

**Title: Advancing Organometallic Catalysis via Incorporating
Weakly-Coordinating Carborane Anions
into Cationic Half-Sandwich Electrophilic Complexes**

Abstract.

In homogeneous transition metal catalysis an “ideal” weakly-coordinating anion constitutes a critical condition for an accessible reactive site at the cationic metal center. Introduction of weakly-coordinating BAr_f^- anion was a significant achievement and led to highly reactive catalysts, capable of C-H bond activation ($\text{BAr}_f^- = [\text{B}(3,5\text{-CF}_3\text{-C}_6\text{H}_3)_4]^-$). The drawback of the BAr_f^- anion is its thermal and chemical instability under acidic conditions. Triflate, another anion traditionally used in cationic complexes, often coordinates strongly and restricts access to the metal center for small molecular substrates. In contrast, carborane anions $\text{CB}_{11}\text{H}_6\text{X}_6^-$ ($\text{X} = \text{H}$ or halogen) are known for their outstanding weakly-coordinating properties and chemical inertness. These properties have been shown to enable carboranes to stabilize extremely reactive cationic organic and main group species. Application of carboranes has been surprisingly limited in transition metal (TM) chemistry. **Proposed here are novel applications of carborane anions for stabilization of reactive TM cationic compounds and catalysis facilitation.** The first proposed carborane-stabilized pentamethyl-cyclopentadienyl nitrosyl ruthenium system belongs to an important class of “half-sandwich” cationic homogeneous catalysts. It has been shown that the catalytic activity of cationic ruthenium complexes, for olefin polymerization and ether oxidation, is significantly enhanced when BAr_f^- anions are used versus triflate anions. It is proposed that these catalytic properties will be enhanced further with less coordinating chemically robust carborane anions. This research will be extended to other reactive systems with Ir(III) and Rh(II). **Bringing carboranes into cationic transition metal complexes will expand our fundamental understanding and command of key metallo-organic transformations.**

Introduction and Background.

Transition metal cationic Lewis–acid systems play an important role in homogeneous catalysis.¹ The question of an “ideal” counter-ion is critically important for these systems.² A reactive site at the metal center can be created via dissociation of a labile neutral ligand, so it is imperative that the counterion is non-coordinating and non-nucleophilic. Introduction of fluorinated tetraarylborate anions such as BAr_f^- was a major advance which has led to the development of powerful cationic catalysts ($\text{BAr}_f = [\text{B}(3,5\text{-CF}_3\text{-C}_6\text{H}_3)_4]^-$).³ Being extremely useful in some systems, BAr_f^- anion is prone to thermal and acidic boron-carbon bond cleavage. In triflate complexes the anion is attached directly to the metal center.⁴ Triflates, known as good leaving groups in organic reactions, are often too nucleophilic and strongly bound to the metal center to generate a vacant site for an incoming molecular substrate.

Carborane anions based on $\text{CB}_{11}\text{H}_{12}^-$ are known for their exceptionally weakly-coordinating properties, spectacular chemical inertness and stabilization of extremely reactive chemical species.^{5,6} These anions can be custom-tailored through alkyl and halogen substitution of hydrogens (Figure 1). Applications of carborane anions in homogeneous catalysis are surprisingly limited and include Turners publications on the carborane-based zirconocene polymerization catalysts at Exxon Mobil⁷ and recent reports on the comparisons of carborane anions to BF_4^- in rhodium- and iridium-based hydrogenation catalysts.⁸ We propose to bring carborane anions into cationic transition metal research, using their attractive characteristics to stabilize novel reactive species, ultimately advancing the homogeneous catalysis field.

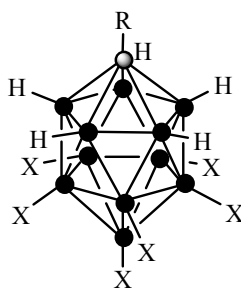


Figure 1. Carborane anion $\text{CB}_{11}\text{H}_5\text{X}_6\text{R}^-$. Dark spheres are boron atoms, light sphere – carbon atom in the cage. Parent carborane: all substituents are hydrogens. Examples of derivatives: 1) R- alkyl, X- hydrogens; 2) R - hydrogen, X – bromine 3) R-hydrogen, X – chlorine.

We started the studies with a well-defined ruthenium pentamethyl-cyclopentadienyl nitrosyl system. This is an ideal system because the metal center in these complexes with triflate anions possesses significant electrophilic character. The reactivity of this system is enhanced by replacing triflate with BAr_f^- anion.^{9,10,11,12} Tetrahydrofuran is catalytically oxidized by molecular oxygen in the presence of $[\text{Cp}^*\text{Ru}(\text{NO})\text{CH}_3(\text{THF})]^+ \text{BAr}_f^-$, which does not occur at all in the presence of triflate complex $[\text{Ru}]\text{CH}_3\text{OTf}$.¹¹ Both triflate and BAr_f^- complexes are reported to catalyze olefin polymerization, giving low molecular weight oligomers.^{10,12} Triflate hampers the reactivity of the system by competitive binding to the available coordination site, while $[\text{Cp}^*\text{Ru}(\text{NO})\text{CH}_3(\text{THF})]^+ \text{BAr}_f^-$ catalyst decomposes at room temperature in solution.

We propose using the $[\text{Cp}^*\text{Ru}(\text{NO})(\text{R})\text{L}]^+$ system as a *first test case* for stabilizing cationic half-sandwich transition metal complexes by weakly-coordinating inert carborane anions $\text{CB}_{11}\text{H}_6\text{X}_6^-$ ((shown on the right, $\text{X} = \text{H}, \text{Cl},$ or Br , $\text{L} =$ neutral coordinated solvent). The effect of various derivatized carborane anions on the reactivity of these complexes with small molecular

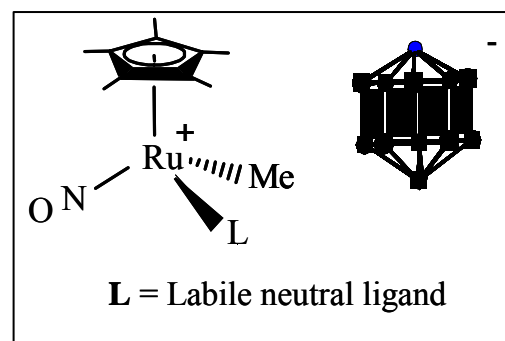


Figure 2.

substrates will be explored in comparison to BAr_f^- and triflate analogs. Decreased coordination of the counter-ion is anticipated to ultimately improve catalytic efficiency of the system. Based on the results of these studies, the research will be extended to electrophilic iridium and rhodium catalytic systems capable of C-H activation (Figure 3). The proposed investigations will expand our fundamental understanding and command of key metallo-organic transformations.

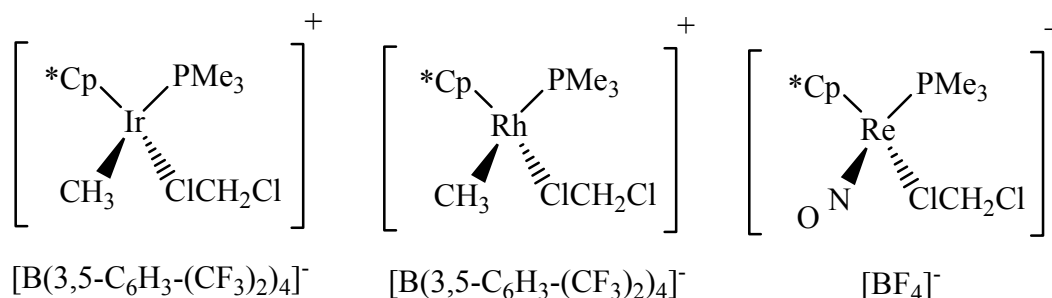
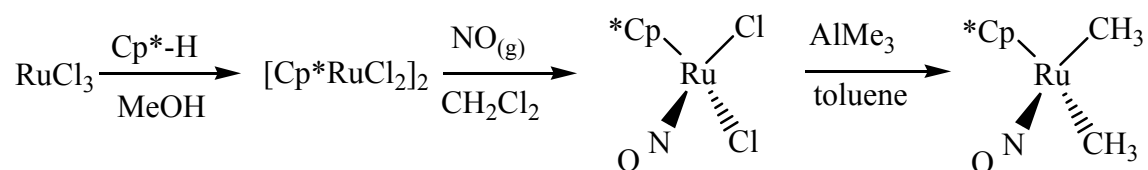


Figure 3. Reactive electrophilic late transition metal cationic complexes.¹³

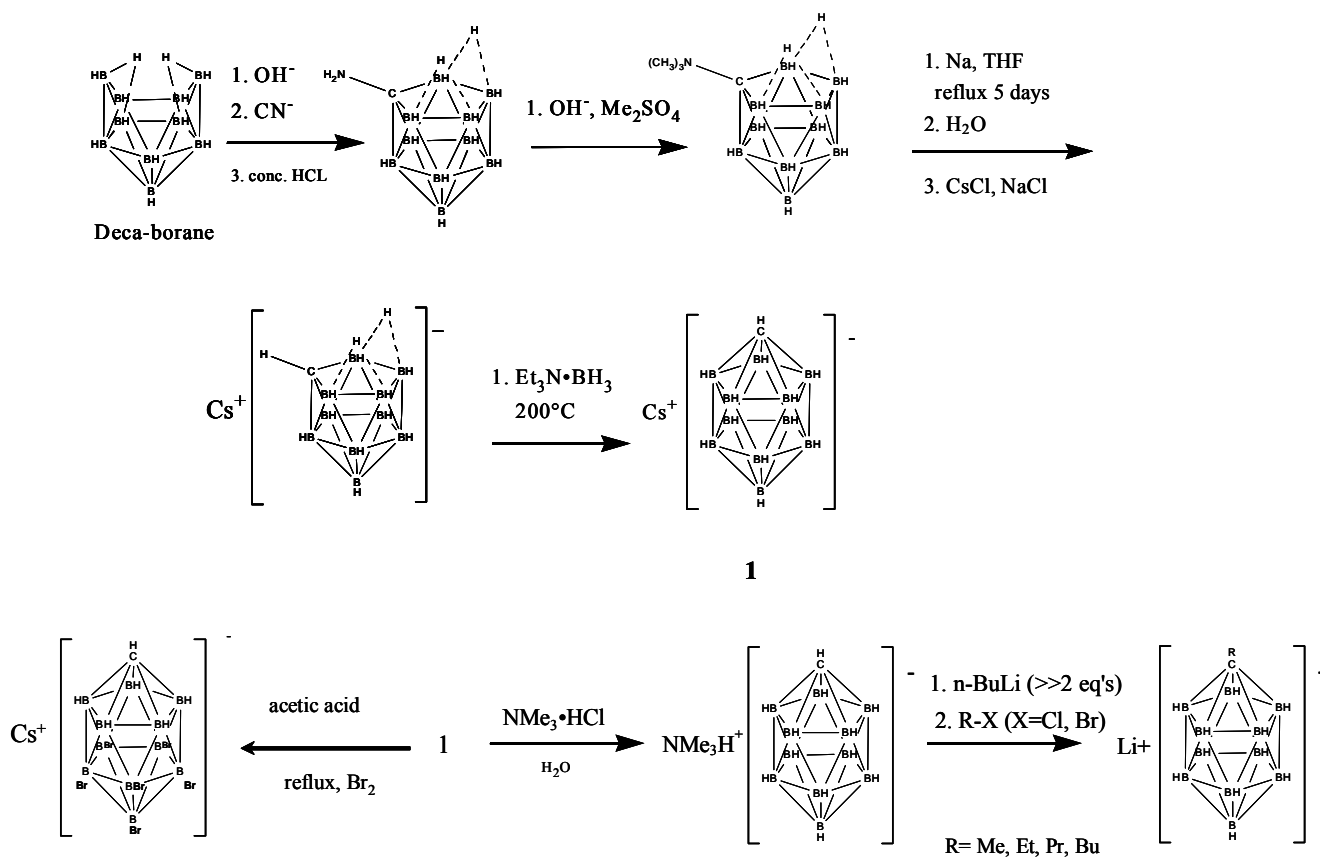
Preliminary results.

All preliminary results were obtained by undergraduate students under the P.I. s' supervision, starting with preparation of carborane salts and Cp*Ru(NO)X₂ complexes on a 10 g scale (X = alkyl, halogen, triflate, Schemes 1, 2).^{14,15}

Scheme 1. Synthesis of starting dimethyl ruthenium complex.¹⁵

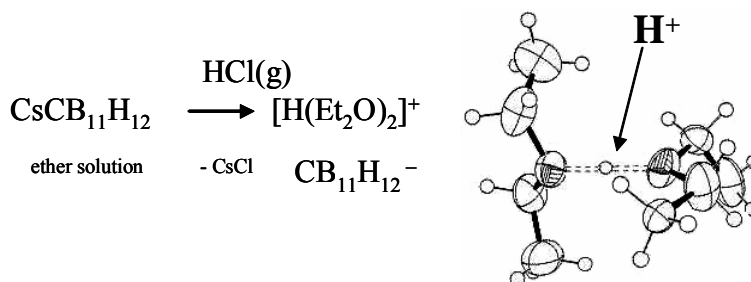


Scheme 2. Synthesis and derivatization of carborane anions.¹⁴

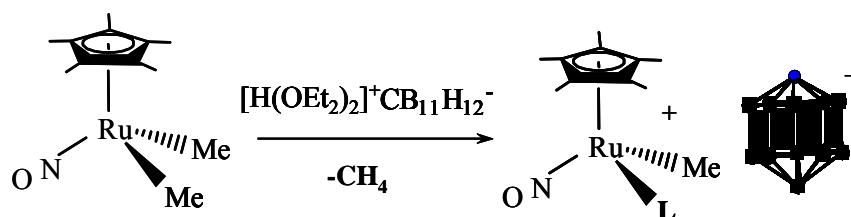


Two new protonated salts of ether with $\text{CB}_{11}\text{H}_{12}^-$ and $\text{CB}_{11}\text{H}_6\text{Br}_6^-$ anions were synthesized and used to obtain desired $[\text{Cp}^*\text{Ru}(\text{NO})\text{R}(\text{L})][\text{carborane}]$ complexes (Schemes 3, 4). *This is the first precedent of using solvated proton salts of carborane for de-alkylation of transition metal complexes.*

Scheme 3. Synthesis of $[\text{H}(\text{OEt}_2)_2]^+[\text{CB}_{11}\text{H}_{12}]^-$. Image of the cation structure is modified from reference 16.



Scheme 4. Synthesis of ruthenium carborane complex via protonation of the di-methyl precursor. Substituents on the carborane cage are not drawn, L = coordinated acetonitrile or dichloromethane.



The spectroscopic analysis of the product is consistent with the assigned formula (Scheme 4).^a The structure is also supported by the preliminary single crystal X-ray diffraction analysis. In another approach, carborane silver salt metathesis reaction with $\text{Cp}^*\text{Ru}(\text{NO})\text{MeCl}$ complex was tested. Starting material in these reactions is consumed rapidly, accompanied by changes in color and NMR spectra of the reaction mixtures.

General plan of procedure.

The top priority is optimizing and scaling up **syntheses** of $[\text{Cp}^*\text{Ru}(\text{NO})(\text{CH}_3)(\text{L})][\text{carborane}]$ complexes via protonation route (carborane is $\text{CB}_{11}\text{H}_{12}^-$, $\text{CB}_{11}\text{H}_6\text{Cl}_6^-$ or $\text{CB}_{11}\text{H}_6\text{Br}_6^-$, L is coordinated solvent). The variety of protonating agents for this reaction spans from protonated ether and THF to super-acidic benzenium salt of carborane.¹⁴ The dichloromethane complex would constitute a highly

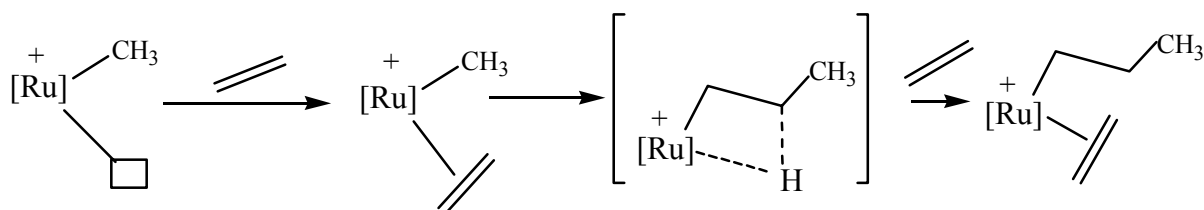
^a ¹H NMR data (CD_3CN , 300 MHz Varian): δ 1.87 (s, Cp^*15H), δ 1.33 ppm (s, Ru-CH_3 , 3H), IR (CD_3CN): ν_{NO} at 1790 cm^{-1} .

reactive organometallic Lewis acid, whose Ir and Rh analogs are capable of C-H bond activation (Figure 3).¹³ Carborane-stabilized complex will be initially isolated with acetonitrile molecule, which can be removed subsequently by redissolving the complex in dichloromethane. The exchange and coordination of dichloromethane to ruthenium center will be monitored by low temperature ¹³C NMR spectroscopy. Investigations into the silver metathesis synthetic route will continue. If successful, the silver route has an advantage of more accessible reagents as compared to solvated proton carborane salts. IR spectroscopy studies will use diagnostic nitrosyl stretch as an indicator of the electrophilicity of the metal center.¹⁷ The effect of the anion bulkiness on the ion pairing in solution will be estimated in ¹¹B and ¹H NMR spectroscopy studies. The material characterization by NMR, IR and UV-vis spectroscopy will be carried out at the Ithaca College facilities. Single crystal X-ray diffraction studies will be done in collaboration with Dr. Emil Lobkovsky (Cornell University) and Professor Phillip Coppens (SUNY Buffalo).

The following **reactivity studies** are planned:

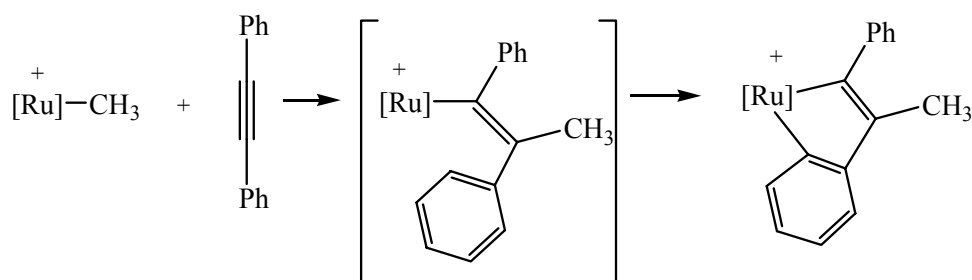
- Treatment of [Cp*Ru(NO)(CH₃)L][carborane] with ethylene is expected to proceed according to Scheme 5 via the addition step, followed by migratory insertion step. These experiments, including kinetics studies, will be monitored by variable temperature high-field multinuclear NMR spectroscopy. Agostic coordination of a beta-hydrogen should be indicated by the presence of far up-field signals in the proton NMR spectrum.¹⁸

Scheme 5. Olefin coordination and migratory insertion into ruthenium carborane complex. Vacant coordination site □ results from dissociation of weakly-coordinated carborane or neutral solvent molecule. [Ru]=[Cp*Ru(NO)]. Carborane portion is not shown.



- Alkyne reactions with the carborane-stabilized complexes and their triflate and BAR_f^- analogs will be studied. The reaction of triflate complex with di-phenyl-acetylene has been reported (Scheme 6).¹⁰ The question is whether the presence of a very different non-nucleophilic counter-ion anion will lead to a different product, allowing coordination of another alkyne molecule. Direct comparisons to the $\text{Cp}^*\text{Ru}(\text{NO})(\text{CH}_3)(\text{THF})^+ \text{BAR}_f^-$ analog will be made.

Scheme 6. Reaction of $[\text{Ru}]\text{CH}_3\text{OTf}$ with di-phenyl-acetylene (triflate groups are omitted).



- The reactivity with CO will be tested. CO addition followed by insertion mechanism has been observed and used for alternating CO-alkene polymerization the late transition metals,¹⁹ and a precedent was reported for CO insertion into Ru-C σ -bond.²⁰
- The mechanism of the catalytic THF oxidation by molecular oxygen in the presence of $[\text{Cp}^*\text{Ru}(\text{NO})\text{Me}]^+$ will be studied by low-temperature UV-vis and IR spectroscopy, both with BAR_f^- and carborane-stabilized complexes. While some precedents for this transformation are believed to occur by radical mechanisms, it is not clear why there is a substantial difference in reactivity between the BAR_f^- and triflate ruthenium compounds.²¹ Carborane anions, due to their non-coordinating inert nature, are ideal counter-ions for such study.
- We are intrigued by the fact that excess of protonating reagent is needed to complete the reaction according to Figure 3. One hypothesis is formation of the hydrogen-bonded intermediates that precede protonation step and release of CH_4 , analogous to protonation of hydride complexes studied by Poli.²² The reactions of protonation using solvated-hydrogen carborane salt will be studied by low temperature stopped-flow UV-vis and IR spectroscopy with regard to possible intermediates.

Feasibility and educational benefits of the project.

We are excited about the research in carborane-stabilized cationic transition metal complexes. Initial investigations have demonstrated that this work is well suited for undergraduates. The organization of the project is perfect for summer program, yet allows for the semester sub-projects. Three undergraduates who worked with the P.I. at Seattle University in 2001, are currently pursuing graduate degrees at the University of Washington. At Ithaca College, undergraduates Jesse Kleingardner and Eric Leibensperger started the carborane salt preparations in 2004. [Currently Eric is in chemistry Ph.D. program at Harvard University.] Nathan Kozlowski and Joseph Livingston (a minority Jamaican student) worked on the carborane derivatization. Matt Pearsall started ruthenium research at IC and received an REU summer internship for a collaborative project with Phillip Coppens (SUNY Buffalo).²³ Joshua Masland is currently making good progress in ruthenium carborane complex syntheses.

All of the members of the chemistry department at IC have research programs supported by current grants (from ACS PRF, NSF, NIH and Research Corporation), each supervising three research students on average. In 2004 eleven students (including Matt Pearsall and Jesse Kleingardner) and two faculty members (including the P.I.) gave a total of thirteen presentations at the national ACS meeting in San Diego. In summer of 2005 twelve undergraduate students carried out research at IC. Student support was provided by academically competitive IC Dana Fellowship (to Josh Masland and Jesse Kleingardner) and through external faculty research grants. With this support we have been able to start cutting-edge research in weakly-coordinating anions for the transition metal chemistry. We are setting up a vigorous, stimulating and sustainable program with undergraduate students pursuing fundamental science, while participating in a relevant research with direct significance to the society.

References:**1. Examples:**

- Malinoski, J.M., White, P.S., Brookhart, M. "Structural Characterization of $[\eta\text{-}2\text{-}(\text{t-Bu})_2\text{PCH}_2\text{C}(\text{O})\text{C}_6\text{H}_5]\text{PdMe}(\eta\text{-}2\text{-}\text{C}_2\text{H}_4)+\text{BAr}_4^-$: A Model for the Catalyst Resting State for Ethylene Polymerization" *Organometallics* **2003**, 22, 621; Taw, F. L.; Bergman, R. G.; Brookhart, M. "Silicon-Hydrogen Bond Activation and Formation of Silane Complexes Using a Cationic Rhodium(III) Complex" *Organometallics* **2004**, 23(4); 886; Stoebenau, E. J., III; Jordan, R. F. "Coordination of Alkenes and Alkynes to a Cationic d^0 Zirconocene Alkoxide Complex" *J. Am. Chem. Soc.* **2003**, 25(11) 3222; Jia, L.; Yang, X.; Stern, C. L.; Marks, T. J. "Cationic Metallocene Polymerization Catalysts Based on Tetrakis(pentafluorophenyl)borate and Its Derivatives. Probing the Limits of Anion "Noncoordination" via a Synthetic, Solution Dynamic, Structural, and Catalytic Olefin Polymerization Study" *Organometallics* **1997**, 16 (5), 842.
2. Strauss, S.H. "The search for larger and more weakly coordinating anions" *Chem. Rev.* **1993**, 93, 927.
3. Brookhart, M.; Grant, B.; Volpe, A.F. Jr. " $[(3,5\text{-}(\text{CF}_3)_2\text{C}_6\text{H}_3)_4\text{B}][\text{H}(\text{OEt}_2)_2]^+$: a convenient reagent for generation and stabilization of cationic, highly electrophilic organometallic complexes" *Organometallics* **1992**; 11(11); 3920.
4. Beck, W. , Suenkel, K. "Metal complexes of weakly coordinating anions. Precursors of strong cationic organometallic Lewis acids" *Chem. Rev.* **1988**, 88(7), 1405.
5. Reed, C. A. "Carboranes: A New Class of Weakly Coordinating Anions for Strong Electrophiles, Oxidants, and Superacids" *Acc. Chem. Res.* 1998, 31(3), 133.
6. Reed, C. A.; Fackler, N. L. P.; Kim, K.-C.; Stasko, D.; Evans, D. R.; Boyd, P. D. W.; Rickard, C. E. F. "Isolation of Protonated Arenes (Wheland Intermediates) with BArF and Carborane Anions. A Novel Crystalline Superacid" *J. Am. Chem. Soc.*, 1999, **121**, 6314.
7. Hlatky, G.G.; Turner, H.W.; Eckman, R.R. "Ionic, base-free zirconocene catalysts for ethylene polymerization" *J. Am. Chem. Soc.* **1989**, 111(7), 2728; "Metallacarboranes as labile anions for ionic zirconocene olefin polymerization catalysts" Hlatky, G.G.; Eckman, R.R.; Turner, H.W.; *Organometallics* **1992**, 11(3), 1413.
8. Rifat, A.; Patmore, N. J.; Mahon, M. F.; Weller, A. S. "Rhodium Phosphines Partnered with the Carborane Monoanions $[\text{CB}_{11}\text{H}_6\text{Y}_6]^-$ (Y = H, Br). Synthesis and Evaluation as Alkene Hydrogenation Catalysts" *Organometallics* **2002**, 21(14), 2856; Rifat, A.; Kociok-Kohn, G.; Steed, J. W.; Weller, A. S.; "Cationic Iridium Phosphines Partnered with $[\text{closo-CB}_{11}\text{H}_6\text{Br}_6]^-$: $(\text{PPh}_3)_2\text{Ir}(\text{H})_2(\text{closo-CB}_{11}\text{H}_6\text{Br}_6)$ and $[(\text{PPh}_3)_2\text{Ir}(\eta\text{-}2\text{-}\text{C}_2\text{H}_4)_3][\text{closo-CB}_{11}\text{H}_6\text{Br}_6]$. Relevance to Counterion Effects in Olefin Hydrogenation" *Organometallics* **2004**, 23(3), 428.
9. Svetlanova-Larsen, A.; Zoch, C. R.; Hubbard, J. L. "Aqueous Organometallic Chemistry of the Electrophilic $[(\text{C}_5(\text{CH}_3)_5\text{Ru}(\text{NO}))]^{2+}$ Fragment" *Organometallics*, **1996**, 15(13), 3076.
10. Burns, R.M.; Hubbard, J.L. "Alkyne Activation by Electrophilic $[(\eta\text{-}5\text{-}\text{C}_5\text{Me}_5)\text{Ru}(\text{NO})(\text{R})]^+$ (R = Me, Ph, p-tolyl) Fragments: .beta.-Migratory Insertion, Isomerization, and Metallacycle Formation" *J. Am. Chem. Soc.* **1994**, 116(21), 9514.
11. Svetlanova (Larsen), A. "Thermodynamics and kinetics of small molecule binding to cyclopentadienyl-Ru-NO and Rh-CO electrophilic centers" Ph.D. Dissertation **1996** Utah State Univ., Logan, UT, USA.
12. Burns, R.M. "Synthesis, structure, and reactivity of nitrosyl and thionitrosyl $(\eta\text{-}5)\text{-pentamethylcyclopentadienyl}$ ruthenium(ii) complexes (pentamethylcyclopentadienyl ruthenium(ii))" Ph.D. Dissertation **1994** Utah State Univ., Logan, UT, USA.; Yi, G.B. "Synthesis, structure, and reactivity of electrophilic ruthenium complexes containing the $[(\eta\text{-}5\text{-}\text{C}_5(\text{CH}_3)_5)\text{Ru}(\text{NO})]$ core" Ph.D. Dissertation **1995** Utah State Univ., Logan, UT, USA.
13. Arndtsen, B. A.; Bergman, R. G. "Unusually Mild and Selective Hydrocarbon C-H Bond Activation Using Positively Charged Iridium(III) Complexes" *Science* **1995**, 270, 1970; Peng, T.-S.; Winter, C. H.;

- Gladysz, J. A. "Generation and Reactivity of Substitution-Labile Dichloromethane and Chlorobenzene Adducts of the Chiral Pentamethylcyclopentadienyl Rhenium Lewis Acid [(eta5-C5Me5)Re-(NO)(PPh3)]⁺" *Inorg. Chem.* **1994**, 33, 2534; Taw, F.L.; Bergman, R.G.; Brookhart, M. "Silicon-Hydrogen Bond Activation and Formation of Silane Complexes Using a Cationic Rhodium(III) Complex" *Organometallics* **2004**, 23, 886.
- 14.** Jelinek, T.; Plesek, J.; Hermanek, S.; Stibr, B. "Chemistry of compounds with the 1-carba-closo-dodecaborane(12) framework" *Collect. Czech.Chem. Comm.* **1986**, 51(4), 819.
- 15.** Chang, J.; Seidler, M.D.; Bergman, R.G. "Synthesis of alkylruthenium nitrosyl complexes. Migratory insertion to coordinated nitric oxide and the mechanism of the conversion of the resultant nitrosoalkyl compounds to oximate, carboxamide, and cyano compounds" *J. Am. Chem. Soc.* **1989**, 111(9), 3258.
- 16.** Stasko, D.; Hoffmann, S. P.; Kim, K.-C.; Fackler, N. L. P.; Larsen, A. S.; Drovetskaya, T.; Tham, F. S.; Reed, C. A.; Rickard, C. E. F.; Boyd, P. D. W.; Stoyanov, E. S. "Molecular Structure of the Solvated Proton in Isolated Salts. Short, Strong, Low Barrier (SSLB) H-bonds" *J. Am. Chem. Soc.* **2002**, 124(46), 13869.
- 17.** Hayton, T. W.; Legzdins, P.; Sharp, W. B.; "Coordination and Organometallic Chemistry of Metal-NO Complexes" *Chem. Rev.* **2002**, 102(4), 935.
- 18.** Bennett, M.A.; McMahon, J.M.; Pelling, S.; Brookhart, M.; Lincoln, D.M. "Protonation of diene complexes of rhodium, iridium, ruthenium, and osmium: a fine balance between terminal and agostic hydrides" *Organometallics* **1992**, 11(1), 127.
- 19.** Brookhart, M.; Rix, F.C.; DeSimone, J.M.; Barborak, J.C. "Palladium(II) catalysts for living alternating copolymerization of olefins and carbon monoxide" *J. Am. Chem. Soc.* **1992**, 114(14), 5894.; Shultz, S.C.; Ledford, J.; DeSimone, J.M.; Brookhart, M. "Kinetic Studies of Migratory Insertion Reactions at the (1,3-Bis(diphenylphosphino)propane)Pd(II) Center and Their Relationship to the Alternating Copolymerization of Ethylene and Carbon Monoxide" *J. Am. Chem. Soc.* **2000**, 122 (27), 6351.
- 20.** Pankowski, M.; Bigorgne, M. "Insertion of carbon monoxide into sigma alkyl metal-carbon bond of carbonyl complexes of iron and ruthenium" *J. Organomet. Chem.* **1983**, 251(3), 333.
- 21.** Fazlur-Rahman, A. K., Tsai, J. -C., Nicholas, K. M. "Rhodium-catalyzed, carbon dioxide-mediated aerobic oxidation of ethers" *J. Chem. Soc., Chem. Com.* **1992**, 1334; Fackler, N.; Zhang, S.; O'Halloran, T. "Stabilization of High Valent Terminal-oxo-complexes: The Interplay of D-orbital Occupancy and Coordination Geometry", *J. Amer. Chem. Soc.*, 1996, 118, 481-482; Hata, E.; Takai, T.; Mukaiyama, T. "Aerobic oxygenation of olefins catalyzed by transition-metal complexes - preparation of epoxides and alfa-hydroxy ketones" *Chem.Lett.* **1993**, 1513; Aresta, M., Fragale, C., Quaranta, E., Tommasi, I. "Carbon dioxide as modulator of the oxidative properties of dioxygen in the presence of transition metal systems" *J. Chem. Soc., Chem. Comm.* **1992**, 315.
- 22.** Belkova, N.V.; Revin, P.O.; Epstein, L.M.; Vorontsov, E.V.; Bakhmutov, V.I.; Shubina, E.S.; Collange, E.; Poli, R. "Kinetics and Mechanism of the Proton Transfer to Cp*Fe(dppe)H: Absence of a Direct Protonation at the Metal Site" *J. Am. Chem. Soc.* **2003**, 125(36), 11106.
- 23.** See enclosed letter of collaboration
-