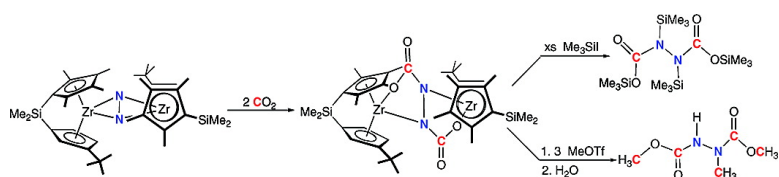


Carboxylation of an *ansa*-Zirconocene Dinitrogen Complex: Regiospecific Hydrazine Synthesis from N and CO

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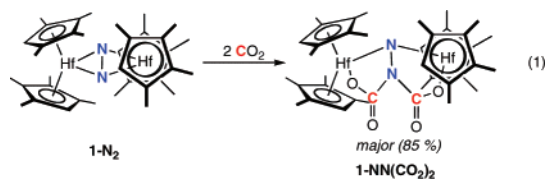
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Dinitrogen, N₂, and carbon dioxide are two abundant and readily accessed atmospheric gases that could, in principle, be useful synthons for organic compounds.¹ The kinetic and thermodynamic stability of both molecules presents significant challenges in designing efficient chemical transformations based on these two potential feedstocks. The discovery of early transition-metal dinitrogen compounds with four electron reduced, [N₂]⁴⁻ ligands²⁻⁴ offers the potential to form new nitrogen-carbon bonds using CO₂ by both cycloaddition⁵ and insertion-type pathways.⁶ Here we describe the regioselective synthesis of *N,N'*-dicarboxylated hydrazines where the selectivity of the N-C bond forming reaction is controlled by a C₂-symmetric *ansa*-zirconocene compound.⁷

Our laboratory has previously reported that the hafnocene dinitrogen complex, [(η⁵-C₅Me₄H)Hf]₂(μ₂, η², η²-N₂) (**1-N₂**), inserted 2 equiv of carbon dioxide to predominately yield **1-NN(CO₂)₂**, where the same nitrogen atom was carboxylated twice (eq 1).⁸ A small amount (~15%) of the *N,N'*-functionalized product was observed. Subsequent treatment of **1-NN(CO₂)₂** with excess Me₃SiI liberated the silylated *N,N'*-dicarboxylated hydrazine. Synthesis of the hafnium congener was inspired by the observation that **1-N₂** has a higher barrier for deleterious side-on, end-on isomerization of the N₂ ligand and is less prone to undergo dinitrogen loss.⁹ Here we report that such functionalization pathways are available to zirconium compounds if the appropriate ligand environment is present.



Based on the hafnium chemistry, our laboratory sought to prepare a zirconocene dinitrogen complex that is resistant to ligand-induced N₂ loss¹² and mimics the carboxylation chemistry of **1-N₂**. The configurational stability and well-established¹⁰ electronic properties of [Me₂Si]-bridged *ansa*-zirconocenes made this class of compounds attractive for N₂ carboxylation. We recently reported the diastereoselective synthesis of the dimeric *ansa*-zirconocene dinitrogen complex, [Me₂Si(η⁵-C₅Me₄)(η⁵-C₅H₃-3-^tBu)Zr]₂(μ₂, η², η²-N₂) (**2-N₂**).¹¹ Both X-ray crystallography and multinuclear NMR studies established sole formation of the C₂ symmetric, homochiral dimer. We were pleased to find that **2-N₂** undergoes extremely slow exchange with ¹⁵N₂ gas, establishing a high barrier for ligand-induced side-on, end-on isomerization.¹¹ In fact, **2-¹⁵N₂** is best prepared from Na(Hg) reduction of the zirconocene diiodide, **2-I₂**, in the presence of ¹⁵N₂. Use of the zirconocene diiodide rather than the dichloride precursor eliminates trace contamination from zirconium(III) monohalide compounds that interfere with subsequent CO₂ chemistry.

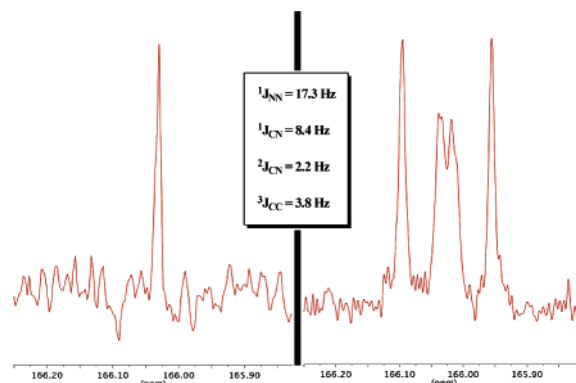
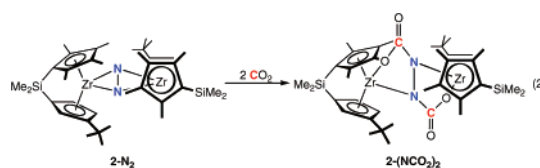


Figure 1. Partial benzene-*d*₆ ¹³C NMR spectrum of **2-(N¹³CO₂)₂** (left) and **2-(¹⁵N¹³CO₂)₂** (right).

Addition of 2 equiv of CO₂ to a green pentane solution of **2-N₂** resulted in immediate formation of an orange precipitate identified as the CO₂ insertion product, **2-(NCO₂)₂**, where N₂ carboxylation has occurred at each nitrogen atom (eq 2). Addition of 1 equiv of CO₂ to **2-N₂** resulted in 50% conversion to **2-(NCO₂)₂**.



Special care must be exercised in handling **2-(NCO₂)₂** as decomposition to insoluble and unidentified products occurred over the course of hours (*t*_{1/2} ~ 30 min) in benzene-*d*₆ solution at 23 °C. Once isolated as a solid, **2-(NCO₂)₂** is stable for weeks in an inert atmosphere. Similar behavior was observed for the hafnocene complex, **1-NN(CO₂)₂**, although solution decomposition occurred on the time scale of days under similar conditions.⁸

Although the instability of **2-(NCO₂)₂** has thus far precluded structural determination by X-ray diffraction, multinuclear NMR experiments, IR spectroscopy, combustion analysis, and reactivity studies definitively establish the regiochemistry of dinitrogen carboxylation. The benzene-*d*₆ ¹H NMR spectrum of **2-(NCO₂)₂** exhibits the number of resonances expected for a C₂ symmetric dimeric zirconocene. Likewise, a single ¹³C resonance was observed at 166.0 ppm, which splits into an AA'XX' pattern upon labeling with ¹⁵N₂ gas (Figure 1). Simulating the data yielded coupling constants similar in magnitude to those reported for **1-NN(CO₂)₂**,⁸ confirming N₂ carboxylation.

¹⁵N NMR spectroscopy also established functionalization of each nitrogen atom. A single resonance centered at 209.5 ppm was observed, comparable to the value of 184.4 ppm for the carboxylated nitrogen in **1-NN(CO₂)₂**.⁸ If the structure of **2-(NCO₂)₂** was analogous to the hafnocene compound where one nitrogen atom

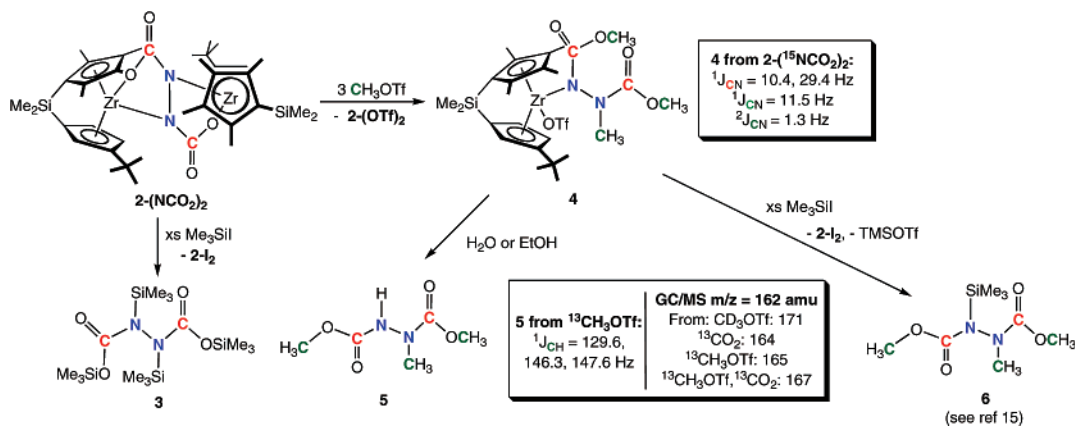


Figure 2. *N,N'*-Dicarboxylated hydrazine synthesis from treatment of 2-(NCO₂)₂ with various electrophiles.

was functionalized twice, *C*₂ symmetry and single ¹³C and ¹⁵N NMR resonances would not be observed. Thus, the *C*₂ symmetry imparted by the *ansa*-zirconocene ligand environment translates onto the regiochemistry of nitrogen carboxylation. The sterically demanding *tert*-butyl substituents likely direct the approach of the inserting CO₂ molecule to the more open lateral positions of the metallocene wedge, although the opposite configuration, whereby the CO₂ inserts *syn* to the 'Bu, has not been definitively eliminated.

Treatment of a benzene-*d*₆ solution of 2-(NCO₂)₂ with excess Me₃SiI rapidly generated 2-I₂ along with *N,N'*-dicarboxylated hydrazine, [(Me₃Si)(Me₃SiO₂C)N]₂ (**3**) (Figure 2). While the mass spectral data of **3** and its ¹³C and ¹⁵N isotopologues are identical to that previously reported for the *N,N*-isomer, the multinuclear NMR spectroscopic data are distinctly different and firmly establish its identity as the *N,N'*-dicarboxylated isomer.¹³

Motivated by these findings, the synthesis of other *N,N'*-dicarboxylated hydrazines coupled to a second N–C bond forming reaction was targeted. Treatment of a benzene-*d*₆ solution of 2-(NCO₂)₂ with 3 equiv of CH₃OTf furnished a 1:1 ratio of the zirconocene bis(triflate), 2-(OTf)₂, and a second zirconium compound, **4**, with new nitrogen–carbon bonds. 2-(OTf)₂ was prepared in a straightforward manner from 2-I₂ and AgOTf. Preparation of various isotopologues of **4** with ¹⁵N₂, ¹³CO₂, ¹³CH₃OTf, and CD₃-OTf along with protonation and 2-D NMR experiments¹³ establish the identity of the product as the *ansa*-zirconocene hydrazido where a total of three new N–C bonds (two from CO₂, one from CH₃-OTf) have been assembled (Figure 2).¹⁴ Because we have been unable to obtain X-ray quality crystals of **4**, the hapticity and the relative stereochemistry of the hydrazido ligand in the zirconocene wedge has not been established.

Although excess methyl triflate is not a sufficiently potent electrophile to cleave to the Zr–N(hydrazido) bond in **4**, free hydrazine, **5**, was obtained upon hydrolysis (Figure 2). A parent ion peak of 162 amu was observed for the natural abundance hydrazine, and the appropriate isotopic perturbations were observed upon preparation of the *d*₉ isotopologue from CD₃OTf, ¹³C₂ isotopologues from independent additions of ¹³CH₃OTf and ¹³CO₂, respectively, and the ¹³C₄ isotopologue from the combination of ¹³CH₃OTf and ¹³CO₂. While excess MeOTf and MeI proved ineffective for removing the free hydrazine (even with heating), addition of excess Me₃SiI to **4** produced a mixture of the previously reported silylated hydrazine, **6**,¹⁵ along with 2-I₂ and Me₃SiOTf (Figure 2).

In summary, a *C*₂-symmetric *ansa*-zirconocene dinitrogen complex promotes selective insertion of 2 equiv of CO₂ into Zr–N bonds resulting in the synthesis of a variety of *N,N'*-dicarboxylated hydrazines from two inert atmospheric gases, N₂ and CO₂. The functionalized product can be treated with silyl- and carbon-based electrophiles to form new N–Si and N–C bonds, respectively.¹⁴ These results open new synthetic pathways for the selective synthesis of organic molecules from abundant chemical feedstocks and demonstrate that such N₂ functionalization with heterocumulenes reactions are available to zirconium.

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Supporting Information Available: Complete ref 1 citation, experimental procedures, and select NMR spectroscopic data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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