JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

COMMUNICATION

pubs.acs.org/JACS

Activation of CO_2 by a Heterobimetallic Zr/Co Complex

Jeremy P. Krogman, Bruce M. Foxman, and Christine M. Thomas*

Department of Chemistry, Brandeis University, 415 South Street, MS 015, Waltham, Massachusetts 02454, United States

Supporting Information

ABSTRACT: At room temperature, the early/late heterobimetallic complex $Co(^iPr_2PNMes)_3Zr(THF)$ has been shown to oxidatively add CO_2, generating $(OC)Co(^iPr_2PNMes)_2(\mu\text{-}O)Zr(^iPr_2PNMes)$. This compound can be further reduced under varying conditions to generate either the Zr oxoanion $(THF)_3Na{-}O{-}Zr(MesNP^iPr_2)_3Co(CO)$ or the Zr carbonate complex $(THF)_4Na_2(CO_3)\text{-}Zr(MesNP^iPr_2)_3Co(CO)$. Additionally, reactivity of the CO_2-derived product has been observed with $PhSiH_3$ to generate the Co-hydride/Zr-siloxide product $(OC)(H)Co(^iPr_2PNMes)_3ZrOSiH_2Ph$.

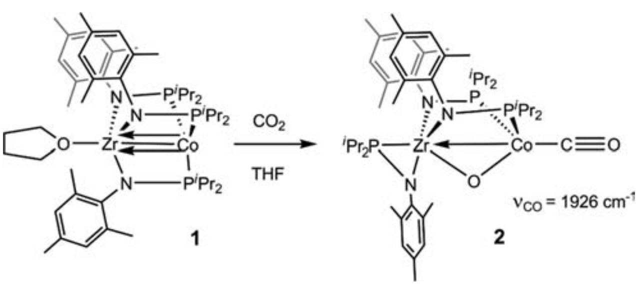
Carbon dioxide has received recent interest as an abundant, economical, and renewable raw material as a C_1 feedstock, a useful organic building block, and a key player in the water-gas shift reaction.[1−5] Along these lines, well-characterized transition metal complexes that activate CO_2 in a well-defined manner have become increasingly desirable targets. Despite recent advances in CO_2 activation by both early and late transition metals, there remains a single example of a well-defined homogeneous catalyst for CO_2 reduction—an N-heterocyclic carbene-supported copper boryl complex reported by Sadighi et al.[6]

Many examples of Zr-promoted CO_2 activation in which CO_2 inserts into a Zr-alkyl or Zr-hydride bond have been reported.[7,8] Disproportionation of CO_2 by Group IV complexes has been reported to give different products based on the nature of the metal center.[9,10] For example, while $Cp_2Ti(CO)_2$ reacts with CO_2 to generate CO and the carbonate-bridged $[(Cp_2Ti)_2(CO_3)]_2$, the corresponding Zr derivative $Cp_2Zr(CO)_2$ reacts with CO_2 to generate CO and the oxo-bridged trimer $(Cp_2ZrO)_3$.[9] Notably, these reactions require elevated temperatures, vast excesses of CO_2, and prolonged reaction times.

Several recent reports of reductive C−O bond cleavage by electron-rich late first row transition metals have been recently reported. These examples include a Ni^0 N-heterocyclic carbene complex that binds and deoxygenates CO_2,[11] reductive disproportionation of CO_2 to CO and CO_3^{2-} by an Fe^I β-diketiminate complex,[12] and an Fe^I tris(phosphine) system capable of CO_2 reductive cleavage and C−C coupling reactions.[13] However, none of these reports addressed the further reactivity of the CO_2-derived products toward further functionalization.

In addition to transition metal mediated CO_2 activation, it has recently been shown that main group Lewis acid/base pairs are capable of activating and functionalizing CO_2.[14−17] Similar Lewis acid/base interactions are also found in early/late heterobimetallic complexes.[18−20] While no examples of C−O bond cleavage by early/late heterobimetallics have been reported to date, there is precedent for CO_2 activation involving insertion of CO_2 into polar metal−metal bonds.[18,21,22] Our group has recently been exploring phosphinoamide-bridged heterobimetallic Zr/Co complexes of the general form $ICo(R_2PNR')_3ZrCl$.[23−26] The dative Co→Zr interactions in these complexes facilitate two electron reduction at potentials ca. 1 V more positive than analogous monometallic Co complexes.[23] The two-electron reduction products, such as $Co(^iPr_2PNMes)_3Zr(THF)$ (**1**) (Scheme 1),[24] feature highly polar metal−metal multiple bonds and are capable of activating small molecules such as alkyl halides and H_2.[25,26] Herein, we report the reactivity of **1** with CO_2 and the further reactivity of this CO_2 activation product.

Scheme 1



Treatment of **1** with one equivalent of CO_2 in THF at low temperature leads to clean formation of $(OC)Co(^iPr_2PNMes)_2(\mu\text{-}O)Zr(^iPr_2PNMes)$ (**2**), in which one of the C═O double bonds of CO_2 has oxidatively added across the metal−metal multiple bond in **1** (Scheme 1). Complex **2** is a paramagnetic complex ($S = 1$, $\mu_{eff} = 2.99\ \mu_B$) with a characteristic infrared $\nu(CO)$ at 1926 cm^{-1}. Notably, one phosphinoamide ligand has dissociated from Co and is bound η^2 to Zr to accommodate the bridging oxo ligand. The ^1H NMR spectrum of **2** is broad and paramagnetically shifted, but the appropriate number of resonances to indicate two inequivalent types of phosphinoamide ligands can be readily identified (Figure S1, Supporting Information). Treatment of **1** with excess CO_2 and treatment of the NaX salt $N_2Co(^iPr_2PNMes)_3Zr\text{-}X\text{-}Na(THF)_5$ with stoichiometric CO_2 both lead to intractable mixtures of products, likely the result of CO_3^{2-} formation. The structure obtained via single crystal X-ray diffraction of **2** is shown in Figure 1. The oxo ligand is nearly symmetrically bridging between the Zr and Co centers. The Zr−Co interatomic distance is significantly elongated

Received: July 31, 2011
Published: August 29, 2011

dx.doi.org/10.1021/ja2071847 | J. Am. Chem. Soc. 2011, 133, 14582–14585

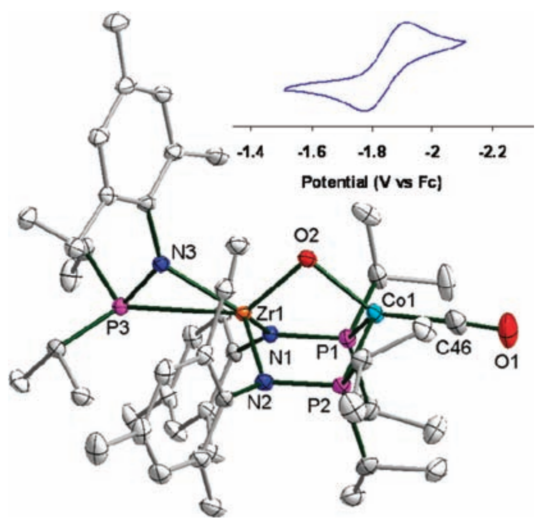
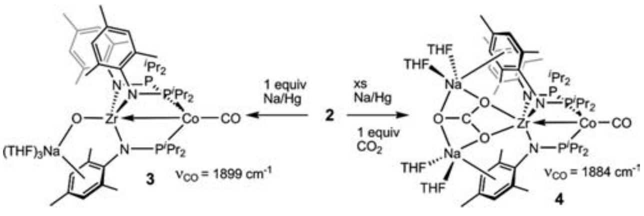


Figure 1. Displacement ellipsoid representation of **2**. Relevant interatomic distances (Å) and angles (deg): Zr1−Co1, 2.8865(5); Zr1−O2, 1.8764(18); Co1−O2, 1.9161(19); Co1−C46, 1.783(3); Zr1−O2−Co1, 99.12(9); Co1−C46−O1, 177.4(3). (Top right) Cyclic voltammogram of **2** (in 0.4 M [^{n}Bu$_4$N][PF$_6$] in THF; scan rate: 100 mV/s).

Scheme 2



(2.8865(5) Å), indicative of very weak, if any, interaction between the two metal centers.

Zirconium oxo moieties are typically bridging and, thus, relatively unreactive. Terminal Zr(IV)═O intermediates have been generated in situ and trapped.[27−29] Moreover, Parkin and co-workers reported the only isolated terminal zirconium oxo to date, (η^5-C$_5$Me$_4$Et)$_2$Zr(═O)(pyridine),[30,31] and the Li-coordinated oxo-anion [Cp*$_2$Zr(H)(OLi(THF)$_2$]$_2$ has been reported by Stephan and co-workers.[33] While the terminal Zr═O fragment is highly reactive,[30,31] Kawaguchi and co-workers have also shown that trimethylsilyl moieties are useful for deoxygenating bridging Zr−O−Zr species via thermodynamically favorable formation of (Me$_3$Si)$_2$O.[32] In the case of the Co−O−Zr heterobimetallic complex **2**, the electronic disparities between the two metal centers spanned by the oxo ligand are anticipated to enhance its reactivity even further.

Complex **2** was investigated using cyclic voltammetry (CV) to ascertain whether **2** could be rereduced at mild potentials. The CV of **2** revealed a fully reversible reduction at −1.85 V (Figures 1 and S5, Supporting Information). Chemical reduction of **2** with 1 equiv Na/Hg leads to formation of the unusual Zr-oxoanion (THF)$_3$Na−O−Zr(MesNP^{i}Pr$_2$)$_3$Co(CO) (**3**) in 24% yield (Scheme 2), among other products. One-electron reduced complex **3** has a substantially lower infrared ν(CO) than **2** (1899 cm^{-1}). Despite the S = $^1/_2$ ground state of **3** (μ_{eff} = 2.00 μ_B), the ^{1}H NMR features are reasonably sharp and shifted only slightly beyond the typical range for diamagnetic species (Figure S2, Supporting Information). The solid state structure of **3** reveals rearrangement to a 3-fold symmetric structure as the previously bridging oxo ligand now occupies a terminal position on Zr while the Zr-bound η^2-phosphinoamide ligand of **2** recoordinates to the Co center in **3** (Figure 2). The Na$^+$ countercation associates strongly with the Zr-bound oxo (Na−O: 2.24(1) Å) and three THF solvate molecules, and fulfills its coordination sphere with a π-interaction to a nearby mesityl substitutent. The Zr−O distance is elongated by comparison to Parkin's terminal Zr═O and Stephan's Zr oxide anion (2.074(4)Å vs 1.804(4) Å and 1.847(9) Å)[31,33] owing to the strong interaction with Na$^+$.

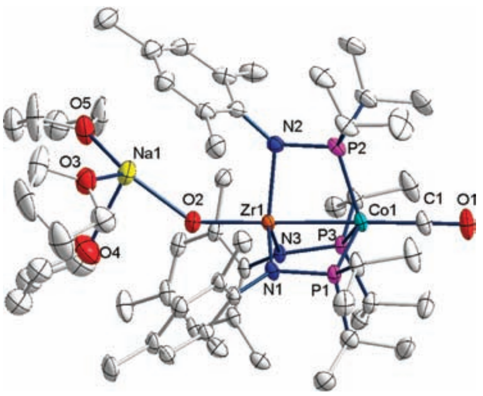


Figure 2. Displacement ellipsoid (50%) representation of **3**. Hydrogen atoms have been omitted for clarity. Relevant interatomic distances (Å) and angles (deg): (avg of 2 molecules in asymmetric unit): Zr1−Co1, 2.5333(5); Zr1−O2, 2.074(4); Co1−C1, 1.740(3); Na1−O2, 2.24(1); Zr1−O2−Na1, 142(1).

Reduction of **2** with excess Na/Hg results in a mixture of products, most notably **3** and the diamagnetic doubly reduced κ^2-CO$_3^{2-}$ dianion (THF)$_4$Na$_2$(CO$_3$)-Zr(MesNP^{i}Pr$_2$)$_3$Co(CO) (**4**, Scheme 2). Appreciable amounts of complex **4** are also observed in the aforementioned reaction with one equivalent of reductant. On the basis of the stoichiometry of this reaction, the isolated yield of **4** is necessarily low, and additional reduced products devoid of CO must be formed; indeed, infrared spectra of the crude reaction mixture reveal stretches around 2040 cm^{-1}, indicative of N$_2$-bound reduced Zr/Co species. Likewise, a higher yield of **4** can be obtained directly via reduction of **2** in the presence of an additional equivalent of CO$_2$. Complex **4** has a slightly lower ν(CO) than **3**, owing to its more reduced nature (1884 cm^{-1}), and characteristic IR stretches for the carbonate moiety are observed at 1684 and 1645 cm^{-1}. The solid state structure of **4** reveals a terminal carbonate bound to Zr in a bidentate fashion, with two Na$^+$ countercations also bound in a κ^2-fashion to the CO$_3^{2-}$ unit (Figure 3). Each Na$^+$ cation is also ligated by two THF solvate molecules and engages in a π-interaction with a mesityl substitutent, similar to that observed in the solid state structure of **3**. A similar coordination motif has been observed in a K$_2$CO$_3$ tris(pyrazolyl)borate Cu complex.[34]

While only one well-defined Zr oxoanion has been reported,[33] several Ti oxoanions have been discussed in the recent literature.[35−37] Recently, Cummins and co-workers reported the Ti oxoanion [((^{t}Bu)(3,5-Me$_2$C$_6$H$_3$)N)TiO][Li(Et$_2$O)$_2$] and its reactivity with CO$_2$ to form the carbonate anion

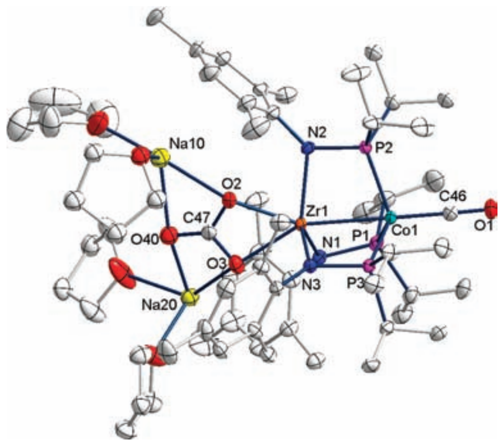
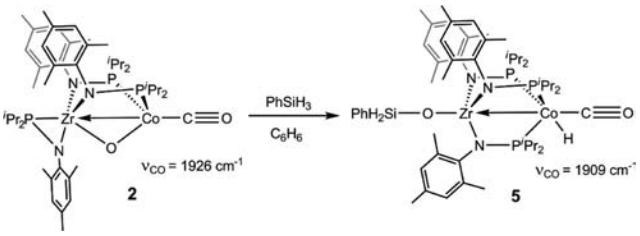


Figure 3. Displacement ellipsoid (50%) representation of **4**. Hydrogen atoms have been omitted for clarity. Relevant interatomic distances (Å) and angles (deg): Zr1−Co1, 2.6111(4); Zr1−O2, 2.254(2); Zr1−O3, 2.257(2); Co1−C46, 1.736(2); C47−O2, 1.303(4); C47−O3, 1.292(4); C47−O40, 1.314(6); O2−Na11, 2.339(3); O40−Na11, 2.355(7); O40−Na20, 2.395(7); O3−Na20, 2.371(4).

Scheme 3



$[((^tBu)(3,5\text{-}Me_2C_6H_3)N)TiOCO_2][Li(Et_2O)_2]$.[35,38] Thus, we can speculate that the mechanism by which **4** is formed is intermolecular and likely involves nucleophilic attack of CO_2 by a terminal Zr-oxo fragment. The mechanism for this reaction, as well as the further reactivity of **3** and **4**, will be the subject of future investigations.

In addition to reduction chemistry, we chose to assess the further reactivity of **2** toward functionalization of the μ-O moiety. Complex **2** was treated with $PhSiH_3$, hoping to take advantage of the favorable formation of Si−O bonds (Scheme 3). The resulting product was diamagnetic, with a single set of resonances for the phosphinoamide ligands, implying a triply bridged species. The infrared ν(CO) of the new product is 1909 cm^{-1}, and an additional broad band is observed at 2129 cm^{-1}. In addition, the ^{1}H NMR spectrum reveals two diagnostic resonances: a quartet at −14.1 ppm corresponding to a Co-bound hydride, and a singlet with ^{29}Si satellites at 4.3 ppm ($^1J_{\text{Si−H}}$ = 210 Hz) corresponding to Si-bound protons. Based on this spectral data, the identity of this $PhSiH_3$ addition product was assigned as $(OC)(H)Co(^iPr_2PNMes)_3ZrOSiH_2Ph$ (**5**). Treatment of **2** with $PhSiD_3$ resulted in an analogous complex **5$^{\mathbf{D}}$**, which was devoid of hydride and Si−H resonances in the ^{1}H NMR, confirming the origin of the cobalt-bound hydride ligand. In addition, the IR spectrum of **5$^{\mathbf{D}}$** revealed a new broad band at 1558 cm^{-1}, corresponding to SiD_2 stretches. The Co−H or Co−D stretches were not discernible in the IR spectra of **5** or **5$^{\mathbf{D}}$**, respectively.

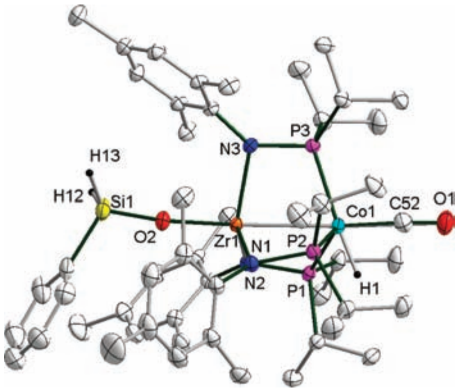


Figure 4. Displacement ellipsoid representation (50%) of **5**. Hydrogen atoms other than those bound to Si or Co have been omitted for clarity. Relevant interatomic distances (Å) and angles (deg): Zr1−Co1, 2.7228(2); Zr1−O2, 1.9688(10); Co1−C52, 1.7422(16)); Zr1−O2−Si1, 171.84(7); Co1−C52−O1, 176.08(15), P1−Co1−P2, 113.663(15); P1−Co1−P3, 111.001(15); P2−Co1−P3, 106.629(15).

The structure of complex **5** was determined unambiguously by single crystal X-ray diffraction, confirming the presence of a Co-bound carbonyl and hydride ligand and the 3-fold symmetric ligand arrangement (Figure 4). In addition, the solid state structure of **5** confirms that the origin of the Si−H protons is a phenylsiloxide ligand bound to Zr. The H atoms of the Co-hydride and siloxide were located in the difference Fourier map and refined. Notably, the geometry about Co remains essentially pseudotetrahedral, with the hydride capping one of the faces. The geometry is perturbed very little by the hydride: the P1−Co−P2 angle is only slightly larger than the other two P−Co−P angles. Thus, we attribute the unperturbed geometry about Co to (1) maximization of orbital overlap for Co−CO π-backbonding, and (2) the steric congestion around the Co center and rigidity of the tridentate ligand framework. The Co−Zr distance in **5** is 2.7228(2) Å, slightly shorter than the interatomic distance in the O-bridged complex **2**, and the Zr−O−Si bond vector is relatively linear (171.84(7) Å).

In summary, we have shown that the highly polar metal−metal multiple bonds in reduced Zr/Co complexes facilitate facile oxidative addition of the C═O bond in CO_2 to generate a terminal CO and bridging Zr−O−Co oxo unit. The hemilability of the phosphinoamide ligand framework is the key to this reactivity, as dissociation of a phosphine ligand from Co provides substrate access to the metal−metal bond. Given the strength of the C−O bonds in CO_2, this transformation itself is remarkable; however, the multielectron reductions of the CO_2 addition product also generate relatively unusual Zr-oxoanion and Zr-carbonate species, with concomitant reversion of the ligand framework to a 3-fold symmetric arrangement. The bridging oxo ligand can also be functionalized via addition of silanes to generate a Zr-siloxide and terminal Co-hydride species. It is important to note that, thus far, CO liberation from any of the CO_2-derived products has not been observed, even using photochemical approaches, so a closed cycle such as that devised by Donahue and co-workers in which the active species is regenerated via CO displacement has proven elusive.[39] Future studies will focus on elucidating such a cycle and investigating the further reactivity of the aforementioned complexes.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental details, additional spectral data, and crystallographic data for complexes **2**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

thomasc@brandeis.edu

■ ACKNOWLEDGMENT

This material is based upon work supported by the Department of Energy under Award No. DE-SC0004019. CMT is grateful for a 2011 Sloan Research Fellowship. The authors also thank Brandeis University for initially funding this project and Mark W. Bezpalko for assistance with X-ray crystallography.

■ REFERENCES

(1) Aresta, M.; Dibenedetto, A. *Dalton Trans.* **2007**, 2975–2992.
(2) Darensbourg, D. J. *Chem. Rev.* **2007**, *107*, 2388–2410.
(3) Lewis, N. S.; Nocera, D. G. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 15729–15735.
(4) Behr, A. *Angew. Chem.* **1988**, *100*, 681–698.
(5) Benson, E. E.; Kubiak, C. P.; Sathrum, A. J.; Smieja, J. M. *Chem. Soc. Rev.* **2009**, *38*, 89–99.
(6) Laitar, D. S.; Muller, P.; Sadighi, J. P. *J. Am. Chem. Soc.* **2005**, *127*, 17196–17197.
(7) Gambarotta, S.; Strologo, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1985**, *107*, 6278–6282.
(8) Hill, M.; Wendt, O. F. *Organometallics* **2005**, *24*, 5772–5775.
(9) Fachinetti, G.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1979**, *101*, 1767–1775.
(10) Alt, H. G.; Schwind, K.-H.; Rausch, M. D. *J. Organomet. Chem.* **1987**, *321*, C9–C12.
(11) Lee, C. H.; Laitar, D. S.; Mueller, P.; Sadighi, J. P. *J. Am. Chem. Soc.* **2007**, *129*, 13802–13803.
(12) Sadique, A. R.; Brennessel, W. W.; Holland, P. L. *Inorg. Chem.* **2008**, *47*, 784–786.
(13) Lu, C. C.; Saouma, C. T.; Day, M. W.; Peters, J. C. *J. Am. Chem. Soc.* **2006**, *129*, 4–5.
(14) Ashley, A. E.; Thompson, A. L.; O'Hare, D. *Angew. Chem., Int. Ed.* **2009**, *48*, 9839–9843.
(15) Berkefeld, A.; Piers, W. E.; Parvez, M. *J. Am. Chem. Soc.* **2010**, *132*, 10660–10661.
(16) Ménard, G.; Stephan, D. W. *J. Am. Chem. Soc.* **2010**, *132*, 1796–1797.
(17) Ménard, G.; Stephan, D. W. *Angew. Chem., Int. Ed.* 2011, 10.1002/anie.201103600.
(18) Gade, L. H. *Angew. Chem., Int. Ed.* **2000**, *39*, 2658–2678.
(19) Wheatley, N.; Kalck, P. *Chem. Rev.* **1999**, *99*, 3379–3420.
(20) Stephan, D. W. *Coord. Chem. Rev.* **1989**, *95*, 41–107.
(21) Memmler, H.; Kauper, U.; Gade, L. H.; Scowen, I. J.; McPartlin, M. *Chem. Commun.* **1996**, 1751–1752.
(22) Hanna, T. A.; Baranger, A. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1995**, *117*, 11363–11364.
(23) Greenwood, B. P.; Forman, S. I.; Rowe, G. T.; Chen, C.-H.; Foxman, B. M.; Thomas, C. M. *Inorg. Chem.* **2009**, *48*, 6251–6260.
(24) Greenwood, B. P.; Rowe, G. T.; Chen, C.-H.; Foxman, B. M.; Thomas, C. M. *J. Am. Chem. Soc.* **2010**, *132*, 44–45.
(25) Thomas, C. M.; Napoline, J. W.; Rowe, G. T.; Foxman, B. M. *Chem. Commun.* **2010**, *46*, 5790–5792.
(26) Zhou, W.; Napoline, J. W.; Thomas, C. M. *Eur. J. Inorg. Chem.* **2011**, *2011*, 2029–2033.
(27) Carney, M. J.; Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 8751–8753.
(28) Carney, M. J.; Walsh, P. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1990**, *112*, 6426–6428.
(29) Carney, M. J.; Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *Organometallics* **1992**, *11*, 761–777.
(30) Howard, W. A.; Waters, M.; Parkin, G. *J. Am. Chem. Soc.* **1993**, *115*, 4917–4918.
(31) Howard, W. A.; Parkin, G. *J. Am. Chem. Soc.* **1994**, *116*, 606–615.
(32) Matsuo, T.; Kawaguchi, H. *J. Am. Chem. Soc.* **2005**, *127*, 17198–17199.
(33) Hoskin, A. J.; Stephan, D. W. *Organometallics* **1999**, *18*, 2479–2483.
(34) Hu, Z.; Gorun, S. M. *Inorg. Chem.* **2001**, *40*, 667–671.
(35) Mendiratta, A.; Figueroa, J. S.; Cummins, C. C. *Chem. Commun.* **2005**, 3403–3405.
(36) Lukens, W. W.; Matsunaga, P. T.; Andersen, R. A. *Organometallics* **1998**, *17*, 5240–5247.
(37) De Angelis, S.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Organometallics* **1995**, *14*, 4505–4512.
(38) Silvia, J. S.; Cummins, C. C. *Chem. Sci.* **2011**, *2*, 1474–1479.
(39) Jayarathne, U.; Chandrasekaran, P.; Jacobsen, H.; Mague, J. T.; Donahue, J. P. *Dalton Trans.* **2010**, *39*, 9662–9671.