

## Samarium-Mediated Functionalization of N=N Bonds: Double Insertion of Carbon Monoxide into the N=N Bond of Azobenzene<sup>1</sup>

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The insertion of carbon monoxide into a metal-carbon bond and olefin metathesis are two fundamental reactions in organometallic chemistry.<sup>3,4</sup> These reactions and their analogues are central to many important stoichiometric and catalytic organometallic transformations. We have recently discovered a new samarium(II)-based reaction which combines CO activation and the multiple-bond breaking and making typical in metathesis reactions. We describe here this remarkable transformation in which an N=N double bond is broken and two N—C bonds and a C—C bond are formed in a single reaction.

(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Sm(THF)<sub>2</sub><sup>5</sup> reacts with C<sub>6</sub>H<sub>5</sub>N=NC<sub>6</sub>H<sub>5</sub> to form a compound identified by X-ray crystallography as [(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Sm](C<sub>6</sub>H<sub>5</sub>)N=N(C<sub>6</sub>H<sub>5</sub>)[Sm(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>] (I).<sup>6</sup> The reductively distorted azobenzene unit found in I contains a 1.25 (1) Å NN bond which is the same length as the 1.247 (3) Å NN double-bond length found in azobenzene.<sup>6</sup> Dark blue I (120 mg, 0.12 mmol) reacts with carbon monoxide at 80 psi over a 1-day period in 10 mL of THF in a 3-oz Fisher-Porter aerosol reaction vessel to form a green solution from which II (100 mg) can be obtained.<sup>7</sup> II was characterized by complexometric metal analysis and <sup>1</sup>H NMR, <sup>13</sup>C NMR, visible, and IR spectroscopy<sup>8</sup> and was identified as (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Sm[μ,η<sup>4</sup>-(PhN)OCCO(NPh)]Sm(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub> by X-ray crystallography.<sup>9</sup> The <sup>1</sup>H NMR spectrum of the bulk reaction product shows that II is the major product with an overall yield of 80%.

Green crystals of II grown overnight from toluene at -30 °C have the structure shown in Figure 1. The molecule has crystallographic C<sub>2h</sub> symmetry with the mirror plane containing C(1), N(1), O(1), Sm(1), and the phenyl rings. The C<sub>2</sub> axis bisects the C(1)–C(1<sup>2</sup>) bond. The pentamethylcyclopentadienyl rings are in the highly unusual eclipsed conformation.<sup>10</sup>

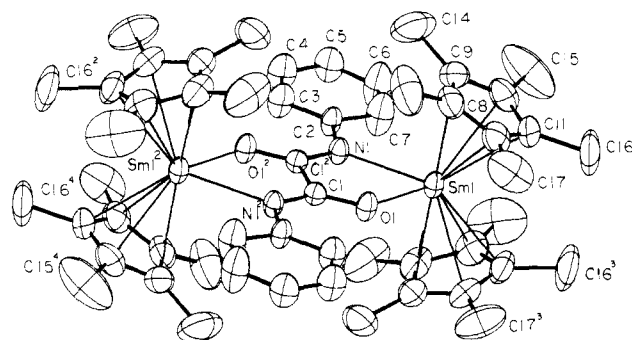
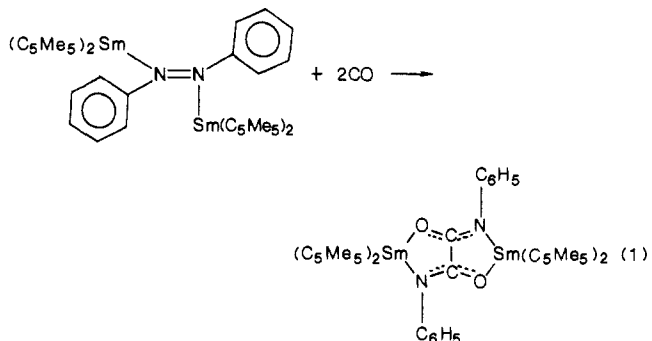


Figure 1. ORTEP plot of [(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Sm]<sub>2</sub>[μ,η<sup>4</sup>-(PhN)OCCO(NPh)]. Thermal ellipsoids are shown at 50% probability. Atoms without superscript labels are related to atoms with superscript 2 by a C<sub>2</sub> axis and to atoms with superscript 3 by a mirror plane. Superscript 4 atoms are related to superscript 3 atoms by a C<sub>2</sub> axis.

The structure of II indicates that two molecules of carbon monoxide formally have been inserted into the NN double bond of azobenzene as shown in eq 1. The C(1)–C(1<sup>2</sup>) distance of 1.57



(2) Å is that of a single bond and the C(1)–O(1) and C(1)–N(1) distances, 1.26 (1) and 1.31 (1) Å, respectively, are consistent with multiple-bond character delocalized over the N–C–O unit.<sup>11</sup> The Sm–O(1) distance of 2.30 (1) Å and the Sm–N(1) distance of 2.49 (1) Å are longer than typical trivalent Ln–OR and Ln–NR<sub>2</sub> single-bond distances, but they are shorter than R<sub>2</sub>O→Ln and R<sub>3</sub>N→Ln donor-bond lengths.<sup>12</sup> The μ,η<sup>4</sup>-[(PhN)OC]<sub>2</sub> unit is formally related to *N,N'*-diphenyloxamide by double deprotonation.

The overall transformation accomplished by treating azobenzene with (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Sm(THF)<sub>2</sub> and then CO is shown in eq 2. The short NN bond in II has been completely cleaved with the generation of two CN bonds and a C–C single bond. This type of bond breaking and bond making involving two carbon and two nitrogen atoms is unusual in organometallic reactions involving four centers. This reaction is furthermore unusual in that the reactivity of II is centered not on its distorted, long C–N bonds

(1) Reported in part at the Seventeenth Rare Earth Research Conference, Hamilton, Ontario, Canada, June 12, 1986.

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(7) All manipulations must be done in the absence of oxygen and water.

(8) Anal. Calcd for [(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Sm]<sub>2</sub>(C<sub>14</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub>): Sm, 27.9. Found: Sm, 27.6. <sup>1</sup>H NMR (C<sub>2</sub>D<sub>8</sub>O) δ 1.84 (s, C<sub>5</sub>Me<sub>5</sub>), resonances attributable to the aryl protons were observed but could not be definitively assigned; <sup>13</sup>C NMR (C<sub>2</sub>D<sub>8</sub>O) 121.41 (C<sub>5</sub>Me<sub>5</sub>, s) 20.12 (C<sub>5</sub>Me<sub>5</sub>, q, J<sub>C-H</sub> = 125 Hz), resonances from the aryl carbons were not observed; IR (KBr) 2940 s, 2900 s, 2860 s, 1590 s, 1570 s, 1540 s, 1495 s, 1450 s, 1380 s, 1340 s, 1260 m, 1200 m, 1170 m, 1100 m, 1020 m, 800 m, 760 m, 680 m cm<sup>-1</sup>; the visible spectrum in toluene contained no distinct maxima; extinction coefficients of the tail of the UV absorption were 50 at 600 nm, 130 at 500 nm, and 700 at 400 nm.

(9) The space group is *A2/m* (nonstandard setting of *C2/m*) with *a* = 15.961 (3) Å, *b* = 14.204 (5) Å, *c* = 15.612 (8) Å, β = 118.14 (3)°, *Z* = 2 for C<sub>calcd</sub> 1.25 g cm<sup>-3</sup>. Least-squares refinement on the basis of 2151 observed reflections converged to a final *R* = 0.053. All non-hydrogen atoms except the toluene carbon atoms were refined anisotropically and no hydrogen atoms were included.

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(12) Based on data in ref 6 and 13–19. The average Sm–C(ring) distance of 2.71 (1) Å is typical for eight-coordinate trivalent (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Sm(X)(Y) complexes.<sup>14</sup>

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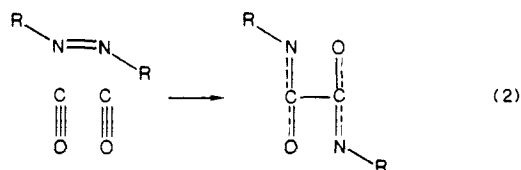
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(1.56 (2) and 1.61 (1) Å vs. a normal 1.42 Å) or its long ortho C-H bonds (stretched by an agostic interaction with samarium), but on the shortest bond in the system, namely, the N=N unit.<sup>4</sup> The utility of this reaction in the derivatization of organic heterocycles<sup>11,20</sup> and in the more general area of organometallic heteroatomic metathesis reactions is under study.

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**Supplementary Material Available:** Tables of crystal data, bond distances, bond angles, final fractional coordinates, and thermal parameters (5 pages); table of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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## Synthesis, Structure, and Reactions of a Zirconocene-Cyclohexyne Complex

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Transition metals have the unique ability to simultaneously stabilize high-energy organic species and to activate them toward selective attack by a variety of chemical reagents. Cyclooctyne is the smallest cycloalkyne to have been prepared in the free state while cycloheptyne and cyclohexyne have been observed as fleeting intermediates by several methods.<sup>1</sup> Several years ago, Bennett and co-workers reported the trapping of in situ generated cyclohexyne and cycloheptyne as their bis(triphenylphosphine)platinum complexes.<sup>2</sup> To date these are the only examples of transition-metal-small-ring cycloalkyne complexes to be reported. We now report the preparation, the X-ray crystal structure, and a number of reactions of the trimethylphosphine adduct of the zirconocene-cyclohexyne complex.

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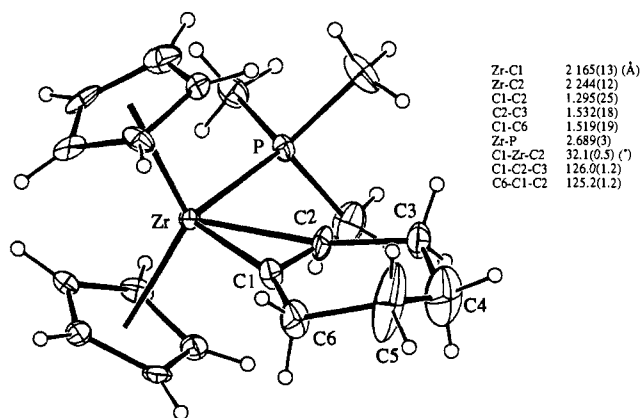
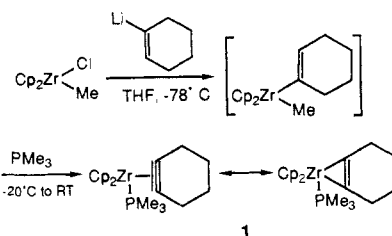
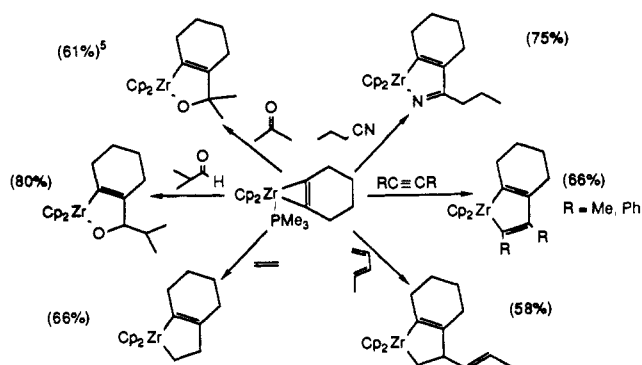


Figure 1. Molecular structure of 1, with selected bonds and angles.

### Scheme I



### Scheme II



The trimethylphosphine adduct of the zirconocene-cyclohexyne complex can be prepared as shown in Scheme I. Yields of 60% of 1 as analytically pure material are obtained in this manner, after recrystallization from ether. Compound 1 has been characterized by <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR, elemental analysis, and X-ray crystallography. Each unit cell contains eight molecules, four each of two independent molecules which are nearly identical within experimental error (3σ). Shown in Figure 1 is one of these two molecules, along with important bond angles and distances (average values for the two molecules). Of greatest interest is the carbon-carbon multiple bond length which averages 1.295 (25) Å. This value is essentially identical with that seen in Bennett's platinum complex.<sup>2</sup> As in that case, a significant amount of back-bonding is apparent causing the carbon-carbon bond length to be between that expected for a simple carbon-carbon double<sup>4a</sup> and triple bond.<sup>4b</sup> That the "cyclohexyne" fragment experiences ring strain only to a small extent can also be seen from the C1-C2-C3 and C6-C1-C2 bond angles of 125.2 (1.2)° and 126.0 (1.2)° which deviate only to a small extent from that observed for simple olefins.<sup>4a</sup> Again, this is very similar to what is observed for the platinum complex.

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