

Reactivity of the Nickel(0)-CO₂-Imine System: New Pathway to Vicinal Diamines

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Received September 2, 2009

Summary: Nickela-2-oxazolidinones, formed by oxidative coupling of imines and CO_2 with Ni^0 , react with LiCl under mild conditions (4 °C, 1 atm) to afford vicinal diamines in up to 89% yield. The reaction is the first organometallic example of reductive imine coupling requiring CO_2 . In this system, CO_2 is participatory and is not incorporated in the reaction products. These results represent an important addition to our understanding of the reactivity of metallacycles derived from CO_2 and unsaturated compounds.

Carbon dioxide (CO₂) is a highly appealing C₁ building block for industrial organic synthesis,¹⁻⁵ since this potent greenhouse gas is inexpensive, abundant, nontoxic, noncorrosive, nonexplosive, and nonflammable. The thermodynamic stability and kinetic inertness of CO₂, however, present significant challenges to converting CO₂ into useful materials. Nickel(0) has a particular affinity for CO₂, as evidenced by the large number of characterized monomeric and oligomeric Ni–CO₂ complexes.^{6–11} The regioselective co-oligomerization of CO₂, Ni⁰, and unsaturated compounds via an oxidative coupling reaction (Scheme 1) takes advantage of this affinity to afford the five-membered chelate ring **1**. The reaction has been shown to proceed at the electron-rich Ni⁰ center with a variety of unsaturated

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compounds,¹² including alkenes,^{13–16} dienes,^{17–19} alkynes,^{20–24} aldehydes (Y = O),^{25–27} and imines (Y = NR³).²⁸ Recent efforts primarily have been dedicated to further developing the chemistry of oxanickelacyclopentenes, formed by the oxidative coupling of Ni⁰ with CO₂ and alkynes (**1b**). For example, Mori et al. reported the regio- and stereoselective synthesis of tri- and tetrasubstituted carboxylated alkenes,⁴ while Louie and co-workers used CO₂, diynes, and a catalytic amount of nickel complex in an efficient, intramolecular [2 + 2 + 2] cycloaddition system.^{2,29,30}

Scheme 1. Nickel-Mediated, Regioselective Oxidative Coupling of Double-Bonded Compounds ($Y = CR^3R^4$, O, NR³) and Alkynes with CO₂



Although nickela-2-oxazolidinones **2** are formed in high yield (ca. 90%) from aliphatic and aromatic imines,²⁸ further investigations on their reactivity have not been reported. Herein, we describe the first results of attempted Ni–C insertion reactions in nickela-2-oxazolidinones and the unexpected, high-yielding production of vicinal diamines by a Ni–CO₂–imine intermediate.

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Published on Web 04/15/2010

Scheme 2. Attempted Synthesis of 3,4-Dihydro-2*H*-1,3-oxazin-2-ones from Imines, Alkynes, CO₂, and Ni⁰



Scheme 3. Ni⁰-CO₂ Mediated Dimerization of Imines



Our initial plan was to build nitrogen-containing heterocyclic products via the insertion of alkynes into the Ni–C bond of nickelacycles 2, with subsequent reductive elimination from the seven-membered chelate ring to afford 3,4dihydro-2*H*-1,3-oxazin-2-ones 3 according to Scheme 2.

Numerous reactions were attempted by combining Ni-(COD)₂ with a wide range of substituted imines and metal ligands in the presence of CO₂. Under all conditions tried, none of the cyclic products were detected and only starting imines, as well as aldehyde and amine from imine hydrolysis, were isolated (see Table S1 in the Supporting Information for a complete list of reaction components). The addition of lithium chloride, a Lewis acid intended to activate the nickelacycle, led to the formation of compounds with peaks in the 4.5–6.0 ppm region in the ¹H NMR spectrum of the crude reaction mixture's organic fraction ($L_2 = bpy$; imine = N-benzylideneaniline; alkyne = 1-hexyne). The reaction products were found by IR spectroscopy not to contain any carboxylate moiety, and olefinic signals expected from alkyne adducts were also absent. NMR and IR spectroscopic analysis in combination with high-resolution mass spectrometry showed these reaction products to be vicinal diamines.

To tetrahydrofuran solutions of Ni(COD)₂ under argon were added equimolar amounts of bpy and imine followed by sparging with CO₂ (1 atm) at 4 °C and the addition of LiCl (2 equiv) to afford vicinal diamines (Scheme 3) in low to excellent unoptimized yields (Table 1). The reaction afforded the highest yields with electron-neutral systems ($R^1 = R^2 =$ Ph). The vicinal diamines were obtained as diastereomeric (*meso:dl*) mixtures with modest diastereoselectivities. The highest stereoselectivity was observed when R^2 was *p*-OMePh (Table 1).

Following the assignment of ¹H NMR signals from diamine mixture **4**, it was clear that other imine-derived substances were present in the product mixtures. One compound that appeared in variable amounts in different preparations ultimately proved to be the imidazolidine **10** (Scheme 4).

Table 1. Ni⁰-CO₂ Mediated Dimerization of Imines

e (%)
7
3.6
D
5.0
2.0

^{*a*} Determined by ¹H NMR analysis⁶⁶ (see the Supporting Information). ^{*b*} Determined by GC and ¹H NMR analysis.

Scheme 4. Formation of Imidazolidines 9 and 10 ($R^1 = R^2 = R^3 = Ph$)



Formation of imidazolidines **9** from the corresponding diamines and either a carbonyl or imino compound is straightforward (Scheme 4), but the origin of the C=X component was unclear. Compound **10** was consistently present in samples of **4** that had been chromatographed on untreated silica gel, and this imidazolidine also appeared when purified diamine samples (chromatographed on deactivated silica—see the Supporting Information) were stored in CDCl₃. It therefore seemed likely that C₂ of **10** must come from the diamine product itself. A possible explanation was offered by Shimizu and Makino,³¹ who found that vicinal diamines readily undergo oxidative cleavage to the corresponding imines in the presence of Lewis acids. The conversion of *dl*-bisamine **4a** into pentaphenyl imidazolidine **10** was followed by ¹H NMR spectroscopy of a crude, aerobic reaction mixture in CDCl₃ over a 4 week period (Figure 1).

The highly stereoselective, if not stereospecific, nature of this reaction was surprising. Imidazolidine **10** steadily formed at the expense of **4a**, but the concentration of *meso*-diamine **4b** remained constant in the same sample. The formation of **10** in purified diamine samples was also promoted by exposure to untreated silica gel. It was subsequently found that treatment of silica with triethylamine largely suppressed imidazolidine formation (data not shown), and similarly, the reaction in CDCl₃ was suppressed by filtering the solvent through basic alumina powder, both results being consistent with acid catalysis of the cleavage reaction. There is no literature precedent for stereoselective decomposition of diaryl diamines, and we can offer no satisfactory explanation for this result.

Periasamy et al. reported the formation of an imidazolidine ($R^1 = R^3 = Ph, R^2 = CH_3$) in 48% yield as a byproduct in the corresponding imine coupling reaction using a TiCl₄/ Et₃N system.³² Given the oxidative lability of many 1,2diamines, it is surprising that reports of imidazolidine byproduct are not more common in the literature.

Spectral data for imidazolidine **10** initially seemed to be inconsistent with the assigned structure. Mass spectrometric analysis gave an m/z value of 451.3 ($[M-H]^+$ calcd for $C_{33}H_{28}N_2$, 451.2), but the ¹H NMR spectrum showed a pattern of ring proton signals more complex than originally

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Figure 1. Evolution of organic product mole fractions from Nimediated imine coupling analyzed by ¹H NMR spectroscopy (CDCl₃): (white circles) *dl*-1,2-diamine **4a**; (black circles) *meso*-1,2-diamine **4b**; (gray circles) imidazolidine **10**; (white squares) *N*-benzylideneaniline; (white triangles) benzaldehyde.

expected, including a pair of doublets at $\delta_{\rm H}$ 4.95 and 5.13 ppm ($J_{H4-H5} = 7.2$ Hz). It is known that for imidazolidines **9** with small C_2 substituents (e.g., $R^3 = CH_3$) rapid ring inversion leads to apparent magnetic equivalence for H₄ and H₅ to produce a singlet for these methine protons at $\delta_{\rm H}$ 3.50 ppm,^{32–35} but none of the compounds in these studies included larger C₂ substituents. The low-field resonances in our product could be explained by assuming that the C_2 phenyl group is rotated out of the plane of the imidazolidine ring so that both C4 and C5 methine protons display significant downfield shifts. Subsequently, we learned that 10 had been reported as a minor product of the silyl radical-promoted coupling of PhCH=NPh³⁶ and that this compound's ¹H NMR spectrum matched that of our material. Compound 10 was synthesized independently by heating an authentic sample of 4a under reflux with benzaldehyde dimethyl acetal and CF₃CO₂H in methanol, again providing material with matching ¹H NMR spectra.

When $R^2 = p$ -CF₃Ph, additional reaction products were observed in the Ni⁰-CO₂ mediated dimerization of imines (Figure 2), presumably through elimination of 4-(trifluoromethyl)aniline under mildly acidic/hydrolytic conditions to afford the corresponding tautomeric enamine (11)-imine (12) pair. An equilibrium between these two forms typically is reached within 2 days.³⁷

The reductive coupling of imines to 1,2-diamines described here is unusual because it requires a low-valent bpyNi(COD) system, CO₂, and LiCl. The omission of any of these components results in quantitative recovery of starting materials. The requirement of CO₂ for reductive imine coupling suggested that the reaction proceeded via nickelaoxazolidinone **2**. When this complex ($R^1 = R^2 = Ph$), synthesized and isolated independently, was suspended in THF saturated with CO₂ and allowed to react with LiCl (1 equiv) under a CO₂ atmosphere, vicinal diamines **4** were

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Figure 2. Side products in the Ni⁰–CO₂ mediated dimerization of imines;. **12a** (R¹ = p-OMePh): HRMS-FAB (m/z) [M + H]⁺ calcd for C₂₃H₂₁F₃O₂N 400.1524, found 400.1507. **12b** (R¹ = p-CF₃Ph): HRMS-FAB (m/z) [M + H]⁺ calcd for C₂₃H₁₅F₉N 476.1060, found 476.1046.

obtained. When the solvent was not presaturated with CO_2 , the isolated nickelacycle decomposed to quantitatively liberate the starting imine. Nickelaoxazolidinone 2 could also be prepared from Ni(acac)₂ and DIBAH in excellent yields (see the Supporting Information) or generated in situ affording, following the addition of LiCl, diamines 4. The LiCl can be added with the bpy, at the beginning of the reaction, or after the CO₂, at the very end, with equivalent results. No diamine products were observed when LiCl was substituted in the above reactions with a range of Lewis acids (ZnI₂, SbI₃, BF₃) that have been used previously as additives to activate nickelalactones toward reaction with alkyl iodides.^{16,38} When MnI₂ was used, trace amounts (4%) of diamines 4 were obtained along with unreacted imine. These results suggest a unique role for the LiCl in the dimerization reaction, possibly both as a weak Lewis acid and as a source of nucleophilic chloride anion.

Reacting nickelaoxazolidinone $2 (R^1 = R^2 = Ph)$ with 1 equiv of imine $(R^1 = R^2 = Ph)$ in the presence of CO₂ and LiCl afforded the diamines 4 in 89% yield (based on 2) with 98% recovery of imine. Similar yields of the diamines 4 were obtained in the absence of additional imine, starting with the corresponding nickelacycle and LiCl. These results suggest that the diamines are not formed through insertion of free imine, or iminium ion formed by the reaction of trace carbonic acid with the imine, into the nickelacycle Ni–C bond. The involvement of an iminium ion is also unlikely, because the addition of organic bases (DABCO, benzylamine, aniline, triethylamine) to the reaction mixture did not reduce the yield of diamine 4, which even formed in the presence of 3 equiv of triethylamine.

The above results suggest that the C–C bond in the diamine coupling reaction is formed by the reaction of two metallacycles, possibly via a bimetallic intermediate, with a key involvement of LiCl. Decarboxylation affords diamines 4-8, which are freed from the metal upon mild oxidative workup.

Vicinal diamines are recurring structural motifs in biologically active compounds,^{39–44} are useful chiral auxiliaries and ligands in asymmetric synthesis,^{45–49} are intermediates

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in the synthesis of N-heterocyclic carbene ligands,⁵⁰ and find application in radiopharmaceuticals.^{51,52} The reductive coupling of imines to vicinal diamines, a less studied variant on the well-known pinacol coupling of carbonyl compounds, has been reported using numerous reagents.^{32,50,53-72} Despite the wide range of metal-containing reagents used in these transformations, nickel-based reductants have received little attention. Catalytic nickel(II) iodide has been shown to significantly improve the samarium(II) iodide mediated coupling of imines,⁶⁴ and Rieke Ni, generated in situ, was shown to promote the pinacol coupling of various carbonyl compounds.⁷³ The advantages of the variant reported here include good to excellent yields of vicinal diamines where R^{1}

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and R^2 are any groups. Our route also affords negligible amounts (<5%) of monoamines resulting from reduction of the corresponding imine. Imine reduction to the monoamine is a significant, competitive process in many literature methods. 54,55,58,61,62,74-76

In summary, nickelaoxazolidinones, formed by oxidative coupling of CO2 with aryl imines, afford vicinal diamines in the presence of LiCl. The reactions proceed under mild conditions (4 °C, 1 atm) starting with Ni(COD)₂ or Ni $(acac)_2$ and represent the first organometallic example of reductive imine coupling requiring CO₂. In this system, CO₂ is participatory and is not incorporated in the reaction products. These results represent an important addition to the growing repertoire of metallacycle chemistry derived from CO₂ and unsaturated substrates.

Acknowledgment. We gratefully acknowledge the National Science Foundation (Award Number 0723265), the Ralph M. Parsons Foundation, and the Oak Crest Institute for financial support and the California Institute of Technology for a Summer Undergraduate Research Fellowships (SURF) award (to C.S.). We thank the Ecole Supérieure de Chimie Organique et Minérale (ESCOM, France) for placing students (A.G., L.S., M.B.F., A.-L. V.) in the Oak Crest program and the California Institute of Technology Division of Chemistry and Chemical Engineering for providing access to NMR and MS facilities. We also thank Nathan Dalleska, John A. Moss, Mona Shahgholi, and David Vander Velde for valuable input.

Supporting Information Available: Text, figures, and tables giving information on experimental procedures and spectral data of 10. This material is available free of charge via the Internet at http://pubs.acs.org.

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