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Unusual Reactivity of Molecular Oxygen with π-Allylnickel(N-heterocyclic carbene) Chloride Complexes

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Significant effort has been afforded to the development and understanding of Pd(II)-catalyzed aerobic oxidations.[1] In contrast, aerobic oxidations with Ni(II) catalysts are uncommon.[2] Due to our recent success with Pd(II) complexes with amine[3] and N-heterocyclic carbene[4] ligands in catalytic aerobic alcohol oxidations, we sought to synthesize and evaluate 1:1 Ni(II)−carbene complexes for reactivity with O_2. Herein, we describe the synthesis of 1:1 Ni(II)−N-heterocyclic carbene complexes and their unusual reactivity with molecular oxygen.

While a number of highly active Ni(0)− and Ni(II)−N-heterocyclic carbene complexes have been prepared and used in catalysis,[5,6] there are no examples of discreet 1:1 Ni−N-heterocyclic carbene complexes reported in the literature. Initially, attempts to directly prepare 1:1-Ni(II)−carbene complexes via ligand substitution were unsuccessful. Inspired by recent work utilizing phosphine adducts of π-allylnickel halide complexes,[7] we set out to prepare the corresponding carbene π-allylnickel halides. For this purpose, a simple, one-pot preparation of π-allylnickel(N-heterocyclic carbene) halides was developed. This is accomplished by in situ formation of dimeric π-allylnickel chloride[8] followed by addition of 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (I*i*Pr) in a toluene solution (Scheme 1) giving the desired N-heterocyclic carbene adduct in near quantitative yield. Structural confirmation was established via X-ray crystallographic analysis of a reddish-brown single crystal of **1** (Figure 1).

As a qualitative test of reactivity with molecular oxygen, samples of **1** in hexanes, THF, and toluene were exposed to the ambient atmosphere. These solutions underwent a rapid color change from orange to violet with precipitation of a purple solid. The purple precipitate was analyzed by ^{1}H NMR to reveal a new Ni−N-heterocyclic carbene species **2**, which lacked resonances associated with an allyl group. To rule out the possibility of a hydrolytic process, **1** was treated with O_2 under strictly anhydrous conditions, again yielding complex **2**. This strongly suggests that O_2 is responsible for the formation of complex **2**.

To ascertain the structure of product **2**, a single purple crystal was analyzed via X-ray crystallography (Figure 2). Intriguingly, **2** is a μ-hydroxo Ni(II) dimer in the solid state, containing an inversion center. The presence of a hydroxo linkage is further evidenced by a sharp OH stretch at 3645 cm^{-1} in the IR spectrum (KBr) and by the presence of a proton resonance at −7.8 ppm (C_6D_6) by NMR.[9] Complex **2** is air-stable, but moisture-sensitive. Additionally, complex **2** appears to be unstable in solution over the course of several days.

Understanding the fate of the π-allyl ligand would provide insight into this unusual transformation. To accomplish this, complex **3** was prepared, containing a nonvolatile allyl group to ease the analysis. Treatment of **3** with molecular oxygen resulted in rapid formation of **2**. Mass spectral and ^{1}H NMR analysis of the organic products showed that cinnamaldehyde (**4**) and phenyl vinyl ketone (**5**) (Scheme 2) were produced cleanly and quantitatively in a 5:3 ratio. To verify that the incorporated oxygen atoms originate from O_2, a solution of **3** in hexanes was exposed to $^{18}O_2$. Analysis by GC−MS clearly shows complete incorporation of ^{18}O in the carbonyls of **4** and **5**. Furthermore, the OH stretch in complex **2** shifted to 3632 cm^{-1}, demonstrating the presence of ^{18}O. This pattern of ^{18}O incorporation is consistent with a mechanism in which oxygen incorporation stems from dissociation of an oxygen−oxygen bond. This Ni(II)-mediated splitting of O_2 is distinctive in that the few examples of Ni(II) involvement in such a process result in C-hydroxylation.[10]

To further investigate the mechanism of this process, a set of kinetic experiments were undertaken to elucidate the concentration

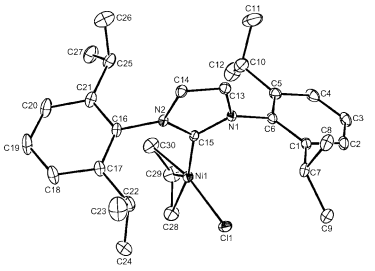


Figure 1. ORTEP diagram of **1**.

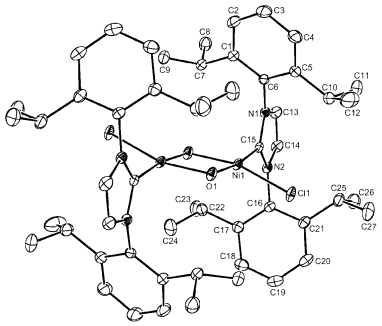
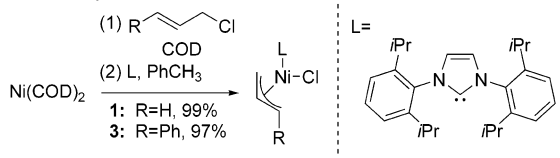
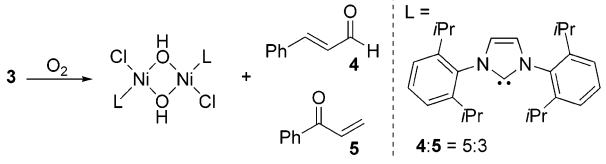


Figure 2. ORTEP diagram of **2**.

Scheme 1. Preparation of π-Allylnickel(N-Heterocyclic Carbene) Chloride Complexes



Scheme 2. Reaction of 3 with O_2



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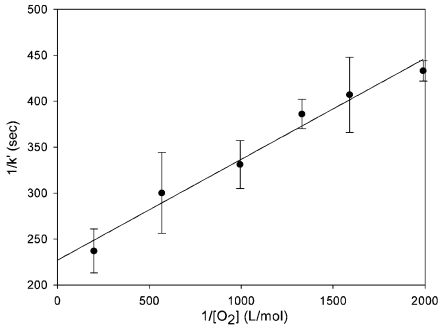
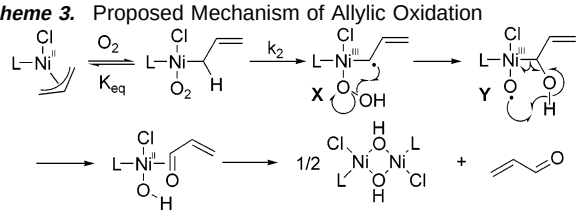


Figure 3. Double-reciprocal plot of O_2 dependence in the oxidation of **1**.

Scheme 3. Proposed Mechanism of Allylic Oxidation



dependence of O_2 and **1**. Kinetics data were collected by measuring the initial rate of the disappearance of **1** by UV−vis spectroscopy at 410 nm in THF at 2.5 °C. The system was found to display saturation behavior, consistent with reversible O_2 binding followed by rate-limiting decomposition of the resulting metal−oxygen species (Scheme 3). A double reciprocal plot of the O_2 concentration dependence yielded a linear fit (Figure 3) with a calculated equilibrium constant for O_2 binding (K_{eq}) of 2100 ± 100 L/mol and the rate of decomposition for the intermediate metal−oxygen complex (k_2) of $4.4 \times 10^{-3} \pm 0.2 \times 10^{-3}$ s^{-1}. This K_{eq} value is very similar to O_2 binding constants reported by Martell and coworkers for Ni(II)−pentaaza complexes.[10b] Under typical reaction conditions, the half-life of the process is ∼7 s (0.03 M at room temperature to 22 °C).

A proposed mechanism for this transformation that accounts for the observed data is shown in Scheme 3. Reversible binding of O_2 leads to an activated complex, which undergoes rate-determining decomposition. A plausible pathway for this decomposition is formation of a Ni(III)−peroxide intermediate **X** in which the oxygen radical abstracts a hydrogen atom from the allyl group. Intramolecular hydroxylation of **X** leads to **Y**, which is set up for a hydrogen atom transfer to yield the carbonyl product and a monomeric hydroxonickel compound. One potential reason for deviation between this process and published Ni-mediated aerobic hydroxylation mechanisms[10a,b] is that the hydroxylated carbon on **Y** is uniquely set up to undergo further oxidation.

In conclusion, 1:1 N-hetereocyclic carbene Ni(II) complexes have been prepared in a convenient, one-pot manner. These complexes react rapidly and quantitatively with molecular oxygen to produce a μ-hydroxo Ni(II) dimer and an (α,β)-unsaturated carbonyl compound. This Ni(II)-mediated splitting of oxygen is unprecedented in the absence of macrocyclic tetra- or pentaaza biomimetic ligands. Mechanistic experiments indicate reversible O_2 binding with a large K_{eq}, followed by rapid, rate-limiting allylic oxidation. While these complexes do not react catalytically with O_2, a clear understanding of the nature of interactions between Ni(II) and molecular oxygen could lead to the development of Ni catalysts for aerobic oxidations. We are currently investigating this possibility as well as applications of these complexes for additional types of new reactivity.

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Supporting Information Available: Experimental procedures, crystallographic data, and spectroscopic data (PDF). X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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