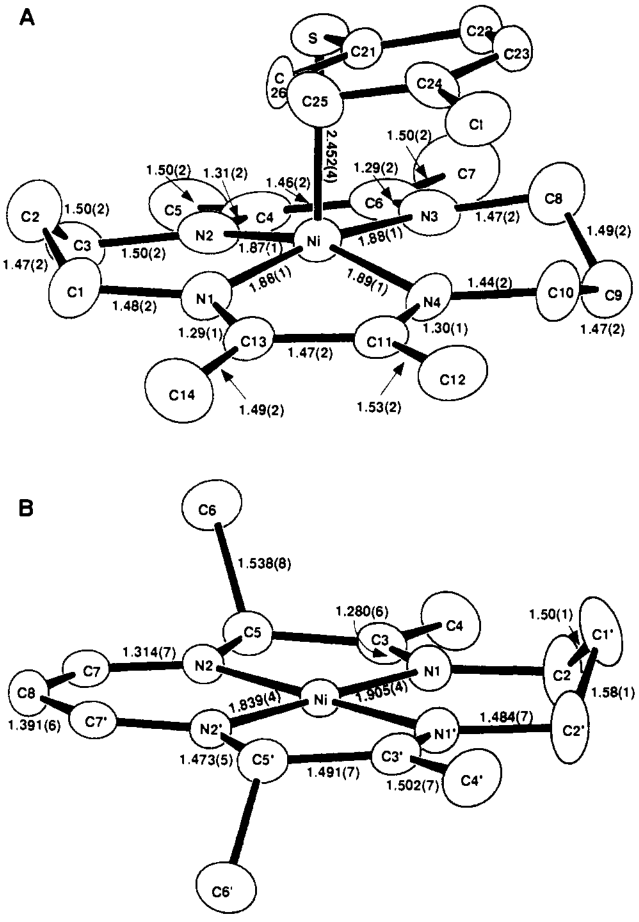
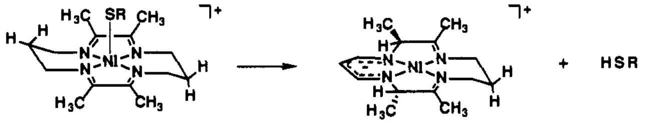


Figure 1. ORTEP plots showing bond lengths (esd) (Å) of [Ni(TIM)S-*p*-C_6H_4Cl]$^+$ (**1**) (A) and the *R,R* enantiomer from a crystal containing a racemic mixture of its reaction product, **2** (B), with the thermal ellipsoids at the 30% probability level and the hydrogen atoms omitted for clarity. For A: N1-Ni-N3 = 169.7 (4)°; N2-Ni-N4 = 162.1 (4)°. For B: Primed atoms are related to unprimed ones by a crystallographic 2-fold axis. Only one position for the disordered C1 is shown. N1-Ni-N2′ = 178.2 (2)°.

Scheme I



1 (R = p-C_6H_4Cl) 2

Black crystals of [Ni(TIM)S-*p*-C_6H_4Cl]PF_6 were obtained from a CH_3CN solution upon slow diffusion of Et_2O at −20 °C.[10] The cation (Figure 1A) is a five-coordinate rectangular pyramid composed of four N donors in the basal plane and an axial S donor. The four N atoms are coplanar to within ±0.062 (9) Å. The Ni atom is displaced from this plane by 0.231 (2) Å toward the

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(5) Abbreviations used: TIM, 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene; L, 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,4,7,10-tetraenato(1−); Pre-H, 3,9-dimethyl-4,8-diazaundeca-3,8-diene-2,10-dione dioximato(1−).

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(8) Anal. Calcd for $C_{20}H_{28}N_4SPF_6Ni$: C, 42.80; H, 5.21; N, 9.98. Found: C, 42.49; H, 5.28; N, 9.73. UV–vis (1.99 mM/acetone): λ_{max} (nm) (ϵ in cm^{-1} M^{-1}) 606 (7700), 386 (4300). IR (Nujol) (cm^{-1}): 1572 m ($\nu_{C=C}$), 1532 m ($\nu_{C=N}$), 1500 m ($\nu_{C=N}$), 1350 s, 1346 s, 1510 s (TIM), 1080 s, 1020 m, 990 m, 850 vs (br, PF_6^-), 748 s, 700 s, 558 s (PF_6^-).

(9) The IR spectrum of a sample of [Ni(TIM)SPh]PF_6 was converted to that of **2** in the solid state within 10 days.

(10) Crystal data for **1**·PF_6: monoclinic space group $P2_1/n$, a = 10.806 (2) Å, b = 8.075 (2) Å, c = 28.984 (6) Å, β = 99.34 (2)°, and Z = 4. Anisotropic refinement of non-hydrogen atoms with hydrogen atoms as fixed isotropic scatterers gave R = 0.051 and R_w = 0.056 for 1189 observed reflections (>3σ_I, 2θ(Mo Kα)$_{max}$ = 42°).

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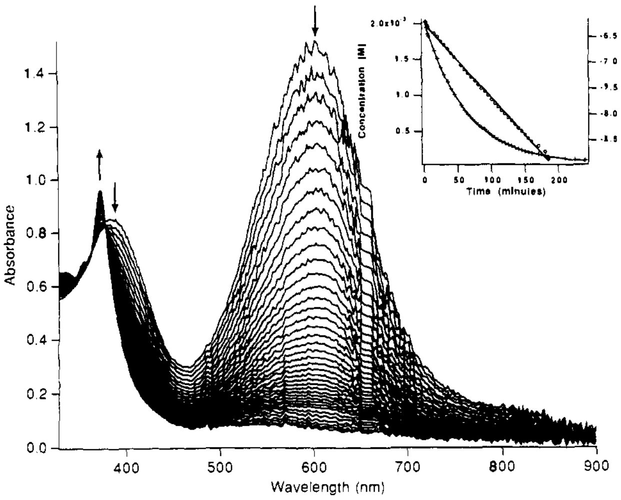

Figure 2. Electronic absorption spectra of a 2.0 mM solution of [Ni(TIM)SPh]PF_6 in acetone at 30 °C taken over 4 h showing isosbestic points at 380 and 362 nm. The inset shows kinetic data for the decrease in the absorption at 603 nm from which first-order rate constants and molar extinction coefficients were extracted. Solid lines represent a fit to a single exponential (left scale) and a least-squares fit to the linear ln A_{603} vs time plot (right scale).

thiolate ligand. The Ni-S distance of 2.452 (4) Å is the longest that has been characterized in a low-spin Ni thiolate complex. The geometry of an analogous Cu(II) complex, [Cu(Pre-H)S-*p*-C_6H_4Cl],[11] is quite similar, but with a larger metal displacement from the basal plane (0.430 Å), smaller trans-basal angles [153.2 (1)°, 156.4 (1)°], and a shorter M-S bond [Cu-S = 2.424 (1) Å].

Solutions of the thiolate complexes are characterized by deep blue colors due to an intense absorption near 600 nm[8] (Figure 2), which is presumably a thiolate → Ni charge-transfer transition. In solution, this color is bleached in a few hours to the orange color of **2**. Red-orange crystals of the product (**2**) were obtained from the reaction of [Ni(TIM)S-*p*-C_6H_4Cl]PF_6 (200 mg, 0.37 mmol) in CH_2Cl_2 followed by the vapor-phase diffusion of Et_2O at ambient temperature under N_2 [isolated yield = 87 mg, 0.22 mmol (60%)].[12,13] The Ni geometry in the cation (Figure 1B) is essentially planar. The four N atoms are coplanar to within ±0.019 (4) Å, and the Ni is required by symmetry to lie in that plane. The six-membered β-diiminate chelate ring is also essentially planar (±0.023 (5) Å, with Ni and C8 required by symmetry to lie in the plane). The Ni-N distances in this delocalized ring are shorter than those involving isolated imines.

The reactions of the Ni(TIM)S-*p*-$C_6H_4R^+$ complexes may be followed spectrophotometrically using UV/vis spectroscopy (Figure 2). The final spectra are not dependent in any significant way on the nature of the thiol or the solvent and are the same as those obtained from isolated samples of **2**. ^1H NMR spectra of reaction product mixtures reveal the peaks assigned to free thiol. The kinetics of the reactions have been studied by monitoring the decrease in absorbance near 600 nm at 30 °C. The reaction is first order in Ni(TIM)S-*p*-$C_6H_4R^+$ (Figure 2).[14] The rates of reaction are sensitive to the basicity of the thiolate[15] and increase with increasing basicity [k (R) × 10^{-2} min^{-1} = 0.15 (NO_2), 1.3 (Cl), 1.6 (H)]. The reaction rates are also sensitive to the nature of the solvent and show an inverse dependence with solvent polarity as expressed by dielectric constants[16] or Z values[17] [k (R = Ph) × 10^{-2} min^{-1} = 0.35 (MeOH), 1.6 (acetone), 2.2 (CH_2Cl_2)].

The solvent dependence of the reaction appears to rule out a dissociative mechanism, since the reaction rate is slower in solvents that would tend to dissociate the complex. A nondissociative mechanism is also supported by the lack of evidence for stable intermediates (e.g., no $Ni(TIM)^{2+}$ is formed) and by the fact that the proton lost is not an acidic proton in $Ni(TIM)^{2+}$. Reaction of $Ni(TIM)^{2+}$ in D_2O in the presence of NaOD leads to deuteration of only the iminyl methyl groups.[18] The first-order kinetics eliminates a bimolecular process and is consistent with a unimolecular, nondissociative mechanism.

A detailed understanding of the mechanism hinges on ascertaining whether the tautomerization drives the deprotonation or vice versa. Tautomerization of the imines to form a β-diimine would generate a ligand with an acidic proton, similar to acetylacetone.[19] This acidic proton could then be removed by the thiolate ligand that is in van der Waals contact[20] with this proton (H-S = 3.12 Å) to form the β-diiminate chelate ring. Alternatively, C-H bond activation involving the axial thiolate could lead to the formation of a carbanion that is stabilized by tautomerization of the imines. The resolution of which alternative best describes the reaction of **1** awaits the completion of activation parameter studies and kinetics studies utilizing isotopically labeled materials that are currently in progress.

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Supplementary Material Available: Additional details of the X-ray studies, atomic coordinates, bond lengths and angles, and hydrogen atom parameters for both **1**·PF_6 and **2**·PF_6 (15 pages). Ordering information is given on any current masthead page.

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(12) Anal. Calcd for $C_{24}H_{23}N_4PF_6Ni$: C, 37.28; H, 5.14; N, 12.42. Found: Cm 36.99; H, 4.96; N, 12.23. UV-vis (1.1 mM/CH_2Cl_2): λ_{max} (nm) (ϵ in cm^{-1} M^{-1}) 372 (11 000), 354 (8000), 339 (sh), 296 (12 000), 267 (15 000). ^1H NMR (300 MHz, CD_2Cl_2): δ = 6.78 (d, 2 H, J, = 6.0 Hz), δ = 4.23 (q, 1 H, J = 6.0 Hz), δ = 3.19 (t, 4 H, poorly resolved), δ = 2.02 (s, 6 H), δ = 1.87 (m, 2 H), δ = 1.49 (br, 2 H), δ = 1.37 (d, 6 H, J = 7.1 Hz). IR (Nujol) (cm^{-1}): 3095 w (ν_{CH}), 1640 s ($\nu_{C=C}$ or $\nu_{C=N}$), 1598 s ($\nu_{C=C}$ or $\nu_{C=N}$), 1506 s ($\nu_{C=C}$ or $\nu_{C=N}$), 1354 s, 1338 m, 1320 s, 1272 s, 1224 m, 1200 w, 1100 s, 850 vs (br, PF_6^-), 558 s (PF_6^-).

(13) Crystal data for **2**·PF_6: monoclinic space group $C_{2/c}$, a = 10.682 (1) Å, b = 20.969 (4) Å, c = 8.653 (1) Å, β = 107.35 (1)°, and Z = 4 (Ni and C8 on 2-fold axis; C1 disordered). Refinement as for **1**·PF_6, but with H atoms on C1 and C2 omitted due to disorder and $2\theta_{max}$ = 50°, gave R = 0.052 and R_w = 0.058 for 1474 observed reflections.

(14) The decrease in absorbance at 606 nm can be fit with a single exponential. Plots of ln (absorbance) vs time are linear over at least 3 half-lives, and the reaction shows no concentration dependence in the range 0.4-2 mM.

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Generation, Dative Ligand Trapping, and N-N Bond Cleavage Reactions of the First Monomeric η^1-Hydrazido Zirconocene Complex, $Cp_2Zr{=}NNPh_2$. A Zirconium-Mediated Synthesis of Indoles

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We report the generation and trapping of $Cp_2Zr{=}NNPh_2$, the first η^1-hydrazidozirconocene complex. This material exhibits reactivity markedly different from that of analogous monomeric

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