

Oxygen-Induced Ligand Dehydrogenation of a Planar Bis- μ -Chloronickel(I) Dimer Featuring an NHC Ligand

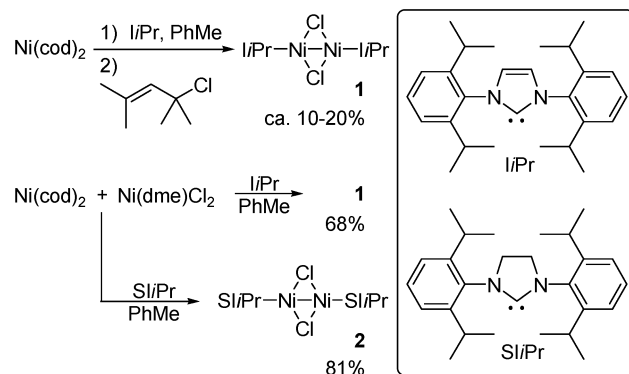
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Planar bis- μ -chloronickel(I) dimers undergo rapid aerobic oxidation to yield bis- μ -hydroxonickel(II) dimers with concomitant ligand dehydrogenation.

Many nickel complexes exhibit high reactivity with O₂, with potential for practical, catalytic aerobic oxidations. One such example is oxygenative C–H bond activation, which several nickel complexes are found to promote in either an intramolecular¹ or intermolecular² fashion, using either O₂ or H₂O₂ as the oxidant. It is thought that these C–H bond activations are similar to oxygenases, proceeding through nickel(III) superoxides as opposed to a direct interaction between nickel and the C–H bond in question. Nickel(III)–dioxygen adducts have been studied wherein nickel(III) species are prepared via the oxidation of nickel(I)³ or nickel(II)^{1c–g,2} complexes at low temperatures. Oxidations of nickel(I) species with dioxygen or peroxides are reported to produce thermally unstable species such as an η^2 -superoxonickel(III) monomer^{3a} or bis- μ -oxonickel(III) dimers.^{3b,c} Bis- μ -hydroxonickel(II) dimers have also been oxidized with hydrogen peroxide to prepare bis- μ -

Scheme 1. Preparation of Bis- μ -chloronickel(I) Dimers **1** and **2**

oxonickel(III) dimers.^{1c–g} Subsequent decomposition of these nickel(III) species leads to ligand oxidation, typically ligand oxygenation. Additionally, the reported oxygenated nickel(III) complexes are either five- or six-coordinate species featuring tri- or tetradentate anionic ligands, respectively. Herein, we report the synthesis of planar, dimeric nickel(I) complexes **1** and **2** containing monodentate, neutral N-heterocyclic carbene (NHC) ligands and their aerobic oxidations, leading to nonoxygenative ligand dehydrogenation.

During studies directed at the preparation of highly substituted π -allylnickel(II) chloride–NHC complexes via the oxidative addition of allylic halides to nickel(0) and subsequent ligation, we attempted the reaction of Ni(cod)₂ with 4-chloro-2,4-dimethyl-2-pentene in the presence of iPr (Scheme 1). This reaction results in the formation of a complex mixture of compounds. However, we were able to isolate and characterize the major product, the unusual bis- μ -chloronickel(I) dimer **1**. In this reaction, nickel(I) presumably forms via homolytic cleavage of a nickel(II)–carbon bond promoted by the size of both the allyl group and the carbene ligand.

Dimer **1** is a fascinating complex in that nickel(I) complexes bearing single, neutral monodentate ligands are a rarity,⁴ which makes an alternative synthesis desirable. We envisioned that a soluble nickel(II) chloride species could chelate nickel(0) through the chlorine atoms to generate a formal bis- μ -chloronickel(I) dimer that would be trapped by the NHC ligand. Gratifyingly, we found that **1** is readily

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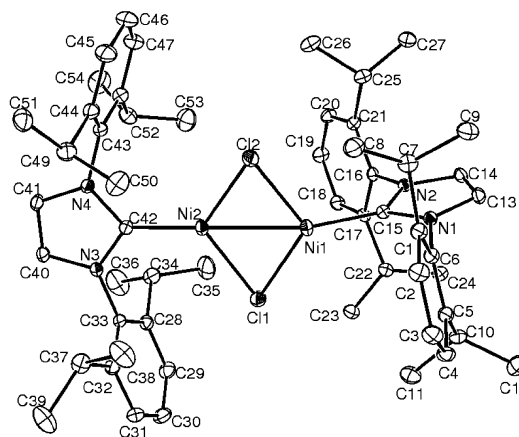


Figure 1. ORTEP plot of **1** (thermal ellipsoids set at 30% probability). Selected bond lengths (Å) and angles (deg): Ni(1)–Ni(2) 2.5194(5), Ni(1)–C(15) 1.871(3), Ni(1)–Cl(1) 2.2084(8), Ni(1)–Cl(2) 2.2212(9), Cl(1)–Ni(1)–Cl(2) 111.44(3).

accessible by equilibrating a 1:1:2 molar ratio of Ni(cod)₂, Ni(dme)Cl₂, and *i*Pr in toluene (Scheme 1). Likewise, we found that the analogous SI⁺Pr complex **2** can be prepared under similar conditions, although the formation of **2** is significantly more sensitive to trace impurities.

Crystallographic analysis of **1** reveals an asymmetric solid-state dimer with a flat bridging structure and a Ni–Ni distance of 2.5 Å (Figure 1). ¹H NMR analysis reveals a single set of ligand resonances between 0 and 8 ppm. The presence of a single set of NMR resonances suggests that the ligand nonequivalence in the crystal structure is not a solution phenomenon. Complex **2** has two-fold symmetry through the center of the Ni–Ni bond in the crystal analyzed, but is otherwise structurally similar to **1**.

Oxidation of **1** with O₂ leads to extremely rapid formation of purple diamagnetic complex **3** (Figure 2). Complex **3** has a visible absorbance spectrum identical to that of the previously reported μ -hydroxo dimer [NiCl(μ -OH)]*i*Pr₂ (**4**),¹ with $\lambda_{\text{max}} = 502$ nm, and the crystal structures of **3** and **4** are highly similar. NMR analysis clearly distinguishes **3** from **4** in that the symmetry associated with complex **4** is completely lost in the spectrum of **3**. Key ¹H NMR resonances for **3** at $\delta = 5.07$ and 5.16 ppm in C₆D₆ reveal the possibility of a terminal olefin. Additionally, **3** has an infrared spectrum almost identical to that of **4**, featuring a μ -OH stretch at 3645 cm⁻¹ and a Ni–O stretch at 546 cm⁻¹. Preparation of **3** using ¹⁸O₂ resulted in shifts in the infrared spectrum, identical to those in **4**, with a μ -¹⁸OH stretch at 3632 cm⁻¹ and a Ni–¹⁸O stretch at 529 cm⁻¹. However, **3** features an additional absorbance at 893 cm⁻¹, regardless of the O₂ isotope used, consistent with a geminal vinylidene C–H bending mode. Therefore, we propose that the oxida-

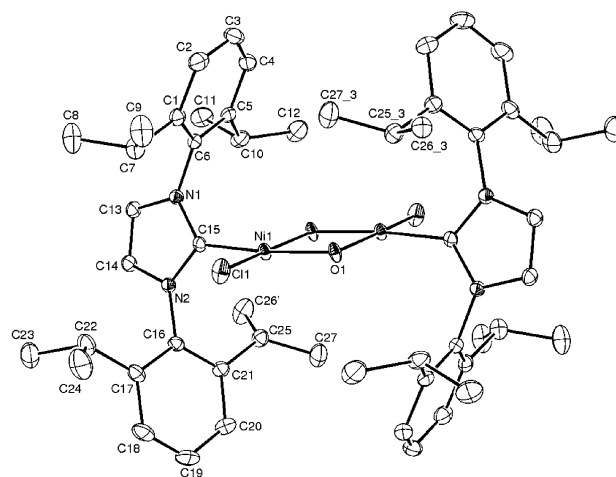
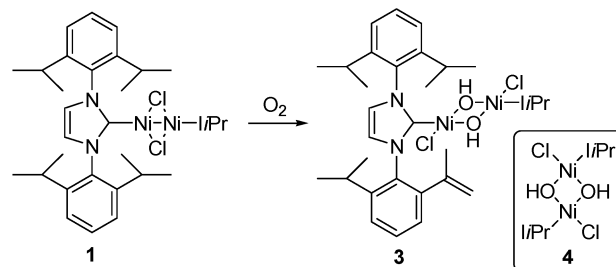


Figure 2. ORTEP plot of **3** (thermal ellipsoids set at 30% probability). Selected bond lengths (Å) and angles (deg): Ni(1)–O(1) 1.847(13), Ni(1)–O(1)#1 1.904(15), Ni(1)–C(15) 1.856(2), Ni(1)–Cl(1) 2.122(4), C(25)–C(26') 1.352(9), C(25_3)–C(26_3) 1.484(8), O(1)–Ni(1)–O(1)#1 84.2(6), C(26')–C(25)–C(27) 121.2(5), C(26_3)–C(25_3)–C(27_3) 113.9(4).

Scheme 2. Oxidation of **1** to Produce Ligand-Dehydrogenation Product **3**



tion of **1** results in bis- μ -hydroxo dimer formation with concomitant dehydrogenation of a single isopropyl group to yield mixed-ligand dimer **3** as shown in Scheme 2.

The presence of an olefin in **3** was not initially detected in the crystallographic analysis, and this structural possibility was perplexing in light of the presence of an inversion center. However, an exhaustive search for the presence of an olefin revealed an interesting scenario. Carbons 25 and 26 were found to fit a 50:50 disorder between olefinic and aliphatic states in the crystal structure. This is consistent with the presence of an inversion center in **3** as well as the proposed structure. The NMR data are consistent with an absence of ligand exchange in **3**, as **4** is not detected in any samples of **3**. If the ligand is at all labile, then the loss of ligand must therefore be a nonconservative pathway leading to decomposition. Both complexes **3** and **4** slowly decompose in solution to produce protonated ligand and an unidentified inorganic nickel product. It should be noted that difficulty in using crystallography to discriminate between an isopropyl and a 2-propenyl group in a complex with multiple isopropyl residues has been observed in another system.⁵

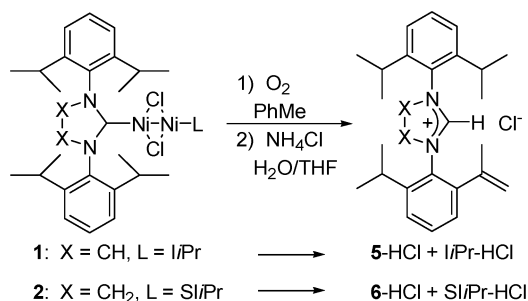
To more rigorously establish the oxidation product(s), we took advantage of the observed instability and subjected complex **3** to mildly acidic conditions to promote ligand

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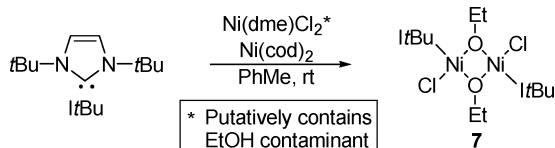
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Scheme 3. Acid-Mediated Decomposition to Yield the Corresponding Protonated Ligand Salts of *S*/I'Pr and *6*/SI'Pr



Scheme 4. Formation of Bis- μ -ethoxonickel(II) Dimer **7**



cleavage. The mixture was characterized using ¹H and ¹³C NMR spectroscopies, as well as high-resolution mass spectrometry. This analysis of the protonated ligand mixture reveals the expected 1:1 combination of I'Pr and dehydrogenated I'Pr **5** hydrochloride salts. Similarly, complex **2** was oxidized and subsequently hydrolyzed to yield a 1:1 mixture of SI'Pr-HCl and **6**-HCl as shown in Scheme 3.

To continue to investigate this process, we set out to prepare structural derivatives by using alternate ligands without isopropyl substituents. When I'Bu, IAd, or IMes was used under conditions identical to those used to prepare **1** and **2**, the reaction mixtures would rapidly develop a dark bluish-purple color, with no nickel(I) products observed. In the case of I'Bu, the bluish-purple complex **7** was crystallized and characterized. Shockingly, **7** was identified as a bis- μ -ethoxonickel(II) dimer (Scheme 4). Because Ni(dme)Cl₂ is typically prepared by drying either [Ni(H₂O)_nCl₂] or [Ni(EtOH)₄Cl₂] with triethyl orthoformate in 1,2-dimethoxyethane (DME),⁶ we propose that the Ni(dme)Cl₂ purchased is contaminated with [Ni(EtOH)_nCl₂]. To test this hypothesis, the experiments were repeated using Ni(dme)Cl₂, which was prepared by drying [Ni(H₂O)_nCl₂] with thionyl chloride in DME.⁷ In this case, neither **7** nor any bis- μ -chloronickel(I) product was observed. However, this nickel(II) source performed similarly to commercially available Ni(dme)Cl₂ in the synthesis of **1**.

To test for the presence of a nickel(III) intermediate, the formation of **3** from the oxidation of **1** was monitored at low temperatures via visible spectroscopy. The reaction proceeds to completion at incredibly high rates. For example, reactions at -78 °C are complete in <15 s at concentrations of <1 mM in **1** and in O₂ with THF or toluene as the solvent. No evidence of any nickel(III) or other intermediate was observed. Given that reported oxygenated nickel(III) com-

plexes are stable at -78 °C or warmer, this suggests two mechanistic possibilities. The first possibility is that **1** does form a nickel(III) intermediate that is orders of magnitude more reactive than reported examples. Alternatively, the oxidation of **1** does not proceed via a nickel(III) intermediate. There are three related cases of dehydrogenation of ligand isopropyl groups reported including hydroperoxopalladium complexes,⁵ a platinum-mediated C-H activation process,⁸ and an aerobic oxidation of Tp-Co(I) [Tp = hydridotris-(3-isopropyl-5-methylpyrazolyl)-borate] that resulted in dehydrogenation of 10% of the isopropyl residues.⁹

Planar nickel(I) complexes **1** and **2** were synthesized by equilibrating nickel(0) and nickel(II) sources. The formation of this bridging motif is strongly ligand-dependent. A recent report on the properties of nickel carbonyl complexes of NHCs reveals that the σ -donating abilities of I'Pr, IMes, and SI'Pr are very similar as determined by carbonyl stretching frequencies.¹⁰ This observation combined with the persistent failure to prepare the IMes analogue of **1** and **2** under identical conditions is suggestive of rigorous steric constraints in this reaction. This is intrinsically interesting because the formation of nickel-NHC complexes has proven to be a generally perplexing field. For example, Ni(IMes)₂ forms readily from Ni(cod)₂,¹¹ Ni(I'Pr)₂ is reported to exist in equilibrium with Ni(cod)₂,¹² and Ni(cod)₂ reacts with I'Bu to form a variety of novel complexes, but not Ni(I'Bu)₂.¹³ Of equal interest is the facile aerobic oxidation that complexes **1** and **2** undergo. The susceptibility of nickel(I) complexes to oxidation is certainly not surprising. However, complexes **1** and **2** are substantially more reactive than those in previously reported cases. Therefore, current and future work is directed at understanding both the unique reactivity of nickel with NHCs and harnessing the extraordinary reactivity toward O₂ exhibited by the resulting complexes.

Acknowledgment. This work was supported by the University of Utah Research Foundation.

Supporting Information Available: Experimental procedures, ¹H NMR spectra, and X-ray structural information. This material is available free of charge via the Internet at <http://pubs.acs.org>. CCDC-265407 (**1**), CCDC-265408 (**2**), CCDC-265409 (**3**), and CCDC-265450 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, U.K.; fax (+44) 1223-336-033; e-mail deposit@ccdc.cam.ac.uk].

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