

Cobalt Dinitrosoalkane Complexes in the C–H Functionalization of Olefins

Jennifer M. Schomaker, W. Christopher Boyd, Ian C. Stewart, F. Dean Toste,* and Robert G. Bergman*

Department of Chemistry, University of California, Berkeley, California 94720

Received January 29, 2008; E-mail: rbergman@berkeley.edu

Metal-mediated organic reactions can be divided into two broad categories: those proceeding via complexation of a substrate to a metal center and those involving the direct interaction of a substrate with ligands bound to the metal center.¹ Examples of the latter include oxidations by metal oxo compounds such as the Fe=O center in cytochrome P450, the Sharpless dihydroxylation of olefins by OsO₄, the reduction of carbonyl compounds by the Noyori reaction, and the hydrosilylation of carbonyl compounds using a (PPh₃)₃Re(O)₂I catalyst developed by Toste.^{2–5} Shvo has also reported ligand–metal bifunctional hydrogenation catalysts that were later studied extensively by Casey and others.⁶

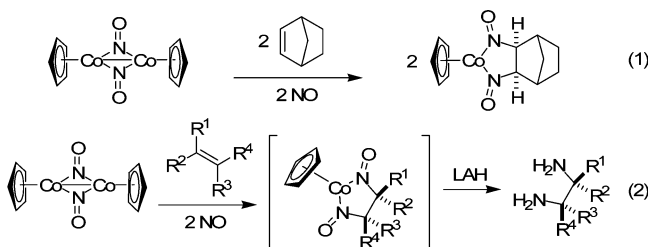
The majority of ligand-attack reactions involve transfer of oxygen and hydrogen to the organic substrate; direct interaction with nitrogen ligands is less frequently encountered. A particularly intriguing example of a nitrogen ligand-based organometallic reaction was described by Brunner in the reaction of norbornene with a cobalt nitrosyl dimer (Scheme 1, eq 1).⁷ Bergman and Becker later demonstrated that cobalt dinitrosyl complexes form direct adducts with a wide range of substituted alkenes, and the overall transformation can be used to generate 1,2-diamines (Scheme 1, eq 2).⁸ In this communication, we report that the ligand-based reactivity of these cobalt dinitrosyl complexes can be used to form a new C–C bond between *unfunctionalized* alkenes and a variety of Michael acceptors.

The proposed mechanism for the use of cobalt dinitrosyl complexes in ligand-based activation of unfunctionalized alkenes toward conjugate addition is shown in Scheme 2. We envisioned the first step to involve the reaction of an olefin with CpCo(CO)₂ in the presence of NO to give cobalt complex **1**, which was previously established to proceed via the intermediacy of CpCo(NO)₂.⁸ Hopefully due to the increased acidity of the protons α to the nitrosyl groups, deprotonation of **1** in the presence of base should occur to generate **2**. The nucleophilic intermediate **2** adds to a Michael acceptor to give the functionalized complex **3**. In the final step, an unusual (but precedented) retrocycloaddition reaction in the presence of excess olefin regenerates the original complex **1**, releasing the functionalized alkene product **4**.⁸

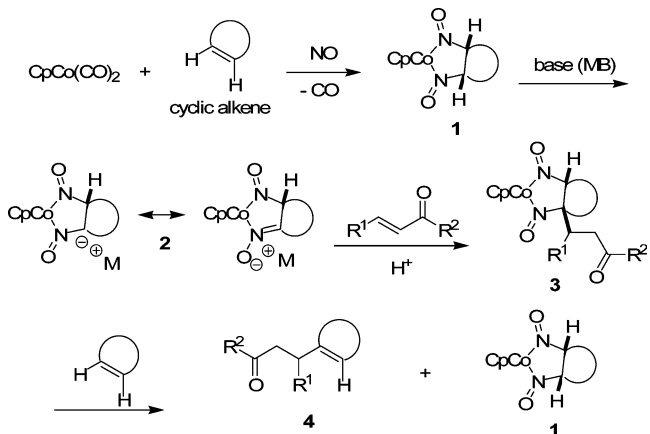
To begin our studies, a variety of stable, isolable cobalt dinitrosoalkane complexes were synthesized by directly treating cobalt dicarbonyl complex **5** with an excess of alkene in the presence of NO (Table 1).⁸

We initially investigated the possibility of forming the anion of the cobalt dinitrosoalkane complex using the silyl complexes **8** and **9** (Table 2). The use of a fluoride source to desilylate a C–Si bond is a common, very mild method for generating a carbon-based anion.⁹ In addition, alkenes in the form of aryl/alkenyl organosiloxanes and boronic esters have been utilized in Pd-, Ru-, or Rh-catalyzed additions to α,β-unsaturated carbonyl compounds.¹⁰ Indeed, treatment of the cobalt dinitrosoalkanes **8** and **9** with Bu₄NF (TBAF) or (NMe₂)₃SSiMe₃F₂ (TASF) in the presence of a Michael acceptor gave the desired products. The use of a com-

Scheme 1. Cobalt Dinitrosoalkane Complexes



Scheme 2. Functionalization of Olefins Using Cobalt Dinitrosoalkane Complexes



mercial solution of TBAF in THF with the less electron-rich Cp group gave moderate yields of the desired conjugate addition products. It was necessary to utilize anhydrous TASF when the cobalt complexes containing the more electron-rich Cp* ligand (Table 2) was treated with Michael acceptors in the presence of a fluoride source.

Having established the viability of forming the anion of the cobalt dinitrosoalkane complex, we turned our efforts toward using unsilylated precursors. Initial attempts to deprotonate the norbornene-derived cobalt complex **7a** using a variety of bases in the presence of a Michael acceptor gave poor yields and decomposition of **7a**. Among the bases screened were Et₃N, DABCO, DBU, and *n*BuLi as well as hydroxides, hydrides, carbonates, and hexamethyldisilazides. KHMDS was the only base found to give the desired conjugate addition product **12**, albeit with a low yield of 21%. Further extensive screening of conditions for the Michael addition yielded LHMDS as the optimum base and a mixture of 5:1 THF/HMPA as the best solvent. In the hope that additives might promote the reaction, a series of Lewis acids was also evaluated. The use of Sc(OTf)₃ as the Lewis acid resulted in an increased yield of the desired product **12** from an initial 39–82% (Table 3).¹¹

The anion of cobalt dinitrosoalkane **7a** was added to a variety of conjugated acceptors using LHMDS as the base, Sc(OTf)₃ as the Lewis acid, and 5:1 THF/HMPA as the solvent to determine

Table 1. Synthesis of Cobalt Dinitrosoalkane Complexes

| entry | alkene | product | yield | entry | alkene | product | yield | |
|-------|--------|-----------|-----------|-------|--------|---------|---------------------|-----|
| 1 | | 6a | 7a | 89% | 7 | | 6g 7g | 77% |
| 2 | | 6b | 7b | 77% | 8 | | 6h 7h | 66% |
| 3 | | 6c | 7c | 87% | 9 | | 6i 7i | 92% |
| 4 | | 6d | 7d | 44% | 10 | | 6j 7j | 72% |
| 5 | | 6e | 7e | 78% | 11 | | 6k 7k | 19% |
| 6 | | 6f | 7f | 74% | 12 | | 6l 7l | 64% |

Table 2. Reaction of Silylated Cobalt Dinitrosoalkane Complexes with Michael Acceptors in the Presence of a Fluoride Source

| entry | substrate | F source | product (Cp', n) | yield |
|-------|-----------|----------|---------------------|-------|
| 1 | 8 | TBAF | 10a (Cp, 1) | 65% |
| 2 | 9 | TASF | 11a (Cp*, 1) | 61% |
| 3 | 8 | TBAF | 10b (Cp, 2) | 76% |
| 4 | 9 | TBAF | 11b (Cp*, 2) | 32% |
| 5 | 9 | TASF | 11b (Cp*, 2) | 65% |

*Reactions using TBAF were performed in THF; reactions using TASF were carried out in 1,2-dimethoxyethane.

Table 3. Evaluation of Lewis Acids

| entry | Lewis acid | yield | entry | Lewis acid | yield |
|-------|-----------------------------------|-------|-------|----------------------|-------|
| 1 | none | 39% | 7 | Hf(OTf) ₄ | 61% |
| 2 | B(OMe) ₃ | 57% | 8 | Sc(OTf) ₃ | 82% |
| 3 | B(OPr) ₃ | 66% | 9 | Y(OTf) ₃ | 39% |
| 4 | B(OPh) ₃ | 18% | 10 | Yb(OTf) ₃ | 61% |
| 5 | BF ₃ ·OEt ₂ | 0% | 11 | Zn(OTf) ₂ | 70% |
| 6 | Cu(OTf) ₂ | 34% | 12 | ZnCl ₂ | 52% |

the electrophile scope. The majority of the electrophiles gave the product as one major diastereomer (Table 4).

To determine the range of alkenes that would participate in this reaction, the cobalt dinitrosoalkanes from Table 1 were screened

Table 4. Conjugate Addition Reactions of **7a**

| entry | E ⁺ | product | dr | isolated yield |
|-------|----------------|------------|-------|-------------------|
| 1 | | 13a | > 9:1 | 69%* |
| 2 | | 12 | > 9:1 | 75-82% |
| 3 | | 13b | 3:1 | 70% |
| 4 | | 13c | 1:1 | 81% |
| 5 | | 13d | > 9:1 | 99%* |
| 6 | | 13e | 2.4:1 | 74% |
| 7 | | 13f | – | 53% disubstituted |
| 8 | | 13g | > 9:1 | 31% |
| 9 | | 13h | 4:1 | 65% |

*Based on recovered starting material.

using 2-cyclohexen-1-one, **A**, or phenyl vinyl sulfone, **B**, as the electrophile (Table 5). Cobalt complexes derived from strained ring systems, such as those containing the [2.2.1]bicycloheptane framework (**7a–c**, Table 5), reacted smoothly to give good yields of the desired products. The new complexes were monosubstituted using **A** as the electrophile (entries 1, 3, and 5) and disubstituted using the less sterically hindered **B** as the Michael acceptor (entries 2 and 4). Substrate **7d** did not react with **A** but gave 50% yield of the disubstituted **15d** using **B** as the electrophile, possibly due to steric effects. The complex formed from *endo* dicyclopentadiene (**7e**) did not undergo Michael addition, but the *exo* complex **7f** did, presumably due to decreased steric interactions. Substrate **7g** was unstable under the basic reaction conditions and did not give useful yields of the product **14g**, even when the reaction temperature was reduced to -78 °C. Cobaltacycle **7h**, formed from highly strained cyclobutene, also gave good yields of conjugate addition products albeit as a 2:1 mixture of diastereomers (entries 11 and 12). Finally, cobalt dinitrosoalkane complexes containing a variety of five-membered rings (**7i–l**) gave products that were obtained in moderate yields but had to be handled quickly due to their propensity to decompose in solution (entries 13–17).

To complete the overall transformation illustrated in Scheme 1, it was necessary to show that treatment of products with an excess of starting olefin could displace the functionalized alkene and regenerate the starting complex.⁸ For example, treatment of **12** with an excess of norbornene at 90 °C gave a nearly quantitative yield of the functionalized alkene **17** by ¹H NMR and regenerated the starting cobalt complex **7a** (Table 6, entry 1). The complex **14b** formed from highly strained norbornadiene required elevated temperatures for retrocycloaddition (entry 2), but additional substitution α to the nitrosyl group attenuated the temperature required for releasing the product alkene **19** (entry 3), perhaps due to steric effects. The cobalt complex **16** required much lower temperatures for the retrocycloaddition reaction with cyclopentene (entry 4).

Table 5. Conjugate Addition Reactions of Cobalt Dinitrosoalkanes

| entry | complex (parent alkene) | product | R ¹ | R ² | yield |
|-------|-------------------------|------------|---|---|-------|
| 1 | 7a | 12 | | -H | 82% |
| 2 | 7a | 15a | | | 56% |
| 3 | 7b | 14b | -C ₆ H ₅ O | -H | 69% |
| 4 | 7b | 15b | -(CH ₂) ₂ SO ₂ Ph | -(CH ₂) ₂ SO ₂ Ph | 61% |
| 5 | 7c | 12 | -C ₆ H ₅ O | -H | 62% |
| 6 | 7d | 14d | -C ₆ H ₅ O | -H | 0% |
| 7 | 7d | 15d | -(CH ₂) ₂ SO ₂ Ph | -(CH ₂) ₂ SO ₂ Ph | 50% |
| 8 | 7e | 14e | -C ₆ H ₅ O | -H | 0% |
| 9 | 7f | 14f | -C ₆ H ₅ O | -H | 73% |
| 10 | 7g | 14g | -C ₆ H ₅ O | -H | 15% |
| 11 | 7h | 14h | -C ₆ H ₅ O | -H | 79% |
| 12 | 7h | 15h | -(CH ₂) ₂ SO ₂ Ph | -(CH ₂) ₂ SO ₂ Ph | 51% |
| 13 | 7i | 14i | -C ₆ H ₅ O | -H | 48% |
| 14 | 7j | 14j | -C ₆ H ₅ O | -H | 57% |
| 15 | 7j | 15j | -(CH ₂) ₂ SO ₂ Ph | -(CH ₂) ₂ SO ₂ Ph | 40% |
| 16 | 7k | 14k | -C ₆ H ₅ O | -H | 37% |
| 17 | 7l | 14l | -C ₆ H ₅ O | -H | 61% |

Table 6. Retrocycloaddition Reactions

| entry | complex | alkene | temp | product | yield |
|-------|---------------------------|--------|--------|-----------|--------|
| 1 | 12 | | 90 °C | 17 | 95%* |
| 2 | 14b | | 120 °C | 18 | 80% |
| 3 | 15b | | 86 °C | 19 | > 90%* |
| 4 | Me₄CpCo | | 75 °C | 20 | 92%* |

16, R = -(CH₂)₂SO₂Ph

*Yields determined by ¹H NMR using mesitylene as an internal standard.

In conclusion, we have demonstrated the use of the ligand-based reactivity of a series of cobalt dinitrosyl complexes for the C–H functionalization of alkenes. Although the alkene scope is still somewhat limited, and we have not yet achieved catalytic turnover, the formation of intermediate cobalt dinitrosoalkane complexes allows for the utilization of masked alkenes as nucleophiles in conjugate addition reactions. The resulting new cobaltacycles can then undergo retrocycloaddition reactions in the presence of the original alkene to regenerate the starting cobalt dinitrosoalkane complex and release the functionalized alkenes. Future studies are directed toward expansion of the scope of the reaction, rendering the reaction asymmetric, and efforts to carry it out under catalytic conditions.

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Supporting Information Available: Experimental procedures and spectral information for all new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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