JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Communication
pubs.acs.org/JACS

Isolation of $(CO)^{1-}$ and $(CO_2)^{1-}$ Radical Complexes of Rare Earths via $Ln(NR_2)_3/K$ Reduction and $[K_2(18\text{-crown-}6)_2]^{2+}$ Oligomerization

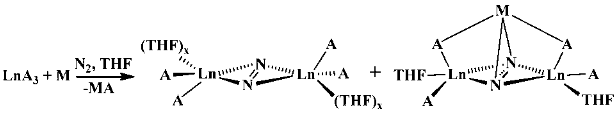
Ming Fang, Joy H. Farnaby, Joseph W. Ziller, Jefferson E. Bates, Filipp Furche, and William J. Evans*

Department of Chemistry, University of California, Irvine, California 92697-2025, United States

Supporting Information

ABSTRACT: Deep-blue solutions of Y^{2+} formed from $Y(NR_2)_3$ (R = $SiMe_3$) and excess potassium in the presence of 18-crown-6 at −45 °C under vacuum in diethyl ether react with CO at −78 °C to form colorless crystals of the $(CO)^{1-}$ radical complex, $\{[(R_2N)_3Y(\mu\text{-}CO)_2][K_2(18\text{-crown-}6)_2]\}_n$, **1**. The polymeric structure contains trigonal bipyramidal $[(R_2N)_3Y(\mu\text{-}CO)_2]^{2-}$ units with axial $(CO)^{1-}$ ligands linked by $[K_2(18\text{-crown-}6)_2]^{2+}$ dications. Byproducts such as the ynediolate, $[(R_2N)_3Y]_2(\mu\text{-}OC{\equiv}CO)\{[K(18\text{-crown-}6)]_2(18\text{-crown-}6)\}$, **2**, in which two $(CO)^{1-}$ anions are coupled to form $(OC{\equiv}CO)^{2-}$, and the insertion/rearrangement product, $\{(R_2N)_2Y[OC({=}CH_2)Si(Me_2)NSiMe_3]\}[K(18\text{-crown-}6)]$, **3**, are common in these reactions that give variable results depending on the specific reaction conditions. The CO reduction in the presence of THF forms a solvated variant of **2**, the ynediolate $[(R_2N)_3Y]_2(\mu\text{-}OC{\equiv}CO)[K(18\text{-crown-}6)(THF)_2]_2$, **2a**. CO_2 reacts analogously with Y^{2+} to form the $(CO_2)^{1-}$ radical complex, $\{[(R_2N)_3Y(\mu\text{-}CO_2)_2][K_2(18\text{-crown-}6)_2]\}_n$, **4**, that has a structure similar to that of **1**. Analogous $(CO)^{1-}$ and $(OC{\equiv}CO)^{2-}$ complexes of lutetium were isolated using $Lu(NR_2)_3/K/18\text{-crown-}6$: $\{[(R_2N)_3Lu(\mu\text{-}CO)_2][K_2(18\text{-crown-}6)_2]\}_n$, **5**, $[(R_2N)_3Lu]_2(\mu\text{-}OC{\equiv}CO)\{[K(18\text{-crown-}6)]_2(18\text{-crown-}6)\}$, **6**, and $[(R_2N)_3Lu]_2(\mu\text{-}OC{\equiv}CO)[K(18\text{-crown-}6)(Et_2O)_2]_2$, **6a**.

Dinitrogen can be reduced to $(N_2)^{2-}$ and $(N_2)^{3-}$ via the combination of a trivalent rare earth salt and an alkali metal as shown in eq 1 (Ln = rare earth, i.e., Sc, Y, lanthanides;



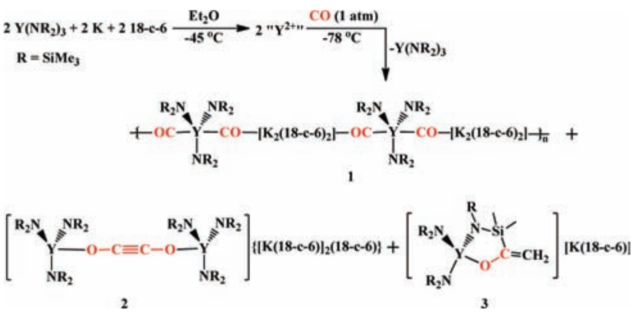
(1)

A = anions such as amides, aryloxides, and cyclopentadienides; M = Na, K).[1] Although the details of the dinitrogen reduction are not known for all the metals, in the case of yttrium, EPR evidence for an Y^{2+} species that reduces dinitrogen has been obtained.[2] We describe here the first studies of the reactivity of the deep-blue solutions of Y^{2+} obtained from $Y(NR_2)_3/K$ reactions (R = $SiMe_3$) with substrates other than dinitrogen. Specifically, the reduction of CO to the $(CO)^{1-}$ radical and CO_2 to the $(CO_2)^{1-}$ radical are presented.[3] The utility of the cyclic polyether, 18-crown-6, in isolating these radicals in surprisingly simple coordination complexes is described, as well as the formation of the dimer of the $(CO)^{1-}$ radical, i.e. $(OC{\equiv}CO)^{2-}$. Analogous CO chemistry with lutetium is also included.

Although CO reduction by potassium has been reported since 1825,[4] complexes of the $(CO)^{1-}$ and $(CO_2)^{1-}$ radicals are rare and have only previously been reported using the carefully designed tris(aryloxide) tacn ligands with uranium.[5] Uranium complexes have also provided an extensive series of CO reduction products, namely the $[(CO)_n]^{2-}$ complexes in which $n = 2–4$.[6] With lanthanides, $n = 3$ examples are known.[7]

CO reduction by Y^{2+} was accomplished in the following way. A deep-blue solution of Y^{2+} was generated at −45 °C from $Y(NR_2)_3$ and excess potassium mirror in diethyl ether under vacuum in the presence of 1 equiv of 18-crown-6. The mixture was filtered from the excess potassium and frozen with liquid nitrogen, and CO was added. After 15 min at −78 °C, the solution was orange. Colorless crystals of polymeric $\{[(R_2N)_3Y(\mu\text{-}CO)_2][K_2(18\text{-crown-}6)_2]\}_n$, **1**, Scheme 1, formed over 2 days at room temperature. The complex, identified by X-ray diffraction, Figure 1, has one $Y(NR_2)_3$ moiety coordinated on each side by (CO)K(18-c-6) units. Hence, formation of one monomeric repeat unit of **1** formally requires 2 equiv of Y^{2+}, arising from two $Y(NR_2)_3/K$ reactions, to reduce two molecules of CO leaving 1 equiv of $Y(NR_2)_3$ as the stoichiometric byproduct. $Y(NR_2)_3$ is observed in the crude product mixture, but quantification is complicated since some could be unreacted starting material.

Scheme 1. Synthesis of Compounds 1, 2, and 3 Where 18-c-6 Stands for the Cyclic Polyether 18-Crown-6



The reaction of CO with the deep-blue solutions formed from $Y(NR_2)_3/K$ is highly sensitive to the form of potassium, the amount of 18-crown-6, the type of ether solvent, and reaction times and temperatures. At least 50 small variations of

Received: November 30, 2011
Published: March 21, 2012

ACS Publications © 2012 American Chemical Society

dx.doi.org/10.1021/ja211220r | J. Am. Chem. Soc. 2012, 134, 6064−6067

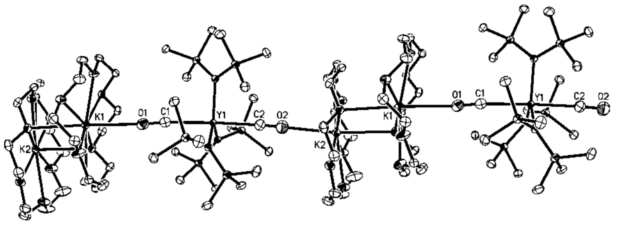


Figure 1. Thermal ellipsoid plot of two repeating units of $\{[(R_2N)_3Y(\mu\text{-CO})_2][K_2(18\text{-crown-6})_2]\}_n$, **1**, drawn at the 50% probability level with hydrogen atoms omitted for clarity.

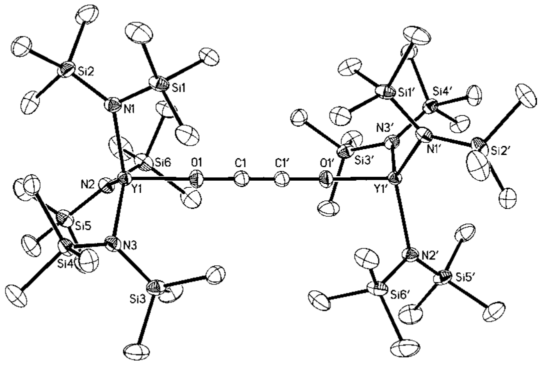
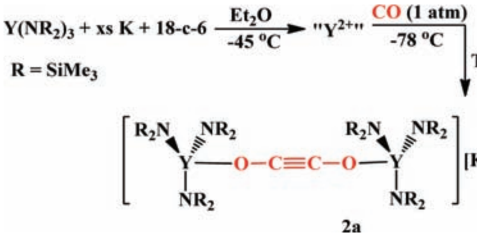


Figure 2. Thermal ellipsoid plot of the dianion $\{[(R_2N)_3Y]_2(\mu\text{-OC}{\equiv}\text{CO})\}^{2-}$ in $[(R_2N)_3Y]_2(\mu\text{-OC}{\equiv}\text{CO})\{[K(18\text{-crown-6})]_2(18\text{-crown-6})\}$, **2**, drawn at the 30% probability level with hydrogen atoms omitted for clarity. See Figure S6 for the complete structure.

these parameters have been explored in order to optimize the results presented here. The $Y(NR_2)_3$/K/CO reaction is complicated by the fact that at least two byproducts are sometimes formed in this reaction, the ynediolate, $[(R_2N)_3Y]_2(\mu\text{-OC}{\equiv}\text{CO})\{[K(18\text{-crown-6})]_2(18\text{-crown-6})\}$, **2**, which was also identified by X-ray crystallography, Figure 2, and the CO insertion/rearrangement product, $\{(R_2N)_2Y[OC(=CH_2)Si(Me_2)NSiMe_3]\}[K(18\text{-crown-6})]$, **3**, Figure S2. Detailed characterization of **1** has been challenging since crystals of **1** do not redissolve in Et_2O and reactions to synthesize **1** when exposed to THF give $[(R_2N)_3Y]_2(\mu\text{-OC}{\equiv}\text{CO})[K(18\text{-crown-6})(THF)_2]_2$, **2a**, Scheme 2, Figure S5, a variant of **2** that differs in its countercation. Complex **2a** also forms when the $Y(NR_2)_3$/K reaction occurs in 1:1 THF/DME.

Scheme 2. Formation of 2a in the Presence of THF



The ynediolate complexes, **2** and **2a**, contain the $(\text{OC}{\equiv}\text{CO})^{2-}$ dianion formally derived by dimerization of two $(CO)^{1-}$ radicals. These complexes are very similar to the U^{4+} complex, $(R_2N)_3U(\mu\text{-OC}{\equiv}\text{CO})U(NR_2)_3$ ($R = SiMe_3$), reported while this research was in progress by Arnold et al.[6b] as well as that of $[U(C_8H_6\{Si^iPr_3\text{-}1,4\}_2)(C_5Me_5)]_2(\mu\text{-OC}{\equiv}\text{CO})$.[6a] Complex **3** is likely to arise initially from insertion of CO into the Y−C bond of the metalated complex, $(R_2N)_2Y[CH_2Si(Me_2)NSiMe_3]K$, known to form from $Y(NR_2)_3$ and K.[2a] Rearrangement of such acyls to enolates is common and would explain the observed structure of **3** (structural details in the Supporting Information (SI)).[8]

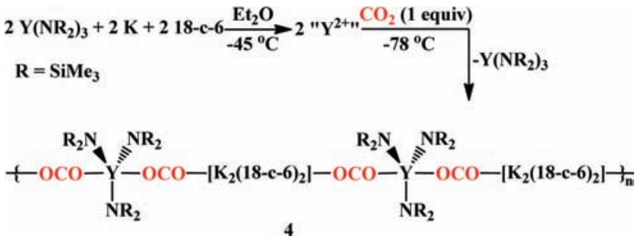
Complex **1** displays an IR absorption at 2091 cm^{-1} that is very close to the 2092 cm^{-1} value observed for the mixed valence U^{3+}/U^{4+} complex $[(L)U]_2(\mu\text{-CO})$ (L = 1,4,7-tris(3,5-di-*tert*-butyl-2-hydroxybenzylate)-1,4,7-triazacyclononane).[5a] The IR spectrum of analogous crystals of **1** synthesized with ^{13}CO lacks this absorption and has a band at 2048 cm^{-1} (calcd, 2043 cm^{-1}), Figure S7. The $^{13}C\{^1H\}$ NMR spectrum of the $(\text{O}^{13}\text{C}{\equiv}^{13}\text{CO})^{2-}$ complex, **2a-^{13}CO**, exhibits a multiplet in the alkyne region[9a] at 55.5 ppm that matches an AA′XX′ simulation,[9b] which uses the coupling constants found for **2a**: $^2J_{YC} = 10.4$ Hz and $^3J_{YC} = 1.7$ Hz, Figure S10.

In **1**, the yttrium atom in the $[(R_2N)_3Y(\mu\text{-CO})_2]^{2-}$ unit has a trigonal bipyramidal geometry with $(CO)^{1-}$ anions in the axial sites. Each potassium ion has a distorted hexagonal bipyramidal coordination environment with one crown ether providing six oxygen donor atoms situated above and below the equatorial plane, a carbonyl monoanion in one axial position, and an oxygen of the second crown ether in the other axial position. The dicationic $[K_2(18\text{-crown-6})_2]^{2+}$ unit that connects the $[(R_2N)_3Y(\mu\text{-CO})_2]^{2-}$ dianions into a polymer has two of these axial K−O(other crown) linkages, and their 2.996(2) and 3.032(2) Å K−O distances are longer than the other 14 K−O distances that range from 2.650(2) to 2.946(3) Å. The $[K_2(18\text{-crown-6})_2]^{2+}$ unit that comprises a link in polymeric **1** has previously been observed in salts of $(Ph_3SiO)^{1-}$,[10] $[Ti(CO)_4(\mu\text{-OC}_6H_5)]_2^{\,2-}$,[11] $\{[Sc(NCS)_6]Cl\}^{4-}$,[12] $(HgSe_8)^{2-}$,[13] and $[Er(NCS)_6(SCN)]^{4-}$,[14] but not in this polymeric form. Neither spectroscopic nor X-ray data (see SI for details) can distinguish Y−C−O−K from Y−O−C−K connectivity in **1**. The Y−C−O−K assignment used in the equations and figures follows the relative Pauling electronegativities of Y (1.22) and K (0.82).

The ynediolate complexes **2** and **2a** differ from **1** in that they are not polymeric even though **2** and **2a**, like **1**, contain dianionic components that are charge balanced by two $[K(18\text{-crown-6})]^{1+}$ cations. The difference presumably arises because the anionic charge from two $(CO)^{1-}$ ions sandwiches a neutral $Y(NR_2)_3$ unit in **1**, whereas the anionic charge of the $(\text{OC}{\equiv}\text{CO})^{2-}$ dianion is sandwiched inside of two neutral $Y(NR_2)_3$ moieties in **2** and **2a**. Complex **2a** has hexagonal bipyramidal potassium like **1**, but the axial positions are occupied by THF of solvation and hence the bridging $—[K_2(18\text{-crown-6})_2]^{2+}—$ connecting unit in **1** is not formed. Complex **2**, which lacks the THF of solvation in **2a**, adopts yet another mode of combining two $[K(18\text{-crown-6})]^{1+}$ cations with a third crown ether bridging the two cations as a bidentate ligand to each potassium to form a $[K_2(18\text{-crown-6})_3]^{2+}$ dication.[15]

The deep-blue Y^{2+} solutions generated as described above also react with CO_2 and surprisingly make complexes of similar overall structure. In this case, a deep-blue Y^{2+} solution prepared at −45 °C as described above was cooled to −78 °C and exposed to 1 equiv of CO_2 which led to an immediate color change to colorless. After workup, crystals of the $(CO_2)^{1-}$ complex, $\{[(R_2N)_3Y(\mu\text{-CO}_2)_2][K_2(18\text{-crown-6})_2]\}_n$, **4**, Scheme 3, Figure 3, were isolated. Complex **4** is polymeric like **1** except that the ligand in between the yttrium and potassium centers is now the $(CO_2)^{1-}$ radical anion instead of the $(CO)^{1-}$ radical. Again, $[K_2(18\text{-crown-6})_2]^{2+}$ units link components in the

Scheme 3. Synthesis of Compound 4



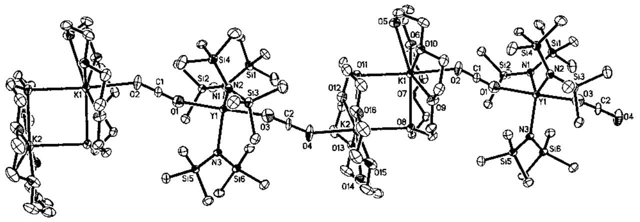


Figure 3. Thermal ellipsoid plot of two repeating units of $\{[(R_2N)_3Y(\mu\text{-}CO_2)_2][K_2(18\text{-crown-}6)_2]\}_n$, **4**, drawn at the 50% probability level with hydrogen atoms omitted for clarity.

extended polymer. The $(CO_2)^{1-}$ anions are nearly linear with 179.1(4)° and 179.2(4)° O−C−O angles similar to the 178.0(3)° angle in the U^{4+} complex of the $(CO_2)^{1-}$ radical anion, $(L')U(\eta^1\text{-OCO})$, L′ = 1,4,7-tris(3-adamantyl-5-*tert*-butyl-2-hydroxybenzylate)-1,4,7-triazacyclononane, previously reported by Meyer et al., which has an IR stretch of 2188 cm^{-1}.[5b] The inequivalent 1.171(4)−1.198(4) Å C−O distances are more similar to each other than the disparate values in $(L')U(\eta^1\text{-OCO})$, 1.122(4) and 1.277(4) Å.[5b] The 2.352(3) and 2.367(3) Å Y−O distances are much longer than the 2.052(3)−2.057(1) Å analogs in **2** and **2a**, which may be a reflection of the fact that the $(OCO)^{1-}$ ligand does not have a full negative charge per oxygen donor atom as in $(OC{\equiv}CO)^{2-}$.

Complex **4** has an IR stretch at 2210 cm^{-1} that shifts to 2150 cm^{-1} in the $^{13}CO_2$ analog, Figure S8. The 2210/2150 = 1.0279 ratio is similar to the 2188/2128 = 1.0282 ratio observed in $^{12}CO_2/^{13}CO_2$ $(L')U(\eta^1\text{-OCO})$ and in free $^{12}CO_2/^{13}CO_2$, 1.0284.[5b]

A reaction analogous to Scheme 1 was examined with lutetium. In this case, $Lu(NR_2)_3$ was treated with K in the presence of 18-crown-6 at −45 °C to give a deep-blue solution. This was frozen at −196 °C, CO at 1 atm was added, the reaction vessel was warmed to −78 °C, and the solution turned to orange yellow. Colorless crystals of an analog of **1**, namely, $\{[(R_2N)_3Lu(\mu\text{-}CO)_2][K_2(18\text{-crown-}6)_2]\}_n$, **5**, were obtained at room temperature. Complex **5** was also characterized by X-ray crystallography, and although not isomorphous, it has a structure similar to that of **1**, Table S1, Figure S9. The lutetium reduction of CO readily forms an ynediolate complex analogous to the byproduct of the yttrium reaction. In the lutetium case, $[(R_2N)_3Lu]_2(\mu\text{-}OC{\equiv}CO)\{[K(18\text{-crown-}6)]_2(18\text{-crown-}6)\}$, **6** (Figure S12), an analog of **2**, can be crystallized as well as $[(R_2N)_3Lu]_2(\mu\text{-}OC{\equiv}CO)[K(18\text{-crown-}6)(Et_2O)_2]_2$, **6a** (Figure S13), an analog of **2a** except that two Et_2O molecules solvate the potassium instead of two THF. The formation of **5**, **6**, and **6a** suggests that the deep-blue solutions obtained from $Lu(NR_2)_3$ and potassium may contain Lu^{2+} in analogy to Y^{2+}.

Density functional calculations described in detail in the SI[16] were attempted on **1** even though semilocal density functionals suffer from various deficiencies for systems with strong noncovalent interactions.[17] Calculations on $[(R_2N)_3Y(\mu\text{-}CO)_2]^{2-}$ did not give good agreement with the structure, but also did not include the interaction of the $(CO)^{1-}$ with potassium. Calculations were then attempted on the entire 172 atom $\{(R_2N)_3Y[(\mu\text{-}CO)K(18\text{-crown-}6)]_2\}$ repeat unit. These also did not give good agreement, but again the full extent of interaction could not be calculated since the interactions between the two $[K(18\text{-crown-}6)]^{1+}$ units in the polymer were not included. The calculations in each case showed very similar energies for triplet, singlet, and closed shell structures as well as structures with Y−O−C−K and Y−C−O−K connectivity.

Although a detailed bonding picture is not available for these compounds, it is clear that the $Y(NR_2)_3/K$ reduction system that generates Y^{2+} can be used to reduce CO and CO_2 and trap these small molecules in crystallizable complexes as the $(CO)^{1-}$ and $(CO_2)^{1-}$ radical anions. Although this first step in CO and CO_2 reduction has previously been demonstrated with tris(aryloxide) tacn uranium complexes, this required the use of a carefully constructed tripodal coordination cavity. The isolation of **1** and **4** shows that these radical anions can be accessed in the more open coordination environments of a simple tris(amide) like $Y(NR_2)_3$; the isolation of **5** shows that this is extendable to the lanthanide series. It is likely that these $(CO)^{1-}$ and $(CO_2)^{1-}$ radicals could be isolated because they formed an extended polymer of low solubility. The polymeric nature of the product was due in part to the linking ability of the $[K(18\text{-crown-}6)]^{1+}$ cations to form bridging $[K_2(18\text{-crown-}6)_2]^{2+}$ moieties. Hence, the use of 18-crown-6 is likely to be a crucial factor in generating these results.

The dimerization of $(CO)^{1-}$ radicals to $(OC{\equiv}CO)^{2-}$ is not unexpected, but in the past this radical has only been postulated in reactions that reductively couple CO. Both lanthanide and actinide complexes can reductively homologate CO to $[(CO)_n]^{2-}$ ions where n = 2−4, but isolating $(CO)^{1-}$ and $(OC{\equiv}CO)^{2-}$ in the same reduction system has not been possible until now. The variable nature of the yields and product mixtures as a function of detailed reaction conditions attests to the high reactivity of these species.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

wevans@uci.edu

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the U.S. National Science Foundation for support of this research through CHE-1010002, CHE-0723168, and CHE-0840513 and Ryan Zarkesh (X-ray) and Dr. N. R. M. Crawford (computations) for experimental assistance.

■ REFERENCES

(1) (a) Fang, M.; Bates, J. E.; Lorenz, S. E.; Lee, D. S.; Rego, D. B.; Ziller, J. W.; Furche, F.; Evans, W. J. *Inorg. Chem.* **2011**, *50*, 1459 and references therein. (b) Jaroschik, F.; Momin, A.; Nief, F.; Goff, X.-F. L.; Deacon, G. B.; Junk, P. C. *Angew. Chem., Int. Ed.* **2009**, *48*, 1117.

(c) Rinehart, J. D.; Fang, M.; Evans, W. J.; Long, J. R. *J. Am. Chem. Soc.* **2011**, *133*, 14236.

(2) (a) Fang, M.; Lee, D. S.; Ziller, J. W.; Doedens, R. J.; Bates, J. E.; Furche, F.; Evans, W. J. *J. Am. Chem. Soc.* **2011**, *133*, 3784. (b) MacDonald, M. R.; Ziller, J. W.; Evans, W. J. *J. Am. Chem. Soc.* **2011**, *133*, 15914.

(3) Reported in part at Pacifichem 2010, Honolulu, Hawaii, December 2010, Symposium 46.

(4) Gmelin, L. *Ann. Phys. Chem.* **1825**, *4*, 31.

(5) (a) Castro-Rodriguez, I.; Meyer, K. *J. Am. Chem. Soc.* **2005**, *127*, 11242. (b) Castro-Rodriguez, I.; Nakai, H.; Zakharov, L. N.; Rheingold, A. L.; Meyer, K. *Science* **2004**, *305*, 1757.

(6) (a) Frey, A. S.; Cloke, F. G. N.; Hitchcock, P. B.; Day, I. J.; Green, J. C.; Aitken, G. *J. Am. Chem. Soc.* **2008**, *130*, 13816. (b) Arnold, P. L.; Turner, Z. R.; Bellabarba, R. M.; Tooze, R. P. *Chem. Sci.* **2011**, *2*, 77. (c) Summerscales, O. T.; Cloke, F. G. N.; Hitchcock, P. B.; Green, J. C.; Hazari, N. *Science* **2006**, *311*, 829. (d) Mansell, S. M.; Kaltsoyannis, N.; Arnold, P. L. *J. Am. Chem. Soc.* **2011**, *133*, 9036.

(7) (a) Evans, W. J.; Grate, J. W.; Hughes, L. A.; Zhang, H.; Atwood, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 3728. (b) Evans, W. J.; Lee, D. S.; Ziller, J. W.; Kaltsoyannis, N. *J. Am. Chem. Soc.* **2006**, *128*, 14176.

(8) (a) Berno, P.; Minhas, R.; Hao, S.; Gambarotta, S. *Organometallics* **1994**, *13*, 1052. (b) Putzer, M. A.; Neumüller, B.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1998**, *624*, 57. (c) Evans, W. J.; Siladke, N. A.; Ziller, J. W. *Chem.—Eur. J.* **2010**, *16*, 796. (d) Manriquez, J. M.; Fagan, P. J.; Marks, T. J.; Day, C. S.; Day, V. W. *J. Am. Chem. Soc.* **1978**, *100*, 7112. (e) Simpson, S. J.; Andersen, R. A. *J. Am. Chem. Soc.* **1981**, *103*, 4063. (f) Petersen, J. L.; Egan, J. W. *Organometallics* **1987**, *6*, 2007. (g) Lee, L.; Berg, D. J.; Einstein, F. W.; Batchelor, R. J. *Organometallics* **1997**, *16*, 1819. (h) Cameron, T. M.; Gordon, J. C.; Scott, B. L.; Tumas, W. *Chem. Commun.* **2004**, 1398.

(9) (a) Sliverstein, R. M., Webster, F. X. *Spectrometric Identification of Organic Compounds*; Wiley & Sons: New York, 1998; Vol. *VI*, p 227. (b) Reich, H. J. WinDNMR: Dynamic NMR Spectra for Windows. *J. Chem. Ed.: Software, Series D*, **1996**, *3D*, No. 2.

(10) McGeary, M. J.; Folting, K.; Streib, W. E.; Huffman, J. C.; Caulton, K. G. *Polyhedron* **1991**, *10*, 2699.

(11) Fischer, P. J.; Yuen, P.; Young, V. G.; Ellis, J. E. *J. Am. Chem. Soc.* **1997**, *119*, 5980.

(12) Petrosyants, S.; Ulyukhin, A. *Russ. J. Coord. Chem.* **2007**, *33*, 155.

(13) Krauter, G.; Weller, F.; Dehnicke, K. *Z. Naturforsch., B: Chem. Sci.* **1989**, *44*, 444.

(14) Chekhlov, A. *Russ. J. Coord. Chem.* **2008**, *34*, 849.

(15) (a) Budzichowski, T. A.; Chisholm, M. H.; Strieb, W. E. *J. Am. Chem. Soc.* **1994**, *116*, 389. (b) Baker, R. J.; Farley, R. D.; Jones, C.; Kloth, M.; Murphy, D. M. *J. Chem. Soc., Dalton Trans.* **2002**, 3844. (c) Uhl, W.; Jasper, B.; Lawerenz, A.; Marschner, C.; Fischer, J. *Z. Anorg. Allg. Chem.* **2007**, *633*, 2321.

(16) TURBOMOLE, V6-2; TURBOMOLE GmbH: Karlsruhe, 2010.

(17) Eshuis, H.; Furche, F. *J. Phys. Chem. Lett.* **2011**, *2*, 983.