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C-H Activation by a Diselenido Dinickel(II) Complex

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ABSTRACT: Addition of selenium to the nickel(I) complex, [Ni(Me₄[12]aneN₄)(CO)]PF₆ effects a redox reaction leading to the diselenido dinickel(II) complex, {[(Ni(Me₄[12]aneN₄)]₂(Se₂)}(PF₆)₂, in 70% crystalline yield. The product's structure features a μ - η^2 : η^2 -Se₂ ligand with Se–Se bond length of 2.379(13) Å. Upon mild heating, {[(Ni(Me₄[12]aneN₄)]₂(μ - η^2 : η^2 -Se₂)}(PF₆)₂ oxidizes 9,10-dihydroanthracene or 1,4-cyclohexadiene forming the terminal hydroselenide, [Ni(Me₄[12]aneN₄)(SeH)]PF₆, and anthracene or benzene, respectively. [Ni(Me₄[12]aneN₄)(SeH)]PF₆, cleanly converts back to the diselenido dinickel(II) adduct upon addition of a phenoxy radical.

Transition metal chalcogenides¹ enjoy a rich history due to their wide-ranging geometric and electronic structures resulting in novel bonding characteristics and applications. Soluble forms, which can be challenging to prepare given the significant driving force favoring binary metal chalcogenides, display a wide array of stoichiometries and structures. Seminal examples date to some of the earliest studies of organometallic chemistry involving metal carbonyls with chalcogenide ligands.² Their renaissance may be traced, in part, to the discovery of these cores in metalloprotein active sites.³

We have explored nickel-oxygen⁴ and -sulfur⁵ complexes, uncovering a range of geometric and electronic structures and patterns of reactivity. In this report, we turn our attention to soluble nickel-selenium complexes, applying the strategy of synthesis via reaction of nickel(I) precursors with selenium. The resulting diselenido dinickel(II) complex exhibits the capacity to activate C– H bonds, a transformation of potential synthetic utility. Metal-selenide C–H activation is rarely seen across the periodic table and unprecedented for nickel.⁶

The reaction of elemental selenium with the nickel(I) complex⁷ [Ni(Me₄[12]aneN₄)CO]PF₆ resulted in a rapid color change from light green to dark brown. Recrystalization lead to isolation of the diselenido dinickel(II) complex, {[(Ni(Me₄[12]aneN₄)]₂(μ - η ²: η ²-Se₂)}(PF₆)₂ (1) in 70% yield (See Supporting Information for synthetic and spectroscopic details). The optical spectrum displays two intense features at 390 nm (ε = 7070 M⁻ ¹cm⁻¹) and 690 nm (1100). The former, assigned as a $(Se_2)^2$ →Ni charge transfer transition, contains a shoulder at 410 nm. The complex is paramagnetic as evidenced by highly dispersed ¹H NMR signals (Figure 1S) and a μ_{eff} = 2.71(2) μ_B.

The cation of 1 consists of a centrosymmetric planar Ni₂(μ - η^2 : η^2 -Se₂) core, Figure 1, with each metal in a distorted octahedral geometry. The Se–Se bond distance of 2.379(13)Å is shorter than that found in {[(PhTt⁻^{Bu})Ni]₂(μ - η^2 : η^2 -Se₂)} (2.479(1)Å)⁸ and longer than in {[(β-diketiminato)Ni]₂(μ - η^2 : η^2 -Se₂)}²⁺ (2.3304(6) Å),⁹ the only other structures available for Ni₂(Se₂) complexes.¹⁰ The intermediate bond length in the title complex is indicative of a moderate level of Se–Se bond activation. Although, it should be noted that the metal coordination number, which can also influence the Se–Se bond length varies from six to five to four through this series of complexes.



Figure 1. Thermal ellipsoid plot of the cation of **1**. Selected bond lengths (Å) and angles (deg): Se–SeA 2.379(13), Ni–Se 2.566(13), Ni–SeA 2.557(13); Ni–Se–NiA 124.68(2), Se–Ni–SeA 55.32(2).

The ability of **1** to oxidize C–H bonds was surveyed initially by reaction with 9,10-dihydroanthracene (DHA), a substrate with activated C–H bonds (first bond dissociation enthalpy = 78 kcal/mol).¹¹ In a typical reaction, a THF solution of DHA was added to **1** in acetonitrile. The dark brown solution was heated at 55°C overnight generating a light green solution, Scheme 1. Analysis of the solution by ¹H NMR spectroscopy and integration relative to an internal standard revealed the consumption of 50% of the DHA and the concomitant production of anthracene in 48% yield, Figure 2. Anthracene production was additionally confirmed by GC-MS analysis.



Figure 2. ¹H NMR spectra in CD₃CN of the reaction of **1** and 9,10-dihydroanthracene (DHA) before (a) and after (b) heating at 55°C to produce anthracene (An) in 48% yield relative to a hexamethylbenzene (HMB) standard. The features at ~6 ppm (#) are attributed to a thermal decomposition product of **2**. Residual solvent (*).

The nickel-containing product was isolated as green crystals following pentane diffusion into a concentrated solution. X-ray diffraction analysis established the crystalline material as the nickel(II) hydroselenide, $[Ni(Me_4[12]aneN_4)SeH](PF_6)$ (2), which was prepared via two independent synthetic strategies and fully char-

acterized (SI). Metathesis of $[Ni(Me_4[12]aneN_4)](PF_6)_2$ with Na₂Se in a THF/acetonitrile solution resulted in conversion to a bright purple solution, from which green crystals were deposited and identified as 2. The same compound was produced upon addition of excess PPh₃ to 1. In each of these reactions, a common intermediate, [Ni(Me₄[12]aneN₄)Se](PF₆) is proposed, which abstracts a hydrogen atom yielding 2. Identifying the source of the H atom is an objective of ongoing experiments. The high-spin nickel(II) complex features a stereochemistry intermediate between trigonal bipyramidal ($\tau = 1$) and square pyramidal ($\tau = 0$) as evidenced by its τ value of 0.53.¹² This represents the first structure of a terminallyligated hydroselenide of nickel¹³ and the second of any nickel triad metal.¹⁴ The Ni–Se distance is 2.389(7) Å. Corroborating evidence for the SeH ligand was provided by IR spectroscopy and mass spectrometry, the former of which revealed a V(Se-H) at 2346 cm^{-1.15} Quantitation of the reaction of 1 with DHA by electronic absorption spectroscopy revealed 2 production in only 15% yield, vide infra.



Figure 3. Thermal ellipsoid plot of the cation of **2**. Selected bond lengths (Å): Ni–N1 2.186(2), Ni–N2 2.0616(16), Ni–N3 2.189(2), Ni–Se 2.389(7).

The origin of the low yield of **2** was of concern and consequently, investigated. **2** is somewhat unstable under the reactions conditions, i.e. **2** decomposed at 55° C in a time course comparable to that of the reaction of **1** with DHA. Further support for this assertion derives from the reaction of **1** with 1,4-cyclohexadiene (CHD), which produced **2** and benzene. Despite the similar C–H BDEs for DHA and CHD, the latter reacts with **1** at lower temperatures, due to the smaller size of the CHD substrate. Consequently, the reaction of **1** and CHD proceeded at 35°C affording **2** in 70% yield and benzene in 66% yield.

The efficacy of the reactions with DHA and CHD point to a lower limit of the effective Se–H bond dissociation enthalpy (BDE) of at least 78 kcal/mol. To determine the BDE with greater accuracy, one could turn to the well documented approach,¹⁶ in which knowledge of the pK_a and the oxidation potential of the conjugate

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58 59 60 base are applied in a thermodynamic analysis to calculate the X–H BDE. This strategy can not be applied with accuracy to 2 because the conjugate base is not accessible. Consequently, to garner insight into the magnitude of the Se-H effective BDE, reaction of 2 with the 2,4,6-tri-*tert*-butylphenoxy radical was assaved.¹⁷ The reaction efficiently resulted in conversion of 2 to 1 and 2,4,6-tri-tert-butylphenol in high yields, Scheme 2. These results lead to the conclusion that the effective enthalpy¹⁸ Se-H bond dissociation of [Ni(Me₄[12]aneN₄)SeH](PF₆) must be intermediate between those of DHA (78 kcal/mol) and 2,4,6-tri-tertbutylphenol (82.3 kcal/mol),¹⁹ i.e. the Se-H effective BDE is 80(2) kcal/mol. By comparison, the Se-H BDE for PhSe-H is estimated at 76-80 kcal/mol.²⁰ The similarity of this measurement to the value determined for 2 is striking as it points to similar stabilization energies of the PhSe and $[Ni(Me_4[12]aneN_4)Se]^+$ fragments.

Scheme 2



In summary, the diselenido dinickel(II) complex prepared in high yield via the reaction of its nickel(I) precursor and elemental selenium features a symmetrically bound μ - η^2 : η^2 -Se₂ ligand. The paramagnetic compound oxidizes the C-H bonds of DHA and CHD yielding the aromatic organic products and the hydroselenide, 2. The hydroselenide reacts cleanly with a phenoxy radical in a presumed proton-coupled electron transfer (PCET) process regenerating 1 and the phenol. The proclivity of these two reactions provides a means to bracket the Se-H effective BDE as 80(2) kcal/mol. Future efforts include mechanistic studies to further elucidate the details of the C-H activation process and exploiting this approach to incorporate selenium into the organic substrates, e.g. Se insertion into C-H bonds to create C-Se-H functionality adding molecular complexity via metalpromoted elemental selenium activation.

ASSOCIATED CONTENT

Supporting Information Available: Experimental details and characterization data including CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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