

Advancing Chemistry with the Lanthanide and Actinide Elements**Final Report, September 2013**

Graduate Students: Benjamin M. Schmiege, Elizabeth Montalvo, Kevin A. Miller, Justin R. Walensky, Michael K. Takase, Thomas J. Mueller, Nathan A. Siladke, Megan E. Fieser, Douglas R. Kindra, Heidi L. Houghton

Postdoctoral**Researchers:**

Ming Fang, Ian J. Casely

Contacts:Department of Chemistry, 1102 Natural Sciences II,
University of California, Irvine, CA 92697-2025Ph: 949-824-5174; FAX: 949-824-2210; wevans@uci.edu**Yearly Budget** \$125,000**Period of Execution** June 15, 2010-June 15, 2013**Year Started** 2010**Overall Research Goals**

The objective of this research is to use the unique chemistry available from complexes of the lanthanides and actinides, as well as related heavy metals such as scandium, yttrium, and bismuth to advance chemistry in energy-related areas. The lanthanides and actinides have a combination of properties in terms of size, charge, electropositive character, and f valence orbitals that provides special opportunities to probe reactivity and catalysis in ways not possible with the other metals in the periodic table. We seek to discover reaction pathways and structural types that reveal new options in reaction chemistry related to energy. Identification of new paradigms in structure and reactivity should stimulate efforts to develop new types of catalytic processes that at present are not under consideration because either the transformation or the necessary intermediates are unknown.

This project is one half of my laboratory's DOE research which was split 50:50 between Catalysis and Heavy Element Chemistry programs in 2010. Hence, this report is for a half-project.

Specific Objectives

The main areas explored in this project have been (a) C-H bond activation, the fundamental organometallic reaction needed to expand the use of hydrocarbons as feedstocks [1, 2, 5, 6, 7], (b) metal complex metal complex reactions (MC/MC), the relatively unexplored competition between combinations of closely related Lewis acids as are often found in metal-based catalyses that use metal co-catalysts, e.g. Ziegler-Natta polymerization [10], and (c) the under-developed chemistry of bismuth with relevance to the use of NaBiO₃ oxidation in nuclear waste streams [4] and an unexpected C-H bond activation that has led to a new series of dianionic organometallic ligands [6, 11]. Collaborative efforts with three theory groups, those of Filipp Furche (University of

California, Irvine), Laura Gagiliardi (University of Minnesota), and Laurent Maron (Toulouse), have also produced publishable results that show the value of combined experimental/theory efforts in inorganic and organometallic chemistry [3, 6, 8, 9,11].

Potential Impact to DOE

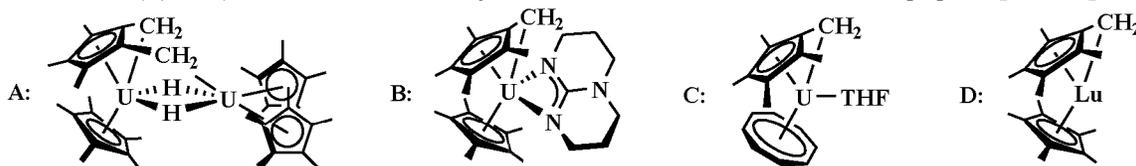
The extreme properties of the large electropositive lanthanide and actinide metals along with yttrium can be useful in identifying new options in reactivity that could form the bases for new catalyses. C-H activation, a reaction that could have enormous value in the energy area if it could be fully utilized, is being studied in this project with these metals as well as with bismuth. Inherent in this study is a comparison of 4f vs 5f metal reactivity that is also of DOE interest since it could provide fundamental insight useful in understanding the separation of lanthanides and actinides in radioactive waste streams. Extension of this project to bismuth was originally prompted by questions in waste stream handling, but unexpected discoveries led to new C-H bond activation chemistry and a new class of organometallic ligands. As the energy relevant chemistry of these heavy metals is advanced, Ph.D. students get trained in the chemistry of the f elements. This half project involved ten graduate students and two postdoctoral associates.

Results from the Three Years of this Half Project

The full details of the research are described in the papers listed at the end of this report [1-11]. Only highlights are presented here.

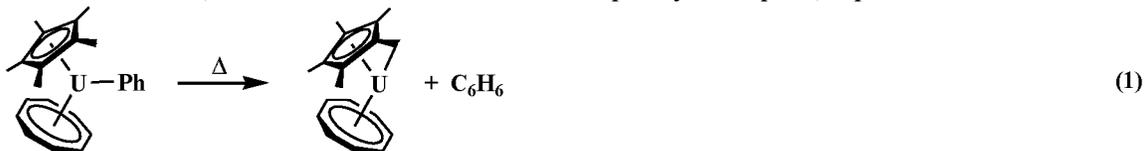
C-H Bond Activation Reactivity.

"Tuck-in" Reactivity. This project produced the first crystallographic data on $(C_5Me_4CH_2)^{2-}$ tuck-in metalated pentamethylcyclopentadienyl complexes of the f elements. The tuck-in complexes are made by C-H bond activation and tuck-in complexes were proposed as intermediates in the first example of C-H activation of methane in solution with $(C_5Me_5)_2LuCH_3$ done at DuPont in the 1980's (*J. Am. Chem. Soc.* **1983**, *105*, 6491). However, since the proposal of tuck-in intermediates in 1983, no crystallographic data on such a species have been obtainable with f element complexes until the following complexes were synthesized in this project: the tuck-in tuck-over dihydride, $(C_5Me_5)U[\mu-\eta^5:\eta^1-\eta^1-C_5Me_3(CH_2)_2](\mu-H)_2U(C_5Me_5)_2$, **A**, the tuck-in cyclic guaninidate, $(C_5Me_5)(hpp)U(\eta^5:\eta^1-C_5Me_4CH_2)$ [(hpp)¹⁻ = 1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-*a*]pyrimidinato], **B**, and the cyclooctatetraenyl tuck-in $(C_8H_8)U(\eta^5:\eta^1-C_5Me_4CH_2)(THF)$, **C**. Their reactivity has been described in three full papers [1, 2, 5].

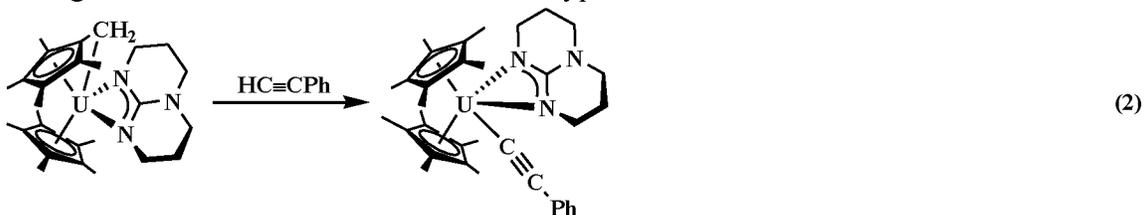


The chemistry of these crystallographically-characterized tuck-in complexes was found to be significantly different from that assumed to occur from the first postulated $(\eta^5:\eta^1-C_5Me_4CH_2)$ tuck-in f element complex, " $(C_5Me_5)Lu(\eta^5:\eta^1-C_5Me_4CH_2)$ ", **D**, suggested to be the species that activates methane in the exchange of $(C_5Me_5)_2LuCH_3$ with $^{13}CH_4$ (*Acc. Chem. Res.* **1985**, *18*, 51). The most striking difference is that **A-C** do not activate

alkanes or even arenes as found for $(C_5Me_5)_2LuCH_3$. In fact, complex **C** is made by the reverse reaction, elimination of benzene from a phenyl complex, eq 1.

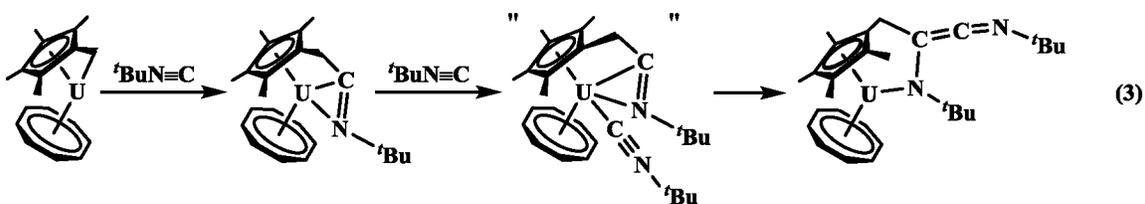


Complexes **A** and **B** were found to react only with hydrocarbons with acidic hydrogens, e.g. $HC\equiv CPh$, eq 2. Complexes **A** and **B** also react with H_2 and both of these reactions are sigma bond metathesis transformations typical of f element-carbon bonds.

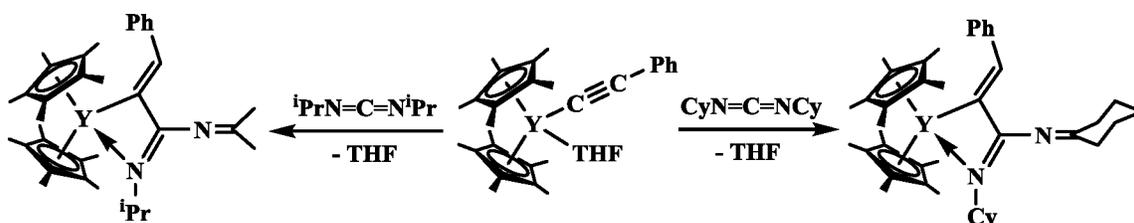


One reason that the spectacular reactivity attributed to the postulated intermediate **D** is not found in the fully characterized **A-C** may be due to lanthanide versus actinide differences. However, such large differences in reactivity are usually not observed for Ln-C vs An-C bonds. Another reason is the difference in ligands since the reactivity of the tuck-in complexes **A-C** varies depending on the ancillary ligands. However, **C** and **D** are very similar metallocene tuck-in complexes. In each case the tuck-in dianion, $(\eta^5:\eta^1-C_5Me_4CH_2)^{2-}$, is attached to a $[(ring)M]^{2+}$ dication (i.e. $[(C_8H_8)U]^{2+}$ and $[(C_5Me_5)Lu]^{2+}$), since the dianionic charge of the $(C_8H_8)^{2-}$ ligand compensates for the higher charge of U^{4+} . Previous studies have shown the steric similarity of $(C_8H_8)^{2-}$ and $(C_5Me_5)^{1-}$ [*Organometallics* **1999**, *18*, 1460]. Differences could also be attributed to the small size of lutetium, but it is also possible that the observed C-H bond activation with methane does not involve a tuck-in intermediate. Further studies are needed to resolve this issue.

Complexes **A-C** are also reactive in terms of insertion, but isolation of single products has been challenging. Eq 3 shows one successful example [5].



Rare Earth Metallocene Chemistry. C-H bond activation was also studied with yttrium metallocenes [7] and resulted in organometallic versions, Scheme 1, of the Alder-ene reaction in which a C-H bond of one unsaturated component is transferred to another while forming a C-C bond.



Scheme 1. An organometallic Alder-ene reaction in which C-H activation of each carbodiimide transfers H to the alkyne while making a carbon-carbon bond.

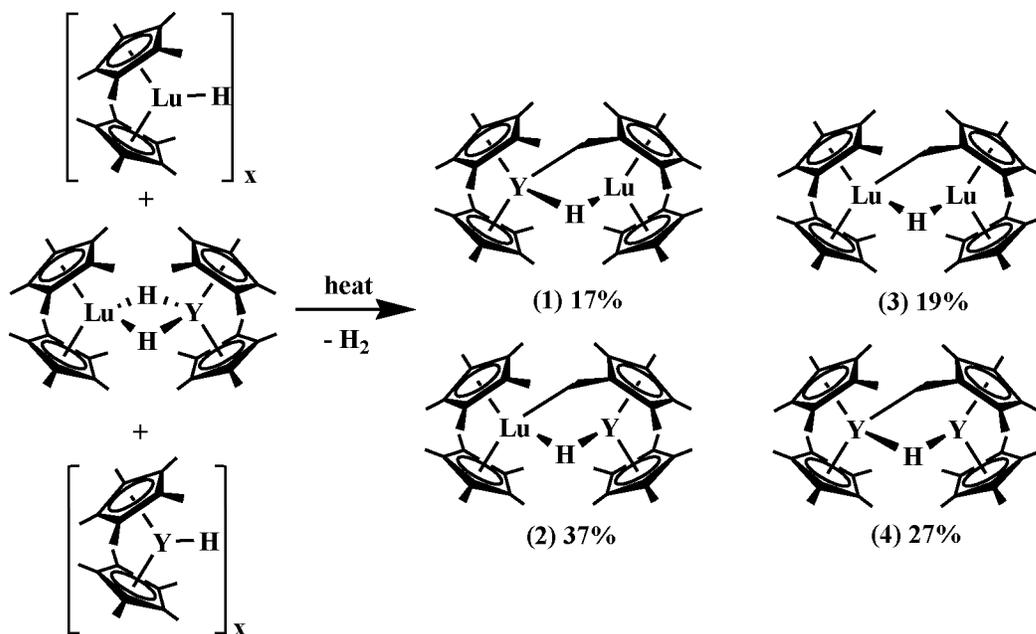
Metal Complex/Metal Complex Reactions.

One of the simplest metal complex/metal complex (MC/MC) reactions is the monomer/dimer equilibrium that can occur in bimetallic complexes, eq 4.



In terms of evaluating the reactivity of two closely related Lewis acidic metal centers, this would involve five species, the monomers and dimers of each metal and the heterobimetallic complex, $(\text{C}_5\text{Me}_5)_2\text{Ln}(\text{bridging ligand})_2\text{Ln}'(\text{C}_5\text{Me}_5)_2$. Obtaining quantitative information on these similar species presents a challenge, since it is unlikely that the heterobimetallic complex can be separated from the homobimetallic analogues.

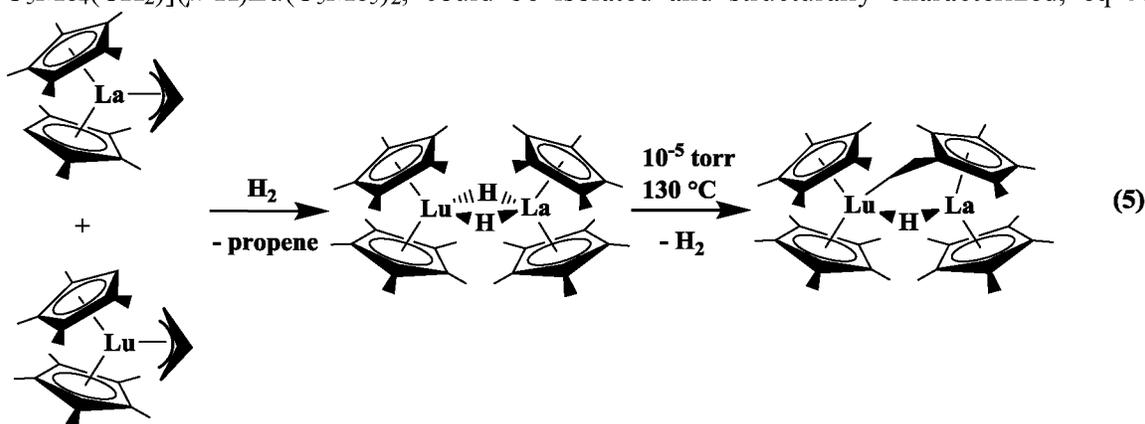
However, examination of the tuck-over bridging $(\mu-\eta^5:\eta^1-\text{C}_5\text{Me}_4\text{CH}_2)^{2-}$ complexes of formula $(\text{C}_5\text{Me}_5)\text{Ln}(\mu-\eta^5:\eta^1-\text{C}_5\text{Me}_4\text{CH}_2)(\mu-\text{H})\text{Ln}(\text{C}_5\text{Me}_5)_2$ has provided a system that allows this type of MC/MC reactivity to be studied. In these complexes, the differing nature of the bridging ligands leads to the hydride ligand being more strongly bound to one metal than the other which produces different observable NMR coupling constants. As a result of the different bridging ligands, this bimetallic system has four components: two distinct homometallic species and two distinct heterometallic complexes. We have found that in the mixed metal yttrium lutetium system shown below in Scheme 2, the Y_2 , Lu_2 , and two types of YLu complexes can all be identified by NMR spectroscopy using ^{89}Y coupling. This system demonstrates the viability of studying MC/MC reactions with closely related rare earth metals: yttrium and lutetium differ in size by only 0.04 Å.



Scheme 2. Formation of four bimetallic tuck-over hydride complexes each identifiable by NMR spectroscopy.

To insure that this tuck-over chemistry applies to open shell rare earth ions as well as $4d^0 4f^0$ Y^{3+} and $4f^{14}$ Lu^{3+} , the $4f^9$ Dy^{3+} tuck-over analog, $(C_5Me_5)Dy[\mu-\eta^5:\eta^1-C_5Me_4(CH_2)](\mu-H)Dy(C_5Me_5)_2$, was also synthesized and characterized to provide a paramagnetic partner for the mixed metal studies.

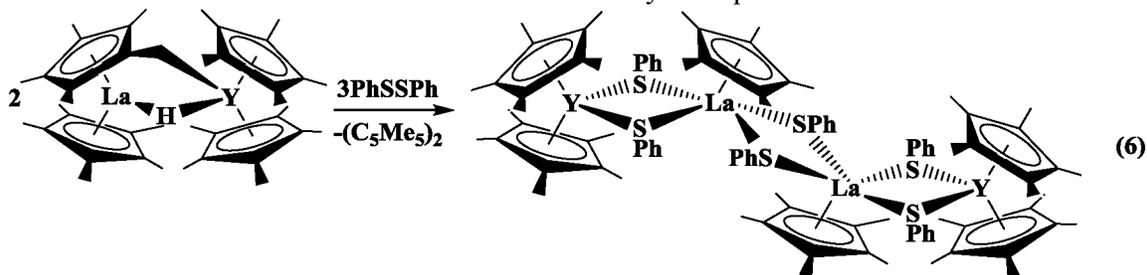
When two metals with a larger size difference are examined, this mixed metal tuck-over hydride system gives fewer variations. With lanthanum and lutetium (metal size difference 0.18 Å), a single mixed-metal tuck-over hydride complex, $(C_5Me_5)La[\mu-\eta^5:\eta^1-C_5Me_4(CH_2)](\mu-H)Lu(C_5Me_5)_2$, could be isolated and structurally characterized, eq 5.



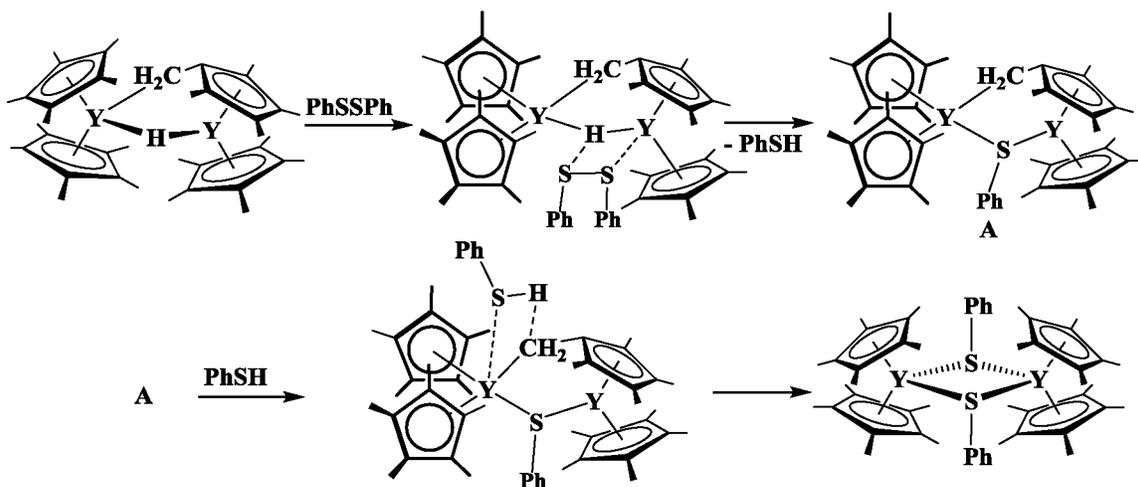
Surprisingly, the observed orientation of the bridging hydride and cyclopentadienyl-alkyl ligands was not that expected on the basis of metal size. As shown in eq 5, the formally seven coordinate metal site is occupied by larger La and the eight coordinate site by smaller Lu. This single product was obtained by heating a heterobimetallic hydride, $(C_5Me_5)_2Lu(\mu-H)_2La(C_5Me_5)_2$, formed by hydrogenolysis of a mixture of

$(C_5Me_5)_2La(allyl)$ and $(C_5Me_5)_2Lu(allyl)$. Combination of the isolated homometallic hydride tuck-over complexes, $(C_5Me_5)La[\mu-\eta^5:\eta^1-C_5Me_4(CH_2)](\mu-H)La(C_5Me_5)_2$ and $(C_5Me_5)Lu[\mu-\eta^5:\eta^1-C_5Me_4(CH_2)](\mu-H)Lu(C_5Me_5)_2$ gave the heterometallic $(C_5Me_5)La[\mu-\eta^5:\eta^1-C_5Me_4(CH_2)](\mu-H)Lu(C_5Me_5)_2$, but surprisingly also left significant amounts of the homometallic tuck-over complexes.

Subsequent reaction of the La/Y analog of the structurally characterized La/Lu complex with PhSSPh provided a new tetrametallic complex, $[(C_5Me_5)_2Y(\mu-SPh)_2La(C_5Me_5)(\mu-SPh)]_2$, eq 6, that demonstrated how these mixed metal complexes can be used to examine the reactivity of closely related metal centers. The structure shown suggests that PhSSPh reacts with Ln-H moieties to make Ln-SH and PhSH products and then the PhSH, generated in situ, reacts, not with any remaining Ln-H bonds, but only with the Ln-CH₂C₅Me₄ bonds to form C₅Me₅ ligands and another Ln-SPh unit. As observed above in the La/Lu complex, the smaller metal Y occupies the 8-coordinate sites and the larger La is in the 7-coordinate locations. This is contrary to expectations.



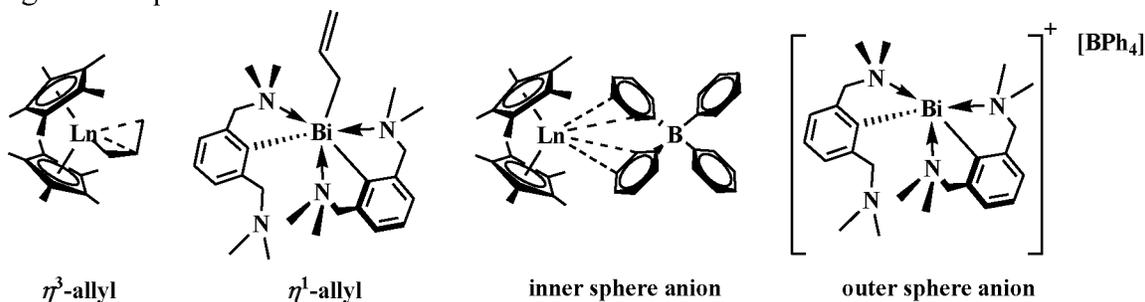
To obtain more information about tuck-over reactivity, the reactions of the homometallic complex, $(C_5Me_5)Y[\mu-\eta^5:\eta^1-C_5Me_4(CH_2)](\mu-H)Y(C_5Me_5)_2$, were examined [10]. The data suggest a very specific sequence of reactions with PhSSPh involving sigma bond metathesis with differentiated reactivity between the Y-C and Y-H bonds, Scheme 3. This demonstrates that these tuck-over hydrides can be used for comparative mixed metal reactivity studies.



Scheme 3. Reaction sequence that rationalizes the formation of $[(C_5Me_5)_2Y(SPh)]_2$ and no $(C_5Me_4CH_2SPh)^{1-}$ products.

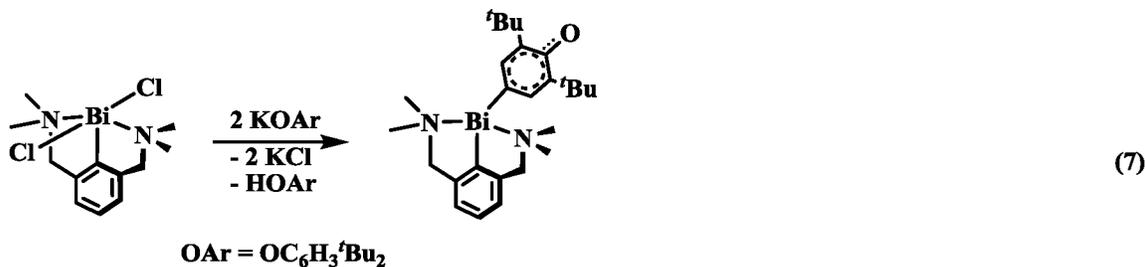
Bismuth Chemistry.

CMPO Complexation. For many years we have wondered if Bi^{3+} , which is similar in size to La^{3+} , would be useful in expanding the type of chemistry done in this study. When Dr. Bruce Mincher at the Idaho National Laboratory (INL) visited UCI for a seminar in Engineering, our discussion revealed that when INL used NaBiO_3 as an oxidant in nuclear waste stream separation schemes, this led to less effective octyl(phenyl)-*N,N*-diisobutylcarbamoyl methylphosphine oxide (CMPO) extraction of lanthanides with typical chelating ligands. A possible explanation was that Bi^{3+} was competing with Ln^{3+} for CMPO. However, to our knowledge a comparative study of Bi^{3+} and Ln^{3+} binding had never been made. Consequently, a comparative study of the binding of cationic lanthanide metallocenes with cations of chelated Bi^{3+} was carried out [4]. The study found that these metals bind very differently despite their similar size and charge, most probably because of their large difference in electronegativity. Pairs of dissimilarly ligated complexes are shown in Scheme 4.

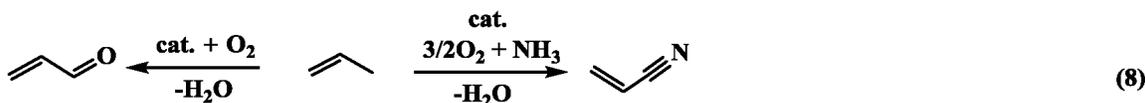


Scheme 4. Pairs of similar Bi^{3+} and Ln^{3+} complexes that have differing bonding modes.

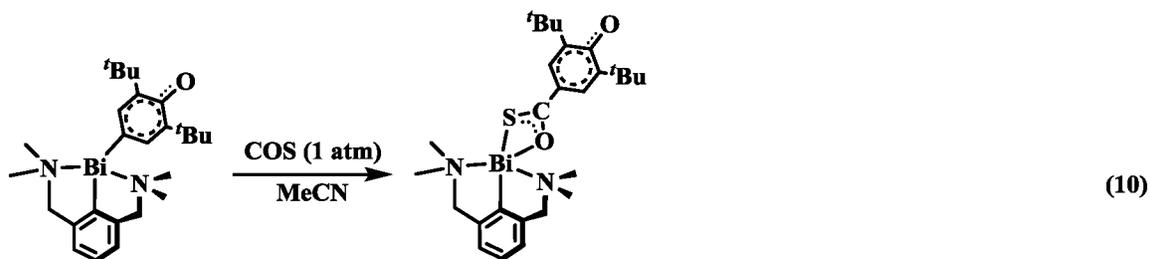
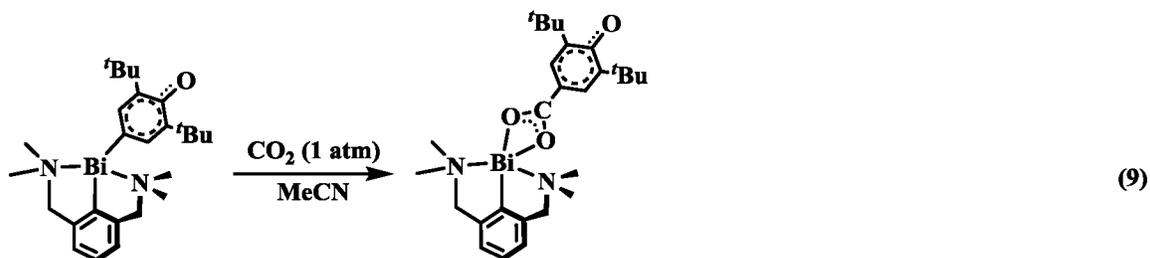
C-H Bond Activation. In the course of investigating the chelated bismuth cations in this study, the unusual C-H activation reaction shown below was discovered, eq 7 [6]. Specifically, two aryloxy anions transform into an aryl alcohol and an oxyaryl *dianion* that is now bound to Bi^{3+} via the C-H activated carbon atom rather than the oxide.



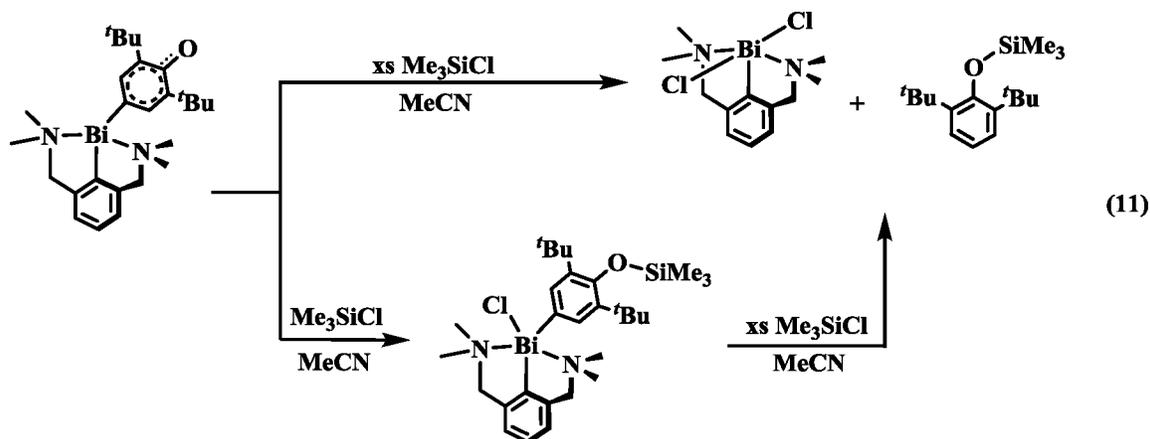
The isolation of a new type of dianionic ligand was most unexpected from this reaction. Bismuth is thought to foster the facile C-H activation observed in the SOHIO process for oxidation and ammoxidation of propene, eq 8. However, C-H bond activation reactions like eq 7 have never been observed for any metal complex.



CO₂ Activation. Since the oxyaryl dianion represents a new organometallic ligand class and arises from C-H bond activation, its chemistry has been pursued. Two major reactions of this unusual dianion have been identified. This ligand leads to the first example of CO₂ insertion chemistry with Bi-C bonds. As shown in eq 9, CO₂ inserts into the Bi-C bond of the oxyaryl dianion [11], a reaction does not occur with normal bismuth aryl complexes like BiPh₃. The CO₂ insertion generates another new type of dianionic ligand, an oxycarboxy species, [O₂CC₆H₂(*t*-Bu)₂O]²⁻. COS reacts analogously, eq 10, to make the first oxythiocarboxy dianion, [OSCC₆H₂(*t*-Bu)₂O]²⁻.

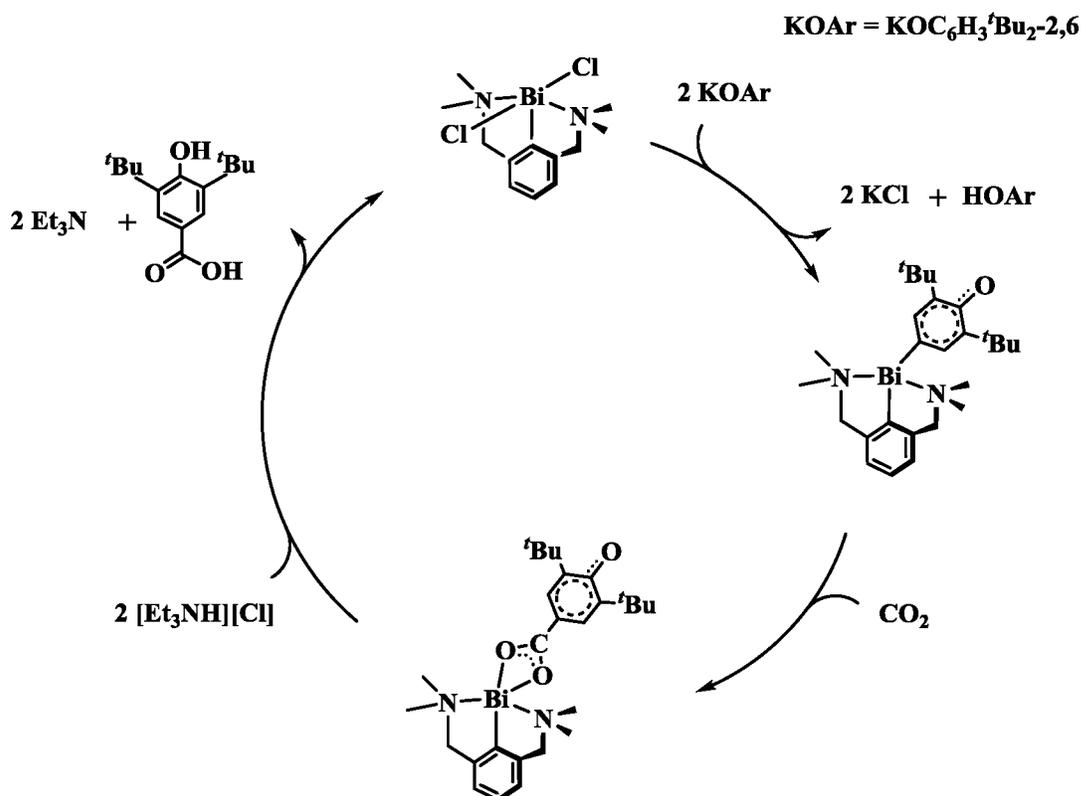


The oxyaryl dianion complex also reacts with trimethylsilyl halides and pseudohalides to add Me₃Si to the oxygen and the halide or pseudohalide to bismuth, eq 11. These reactions are formally oxidative additions that occur over five bonds.



Combining C-H and CO₂ Activation Into a Cycle. The C-H bond activation of eq 7 and the CO₂ activation in eq 9 provide a basis to use bismuth catalytically in a cyclic process to make 3,5-di-*tert*-butyl-4-hydroxybenzoic acid, a compound used in biomedical applications as a precursor to anti-viral compounds. Although this is not an expensive chemical, the published syntheses, which are largely in the patent literature, typically

functionalize the parent phenol with carbon dioxide by heating (80-210 °C) under high pressure (5-15 atm) with exposure to strong base. The process shown in Scheme 5 demonstrates that bismuth, a metal rarely used in catalysis or with CO₂, can effect this synthesis in a cyclic manner at ambient temperatures under an atmosphere of carbon dioxide.



Scheme 5. Bismuth-catalyzed C-H bond activation and CO₂ insertion lead to a cyclic process to make a carboxylic acid under mild conditions.

Lanthanide-Based CO₂ Insertion. In the course of the CO₂ insertion studies described above, we did an additional CO₂ insertion reaction with [(C₅Me₅)₂Sm]₂(μ-O) to help the theory group of Laurent Maron in Toulouse. They needed this to calibrate their studies of reductive coupling of CO₂ to oxalate by organometallic samarium complexes, a reaction originally reported by our group. We were surprised to see that the oxide complex, usually the final decomposition product in samarium metallocene reactions, *does* react with CO₂ to make carbonate. Hence, the calculations correctly predicted a new reaction that was experimentally verified [8].

Unspent Funds

No unspent funds will remain at the end of this funding period.

Current and Pending Support

Agency	Title of Project	Amount	Period Of Support
National Science Foundation	Expanding Reductive Chemistry with the Rare Earth Metals	\$560,999	2013-2016
Department of Energy Basic Energy Sciences Heavy Element Chemistry	Expanding the Fundamental Chemistry of Actinide Complexes	\$610,000	2013-2016

Pending Proposals: None

Publications Since the June 2010 Beginning of This Half Project Funded by Catalysis (DE-FG03-86ER13514)

1. "Utility of the 1,3,4,6,7,8-Hexahydro-2H-pyrimido[1,2-a]pyrimidinato Ligand, (hpp)⁻, in Stabilizing Uranium Metallocene Mono-Alkyl and "Tuck-in" Complexes" Elizabeth Montalvo, Joseph W. Ziller, Antonio G. Di Pasquale, Arnold L. Rheingold, William J. Evans *Organometallics* **2010**, *29*, 2104-2110. **DOI:** 10.1021/om100076s
2. "Reactivity of Tuck-in and Tuck-over Uranium Metallocene Complexes" Elizabeth Montalvo, Kevin A. Miller, Joseph W. Ziller, and William J. Evans *Organometallics* **2010**, *29*, 4159-4170. **DOI:** 10.1021/om1007538
3. "DFT and CASPT2 Analysis of Polymetallic Uranium Nitride and Oxide Complexes: The Power of Theory When X-ray Analysis is Inadequate" Tanya K. Todorova, Laura Gagliardi, Justin R. Walensky, Kevin A. Miller, and William J. Evans *J. Am. Chem. Soc.* **2010**, *132*, 12397-12403. **DOI:** 10.1021/ja103588w
4. "Bismuth Coordination Chemistry with Allyl, Alkoxide, Aryloxy, and Tetraphenylborate Ligands and the {[2,6-(Me₂NCH₂)₂C₆H₃]₂Bi}⁺ Cation" Ian J. Casely, Joseph W. Ziller, Bruce J. Mincher, and William J. Evans *Inorg. Chem.* **2011**, *50*, 1513-1520. **DOI:** 10.1021/ic102119y
5. "Synthesis and Insertion Chemistry of a Cyclooctatetraenyl Uranium "Tuck-in" Metallocene, (η⁸-C₈H₈)(η⁵:η¹-C₅Me₄CH₂)U" Michael K. Takase, Nathan A. Siladke, Joseph W. Ziller, and William J. Evans *Organometallics*, **2011**, *30*, 458-465. **DOI:** 10.1021/om100700p
6. "Facile Bismuth-Oxygen Bond Cleavage, C-H Activation, and Formation of a Monodentate Carbon-Bound Oxyaryl Dianion, (C₆H₂^tBu₂-3,5-O-4)²⁻" Ian J. Casely, Joseph W. Ziller, Ming Fang, Filipp Furche, and William J. Evans *J. Am. Chem. Soc.* **2011**, *133*, 5244-5247. **DOI:** 10.1021/ja201128d

7. "C–H Activation via Carbodiimide Insertion into Yttrium–Carbon Alkynide Bonds: An Organometallic Alder-ene Reaction" Ian J. Casely, Joseph W. Ziller, and William J. Evans *Organometallics* **2011**, *30*, 4873–481. **DOI:** 10.1021/om200419k

8. "Insights into the Mechanisms of the Reactions of $(C_5Me_5)_2Sm^{II}(thf)_2$ with CO_2 and COS by DFT Studies" Ludovic Castro, Stéphanie Labouille, Douglas R. Kindra, Joseph W. Ziller, François Nief, William J. Evans, and Laurent Maron *Chemistry, A European Journal* **2012**, *18*, 7886–7895. **DOI:** 10.1002/chem.201103192

9. "Ligand Influence on the Redox Chemistry of Organosamarium Complexes: Experimental and Theoretical Studies of the Reactions of $(C_5Me_5)_2Sm(THF)_2$ and $(C_4Me_4P)_2Sm$ with Pyridine and Acridine" Stéphanie Labouille, François Nief, Xavier-Frédéric Le Goff, Laurent Maron, Douglas R. Kindra, Heidi L. Houghton, Joseph W. Ziller, and William J. Evans *Organometallics* **2012**, *31*, 5196–5203. **DOI:** 10.1021/om300573z

10. "Reactivity of the Y^{3+} Tuck-over Hydride Complex, $(C_5Me_5)_2Y(\mu-H)(\mu-CH_2C_5Me_4)Y(C_5Me_5)$ " Benjamin M. Schmiede, Megan E. Fieser, Joseph W. Ziller, and William J. Evans *Organometallics* **2012**, *31*, 5591–5598. **DOI:** 10.1021/om300546t

11. "Insertion of CO_2 and COS into Bi–C Bonds: Reactivity of the Oxyaryl Dianion in the Bismuth NCN Pincer Complex, $[2,6-(Me_2NCH_2)_2C_6H_3]Bi(C_6H_2^tBu_2O)$ " Douglas R. Kindra, Ian J. Casely, Megan E. Fieser, Joseph W. Ziller, Philipp Furche, and William J. Evans *J. Am. Chem. Soc.* **2013**, *135*, 7777–7787. **DOI:** 10.1021/ja403133f

Publications Since the June 2010 Beginning of this Half Project Funded by Heavy Element Chemistry (DE-FG02-10ER16161)

These are included for your information to show the total output of DOE research during the past three years was 21 papers.

a. "Synthesis and Reactivity of a Silylalkyl Double Tuck-in Uranium Metallocene, $(\eta^5:\eta^1-C_5Me_4SiMe_2CH_2)_2U$, and Its Conversion to Bis(tethered) Metallocenes" William J. Evans, Nathan A. Siladke, and Joseph W. Ziller *Chem., Eur. J.* **2010**, *16*, 796–800. **DOI:** 10.1002/chem.200902428

b. "Reactivity of the Tethered Alkyl Uranium Bonds of $(\eta^5:\kappa^1-C_5Me_4SiMe_2CH_2)_2U$ " William J. Evans, Nathan A. Siladke, and Joseph W. Ziller *Compt. Rend. Chim.* **2010**, *13*, 775–780. **DOI:** 10.1016/j.crci.2010.02.003

c. "Importance of Energy Level Matching for Bonding in Th^{3+} - Am^{3+} Actinide Metallocene Amidinates, $(C_5Me_5)_2[{}^1PrNC(Me)N^1Pr]An$ " Justin R. Walensky, Richard L. Martin, Joseph W. Ziller, and William J. Evans *Inorg. Chem.* **2010**, *49*, 10007–10012. **DOI:** 10.1021/ic1013285

d. "Insertion, Isomerization, and Cascade Reactivity of the Tethered Silylalkyl Uranium Metallocene $(\eta^5-C_5Me_4SiMe_2CH_2-\kappa C)_2U$ " Nathan A. Siladke, Joseph W. Ziller, and William J. Evans *J. Am. Chem. Soc.* **2011**, *133*, 3507–3516. **DOI:** 10.1021/ja109491k

- e. "Unprecedented Bending and Rearrangement of f-Element Sandwich Complexes Induced by Superbulky Cyclooctatetraenide Ligands" Volker Lorenz, Benjamin M. Schmiege, Cristian G. Hrib, Joseph W. Ziller, Anja Edelmann, Steffen Blaurock, William J. Evans, and Frank T. Edelmann *J. Am. Chem. Soc.* **2011**, *133*, 1257-1259. **DOI:** 10.1021/ja109604t
- f. "Synthesis, Structure, and Magnetism of an f Element Nitrosyl Complex, (C₅Me₄H)₃UNO" Nathan A. Siladke, Katie R. Meihaus, Joseph W. Ziller, Ming Fang, Philipp Furche, Jeffrey R. Long, and William J. Evans *J. Am. Chem. Soc.* **2012**, *134*, 1243-1249. **DOI:** 10.1021/ja2096128
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