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PRINCIPAL INVESTIGATOR	Anna Larsen	PHONE	(607)274-3473
ACADEMIC RANK	Assistant Professor	FAX	(607)274-1848
DEPARTMENT	Chemistry	E-MAIL	alarsen@ithaca.edu
INSTITUTION	Ithaca College		
INSTITUTION ADDRESS	Ithaca NY 14850	APPOINTMENT DATE	Started on Aug 15th 2003

EDUCATION AND EXPERIENCE (All degrees, postdoctoral appointments, PhD and postdoctoral mentors, previous employment dates and locations. See instructions for format.)

2003-present Ithaca College, Ithaca, New York, Tenure-track assistant Professor
 2001-2003 University of Washington, Seattle, WA, Postdoctoral Associate, Mentor: Professor Jim Mayer
 2000-2001 Seattle University, Seattle, WA, Visiting Assistant Professor
 1997-2000 University of California-Riverside, CA, Postdoctoral Associate, Mentor: Professor Chris Reed
 1991-1997 Utah State University, Logan, UT, Ph.D. (inorganic chemistry), Adviser: Professor John Hubbard
 1985-1991 Moscow State University, College of Chemistry, Moscow, Russia, B.S./M.S. (organic chemistry), Advisers: professor Vladimir Palyulin and professor Nikolai Zefirov

TITLE OF PROPOSAL (Must fit on two lines and not exceed 130 characters.)

Non-coordinating carborane counterions for cationic organometallic catalysis

ABSTRACT: In the following space, provide a summary of your proposal plan. (Maximum 200 words.)

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 virtually non-coordinating and chemically inert. These properties 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 $[\text{Cp}^*\text{Ru}(\text{NO})]$ system belongs to "half-sandwich" cationic homogeneous catalysts, and its catalytic activity, for olefin polymerization and ether oxidation, is significantly enhanced with BAR_f^- anions 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), as well as perfluorinated Ru and Pt complexes. **Bringing carboranes into cationic transition metal complexes will expand our fundamental understanding and command of key metallo-organic transformations.**

PUBLICATIONS OF PRINCIPAL INVESTIGATOR (List all during last five years [**no** abstracts or talks]; attach additional page if necessary.)

"Hydrogen Atom Transfer from Iron(II)-tris[2,2'-bi(tetrahydropyrimidine)] to TEMPO" Mader, E.A., Larsen, A.S., Mayer, J.M. *J. Am. Chem. Soc.* in press

"Non-Organometallic Mechanisms for C-H Bond Oxidation. Hydrogen Atom vs. Electron vs. Hydride Transfer" Mayer, J.M., Larsen, A.S., Bryant J.R., Wang, K., Lockwood, M., Rice, G., Won, T.-J. *ACS Symposium Series*, **2003**, in press

"Electron and Hydrogen Atom Self-Exchange Reactions of Iron and Cobalt Coordination Complexes" Yoder, J.C.; Roth, J.P.; Gussenhoven, E.M.; Larsen, A.S.; Mayer, J.M. *J. Am. Chem. Soc.* **2003**, 125(9); 2629-2640

"Hydrocarbon Oxidation by *Bis*- μ -Oxo Manganese Dimers: Electron Transfer, Hydride Transfer, And Hydrogen Atom Transfer Mechanisms" Larsen, A.S.; Wang, K.; Lockwood, M. A.; Rice, G.L.; Won, T.J.; Lovell, S.; Sadilek, M.; Tureček, F.; Mayer J.M. *J. Am. Chem. Soc.* **2002**, 124(34); 10112-10123

"Molecular Structure of the Solvated Proton in Isolated Salts. Short, Strong, Low Barrier (SSLB) H-bonds" Stasko, D. ; Hoffmann, S.; 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.; Tsang, C.W.; Mak, T. C. W. , Xie, Z. *J. Am. Chem. Soc.* **2002**, 124 (46); 13869-13876.

"Designing Ionic Liquids: Imidazolium Melts with Inert Carborane Anions" Larsen, A.S.; Holbrey, J. D.; Tham, F. S.; Reed, C.A. *J. Am. Chem. Soc.* **2000**, 122(30), 7264-7272.

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PROPOSED BUDGET - Indicate with an asterisk [*] any item for which a match is being provided. List item and amount under Budget Rationale below.

	YEAR 1	YEAR 2
a) EQUIPMENT AND SUPPLIES (<i>itemize capital equipment</i>):		
Starting materials for the carborane syntheses, Organic Solvents, Deuterated solvents	1,000	1,000
Vacuum/ Schlenk line hardware, Glassware Instrumentation: Dry box	1,000 24,000*	500
b) STIPENDS (<i>not to exceed rates indicated</i>):		
Faculty Summer Stipend [Rate: up to \$7,500 for 8 weeks] Weeks: <u> 8 </u>	7,500	7,500
Undergraduate Summer Stipend [Rate: up to \$3,500 for 10 weeks] Weeks: <u> 10 </u> Students per year: <u> 1 </u>	7,000*	7,000*
FICA/Medicare (<i>7.65% of stipend</i>)	535	535
(<i>Note: no other benefits or indirect costs are allowed</i>)		
c) OTHER		
Travel	500	500
TOTALS	<u>41,535</u>	<u>17,035</u>
TOTAL BUDGET		<u>58,570</u>
LESS MATCHING FUNDS FROM INSTITUTION		(<u>19,535</u>)
REQUESTED FROM RESEARCH CORPORATION		<u>39,035</u>

ADDITIONAL SUPPORT - List periods and direct cost amounts of all additional support [internal and external] including start-up received and requested for [1] this research, or [2] other research; identify requests that duplicate this one.

One undergraduate research student is expected to be supported by internal IC scholarship in summer for both of the two years (stipend of \$3,500/yr x 2 + 535= 7535). 50% of the dry-box cost (\$12,000) will be matched by Ithaca College as the instrument will be used in teaching labs. [2] Other research in low-melting carborane salts is not externally supported. Part of this proposal was submitted to the ACS PRF (in September 2005) and is pending.

BUDGET RATIONALE - Include the source of other items [equipment/supplies], which are needed for this research beyond those requested from RC. Explain travel related to research and other budget items that require further clarification. List any items from Proposed Budget above for which a match is being provided and give dollar amount of the match.

Among the instrumentation available for this research, as well as for teaching purposes, Ithaca College has Varian XL-300NB FT-NMR (to be replaced by 400 MHz JEOL) & Sun Workstation; PE 1310 Infrared, Varian 634S UV-VIS, PE 137 Infrared, Nicolet Magma 550 FT-IR Spectrometer, HP 8452A Diode Array Spectrophotometer, Cary 14 UV-VIS NIR, BAS CV-1B Cyclic Voltammograph with Houston X-Y recorder, BAS CD-27 Voltammograph, Shimadzu UV-2101PC Spectrometer, M. Braum MB 150m Dry Box (unreliable condition).

Travel for the faculty to present results at conferences is covered by IC up to 800\$/year.

Nitrogen gas is covered by IC.

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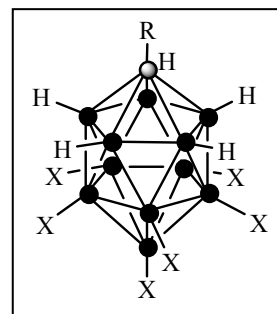
CCSA Application

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STATEMENT OF THE PROBLEM AND SCIENTIFIC SIGNIFICANCE OF PROPOSED RESEARCH (State succinctly the problem that is to be addressed. Clearly outline the importance of the problem, the originality of the approach and the impact it may have on the field if successful. Give an overview of the broader significance as well as the immediate impact of this research.)

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, another anion 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.

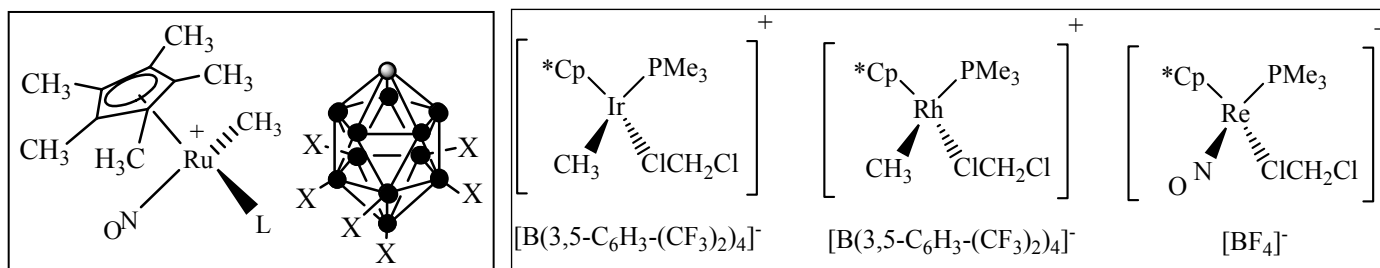
Carborane anions based on $\text{CB}_{11}\text{H}_{12}^-$ are known for their exceptionally weakly-coordinating properties, spectacular chemical inertness and stabilization of extremely reactive chemical species.^{5,6} These anions can be custom-tailored through alkyl and halogen substitution of hydrogens as shown (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; derivatives: $\text{R} = \text{alkyl}$, $\text{X} = \text{H}$; $\text{R} = \text{H}$, $\text{X} = \text{Br}$ or Cl)



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.

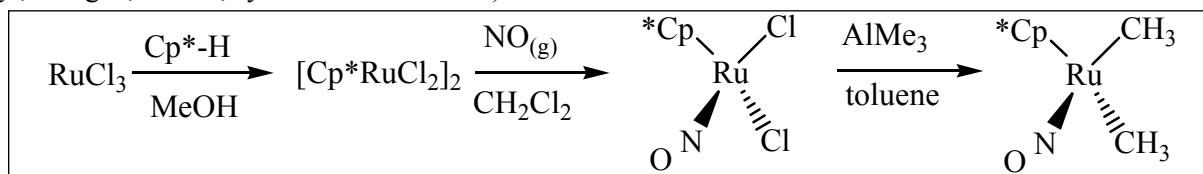
For these studies we chose a well-defined ruthenium pentamethyl-cyclopentadienyl nitrosyl system. This is a suitable model because the metal center in its complexes with triflate anions has been shown to possess significant electrophilic character.^{9,10,11,12} The reactivity of this system is clearly enhanced by replacing triflate with less coordinating BAR_f^- anion. 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 (latter to the higher extent) 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 stabilization of reactive cationic transition metal complexes by weakly-coordinating inert carborane anions $\text{CB}_{11}\text{H}_6\text{X}_6^-$ using the $[\text{Cp}^*\text{Ru}(\text{NO})(\text{R})\text{L}]^+$ system as a first test case (shown below, left, with $\text{X} = \text{H}$, Cl , or Br ; top six carborane hydrogens are omitted; $\text{L} = \text{coordinated solvent, CH}_3\text{CN}$ or CH_2Cl_2). The effect of derivatized carborane anions on the reactivity of these complexes with small molecular substrates will be explored in comparison to BAR_f^- and triflate analogs. Decreased coordination and enhanced stability of the counter-ion is anticipated to ultimately improve catalytic efficiency of the system. The research will be extended to electrophilic iridium and rhodium catalytic systems capable of C-H activation (shown below, right)¹³ and to perfluorinated platinum and ruthenium hydrogenation catalysts (*vide infra*).¹⁴ The proposed investigations will expand our fundamental understanding and command of key metallo-organic transformations.

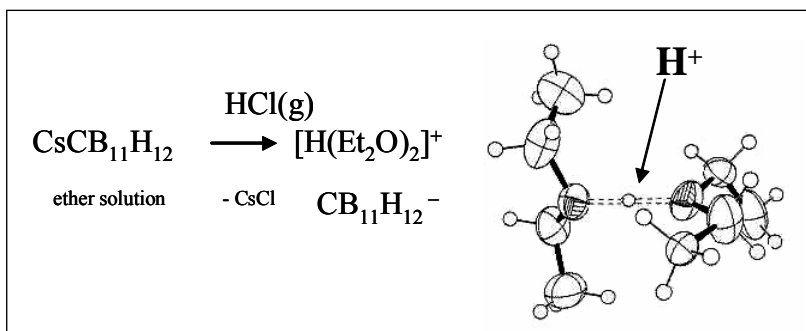


PLAN OF PROCEDURE (Outline the initial approach to the problem and its feasibility. Point out innovative features, relate it to previous work including pertinent references, and indicate how this plan may contribute to the solution of the broader problem posed.)

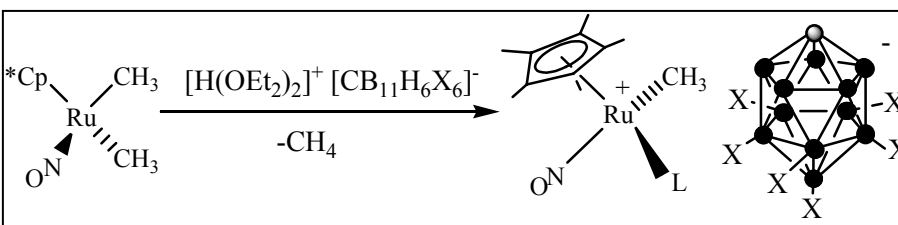
Preliminary Results and General Plan of Procedure. All preliminary results were obtained by undergraduate students under the P.I. s' supervision, starting with preparation of carborane salts and Cp*Ru(NO)X₂ complexes (X = alkyl, halogen, triflate, synthetic route shown).^{15,16}



Two new protonated salts of ether with CB₁₁H₁₂⁻ and CB₁₁H₆Br₆⁻ anions were synthesized and used to obtain desired [Cp*Ru(NO)R(L)][carborane] complexes (shown on the left and below; the [H(OEt₂)₂]⁺ cation structure image is modified from reference 17). *This is the first precedent of using solvated proton salts of carborane for protonolysis of alkyl metal complexes.*



The NMR and IR spectroscopic analysis of the product is consistent with the assigned structure shown below (where L = CH₃CN). (¹H NMR data (CD₃CN, 300 MHz Varian): δ 1.87 (s, Cp*15H), δ 1.33ppm (s, Ru-CH₃, 3H), IR (CD₃CN): ν_{NO} at 1790 cm⁻¹). The structure is also supported by the preliminary single crystal X-ray diffraction analysis.



In another approach, carborane silver salt metathesis reaction with Cp*Ru(NO)MeCl complex was tested. Starting material in these reactions is consumed rapidly, accompanied by changes in color and NMR spectra of the reaction mixtures. We are developing a reliable and safe synthetic route to protonated arene carboranes which would have superior acidity compared to protonated ether salts.

The top priority now is optimizing and scaling up **syntheses** of [Cp*Ru(NO)(CH₃)(L)] [carborane] complexes via protonation route (carborane is CB₁₁H₁₂⁻, CB₁₁H₆Cl₆⁻ or CB₁₁H₆Br₆⁻, 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 reactive organometallic Lewis acid, whose Ir and Rh analogs are capable of C-H bond activation.¹² 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.¹⁸ The effect of the anion bulkiness on the ion pairing in solution will be estimated in ¹¹B and ¹H NMR spectroscopy studies. The IR, UV and NMR spectroscopic characterization will be carried out at the Ithaca College facilities (the department just acquired a new 400 MHz NMR spectrometer). Single crystal X-ray studies will be done in collaboration with Dr. Emil Lobkovsky (Cornell University) and Professor Phillip Coppens (SUNY Buffalo).

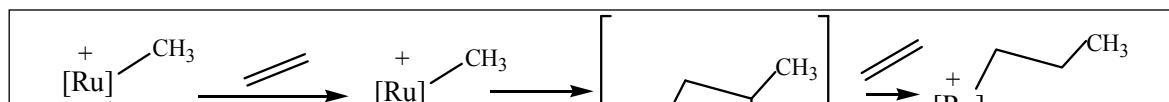
The following reactivity studies are planned:

•Treatment of [Cp*Ru(NO)(CH₃)L][carborane] with ethylene is expected to proceed as shown on the next page, via the addition step followed by migratory insertion step (below [Ru] = [Cp*Ru(NO)]). Vacant coordination site □ will result from dissociation of weakly-coordinated carborane or neutral solvent molecule. These experiments, including kinetic studies, will be monitored by variable temperature high-field multinuclear NMR. Agostic coordination of a beta-hydrogen should be indicated by the presence of far up-field signals in the ¹H NMR spectrum.¹⁹

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PLAN OF PROCEDURE, continued



References:

1. Malinoski, J.M et al. "Structural Characterization of $[\eta\text{-}2\text{-}(\text{t-Bu})_2\text{PCH}_2\text{C}(\text{O})\text{C}_6\text{H}_5]\text{PdMe}(\eta\text{-}2\text{-}\text{C}_2\text{H}_4)+\text{BARf}_4^-$: A Model for the Catalyst Resting State for Ethylene Polymerization" *Organometallics* **2003**, 22, 621; Taw, F. L. et al. "Silicon-Hydrogen Bond Activation and Formation of Silane Complexes Using a Cationic Rhodium(III) Complex" *Organometallics* **2004**, 23(4); 886; Stobenau, E. J., et al "Coordination of Alkenes and Alkynes to a Cationic d^0 Zirconocene Alkoxide Complex" *J. Am. Chem. Soc.* **2003**, 25(11) 3222; Jia, L. et al. "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.
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9. 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: β -Migratory Insertion, Isomerization, and Metallacycle Formation" *J. Am. Chem. Soc.* **1994**, 116(21), 9514.
10. 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.
11. Burns, R.M. "Synthesis, structure, and reactivity of nitrosyl and thionitrosyl cyclopentadienyl ruthenium(ii)" Ph.D. Dissertation **1994** Utah State Univ., Logan, UT, USA.; Yi, G.B. "Synthesis, structure, and reactivity of electrophilic ruthenium complexes" Ph.D. Dissertation **1995** Utah State Univ., Logan, UT, USA.
12. Arndtsen, B. A. et al. "Unusually Mild and Selective Hydrocarbon C-H Bond Activation Using Positively Charged Iridium(III) Complexes" *Science* **1995**, 270, 1970; Peng, T.-S.; et al "Generation and Reactivity of Substitution-Labile Dichloromethane and Chlorobenzene Adducts of the Chiral Pentamethylcyclopentadienyl Rhenium Lewis Acid $[(\eta\text{-}5\text{-}\text{C}_5\text{Me}_5)\text{Re}(\text{NO})(\text{PPh}_3)]^+$ " *Inorg. Chem.* **1994**, 33, 2534; Taw, F.L. et al "Silicon-Hydrogen Bond Activation and Formation of Silane Complexes Using a Cationic Rhodium(III) Complex" *Organometallics* **2004**, 23, 886.
13. Butikofer, J.L.; Roddick, D.M. et al "Synthesis and Reactivity of $[(\text{C}_2\text{F}_5)_2\text{MeP}]_2\text{Pt}(\text{Me})\text{X}$ (X = Me, O_2CCF_3 , OTf, OSO_2F): A Reactivity Comparison with Chelate Acceptor Analogues" *Organometallics*, **2004**, 23, 400-408; Ontko, A.C.; Roddick, D.M. et al "Protonation and H_2 Heterolysis Reactions of Electrophilic $(\text{C}_5\text{R}_5)\text{Ru}(\text{dfepe})(\text{X})$ (R = H, Me; X = H, OTf) Complexes", *Organometallics*, 1998, 17, 5467-5476.
14. Jelinek, T.; et al. "Chemistry of compounds with the 1-carba-closo-dodecaborane(12) framework" *Collect. Czech.Chem. Comm.* **1986**, 51(4), 819.
15. Chang, J.; et al "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. et al. "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. et al. "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. et al "Palladium(II) catalysts for living alternating copolymerization of olefins and carbon monoxide" *J. Am. Chem. Soc.* **1992**, 114(14), 5894
20. Pankowski, M.; et al. "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, et al. "Rhodium-catalyzed, carbon dioxide-mediated aerobic oxidation of ethers" *J. Chem. Soc., Chem.Com.* **1992**, 1334; Fackler, N.; et al "Stabilization of High Valent Terminal-oxo-complexes: The Interplay of D-orbital Occupancy and Coordination Geometry", *J. Amer. Chem. Soc.*, 1996, 118, 481-482;
22. See enclosed collaboration letter from Professor Dean Roddick.
23. Belkova, N.V.; Poli, R. Et al "Kinetics and Mechanism of the Proton Transfer to $\text{Cp}^*\text{Fe}(\text{dppe})\text{H}$: Absence of a Direct Protonation at the Metal Site" *J. Am. Chem. Soc.* **2003**, 125(36), 11106.

Supported for 2+ years starting in summer 2006

24. See enclosed letter of collaboration from professor Phillip Coppens

Supported for 2+ years starting in summer 2006



University at Buffalo
State University of New York
Department of Chemistry

Crystallography Laboratory
(716) 645-6800 ext. 2217
FAX: (716) 645-6948
E-mail: coppens@acsu.buffalo.edu
<http://harker.chem.buffalo.edu/>

September 7, 2005

Prof. Anna Larsen
359 Center for Natural Sciences
Ithaca College
953 Danby Road
Ithaca, NY 14850

Dear Anna:

This is to confirm that I am happy to collaborate with you and your students on the proposed project entitled "Bringing weakly-coordinating carborane anions to cationic half-sandwich electrophilic complexes".

As your student Matthew Pearsall spent the summer with us under the REU project, you and he are familiar with our crystallographic and spectroscopic instrumentation. We will provide the technical support that your project may require in these areas, train your students in use of the instrumentation, and collaborate on our overlapping interests in this important field.

I am looking forward to our continued interaction.

Sincerely,

A handwritten signature in black ink that reads "Philip Coppens". The signature is written in a cursive style with a large, sweeping initial 'P'.

Philip Coppens
Distinguished Professor of Chemistry,
Henry M. Woodburn Chair of Chemistry

PC/in

UNIVERSITY OF WYOMING

Dr. Dean M. Roddick
Chemistry, Dept. 3838
University of Wyoming
1000 E. University Ave.
Laramie, WY 82071
Voice: 1 (307) 766-2535
FAX: 1 (307) 766-2807
Internet: DMR@UWYO.EDU

November 9, 2005

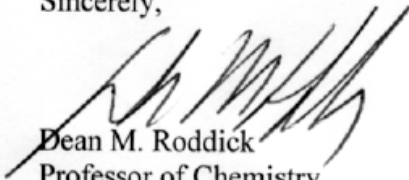
To whom it may concern

Re: Collaborative research with Anna Larsen

I am excited to have the opportunity to engage in mutually beneficial research with Dr. Larsen. Her proposal to extend the use of carborane acids in the preparation of highly reactive metal cationic systems dovetails perfectly with my current research goals: We have recently prepared a series of very elusive electron-poor cationic platinum complexes, $(dfepe)Pt(Me)^+$, $(dfepe)Pt^{2+}$ and $[(dfmp)_2Pt(Me)]^+$ ($dfepe = (C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$; $dfmp = (C_2F_5)_2PMe$) that are only stable in neat superacidic media. Moreover, the formation of highly acidic H_2 adducts, one of our avenues of research, is not compatible with standard fluorinated borate anions. We expect that the combination of our metal cation systems with halogenated carborane anions will lead to stable isolable "super-electrophiles" and allow us to study their fundamental properties and catalytic applications. Extensions to other research projects in our group including ionic hydrogenation catalysis using highly acidic $CpRu(dfepe)(H_2)^+$ cations is also of great interest to us.

Collaborating with Dr. Larsen's research group and building upon her background and experience with carborane anion work will be mutually beneficial to both of our research efforts. I look forward to working with her in this fruitful research area.

Sincerely,



Dean M. Roddick
Professor of Chemistry
University of Wyoming

Supported for 2+ years starting in summer 2006

LIST OF REVIEWERS

The reviewer list should include at least eight "outsiders," individuals with whom you have had no substantive contact, who are experts in your area of research, and at least two "insiders," preferably former mentors. Do not hesitate to use industrial reviewers and scientists from abroad. We may also select reviewers of our choice. Please include complete names (initials are not enough), mailing addresses, phone and fax numbers, and e-mail addresses. **You must note briefly the nature and extent of your interactions with each of the outside reviewers. Examples: Met at a meeting, interviewed with, no interaction, never met, etc. No more than one page.**

- Professor James M. Mayer
Department of Chemistry, Box 351700, University of Washington
Seattle, WA 98195-1700 ; phone: (206) 543-2083, fax: (206) 685-8665
mayer@chem.washington.edu

Insider:
Former postdoctoral mentor
- Professor Chris Reed,
Department of Chemistry – 027, University of California, Riverside
Riverside, CA 92521-0403 Phone: 951-827-5197 Fax: 951-827-2027
chris.reed@ucr.edu

Insider:
Former postdoctoral mentor
- Professor Daniel Rabinovich,
Department of Chemistry, Burson Bldg. Room 200, UNC Charlotte
9201 University City Blvd. Charlotte, NC 28223
phone (704)687-4442, FAX 704-687-4765
drabinov@email.uncc.edu

Outsider:
Attended the same conference
- Professor Ana de Bettencourt-Dias,
Department of Chemistry, Syracuse University, Syracuse, NY 13244
Tel.: 315 443 2006; Fax: 315 443 4070
debetten@syr.edu

Outsider:
Attended her seminar
- Professor Marina Petrukhina, Assistant Department of Chemistry
1400 Washington Avenue University at Albany, SUNY Albany, NY 12222
Phone: 518-442-4406; Fax: 518-442-3462
E-mail: marina@albany.edu

Outsider:
Attended the same conference
- Professor Rinaldo Poli, ENSIACET
+ 33-5.62.88.58.63 (tel); Laboratoire de Chimie de Coordination (LCC - UPR
8241) 205 Route de Narbonne, 31077 Toulouse Cedex (France)
+ 33-5.61.33.31.95 (tel); + 33-5.61.55.30.03 (fax)
poli@lcc-toulouse.fr

Outsider:
Attended his lecture in 1995
- Professor Sunhee Choi
Department of Chemistry, Middlebury College, Middlebury, Vermont 05753
Phone: (802) 443-5716, FAX: (802) 443-2072
choi@middlebury.edu

Outsider:
Attended a conference in 2003
- Professor Steven Strauss
Department of Chemistry, Colorado State University, Fort Collins, CO 80523
USA
steven.strauss@colostate.edu
970-491-5104 voice -1801 fax

Outsider:
No personal communication
- Dr. Howard Turner
Symyx Technologies, Inc. 3100 Central Expressway
Santa Clara, CA 95051 hturner@symyx.com, Phone: 408-764-2000
Fax: 408-748-0175

Outsider:
Interviewed with in 1998.
- Professor Stanton Ching, Department of Chemistry, Connecticut College
New London, CT 06320, (860) 439-2753, FAX (860) 439-2818
sschi@conncoll.edu

Outsider:
Attended the same conference

ENDORSEMENT PAGE – see scanned next page

Conditions of Research Corporation Awards

A RESEARCH CORPORATION AWARD is a contribution to the scientific and academic program of the institution and is to be used for support of work described in the application prepared by the principal investigator and adopted by the institution.

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The amount of the award is the total of the items approved in the budget submitted as part of the application. If it differs from the amount requested, the differences are noted in the letter of notification from the Vice President. The principal investigator may, as dictated by the work, reallocate the budget among approved funding categories. Faculty salaries not approved in the budget, indirect costs or overhead, and secretarial assistance are not chargeable to the award.

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APPLICANT: Anna Larsen

PROJECT TITLE: Non-coordinating carborane counterions for cationic organometallic catalysis

SUBMITTED BY: Ithaca College

Name of institution adopting and assuming responsibility for the above project, believing the principal investigator is qualified to conduct the project, and accepting the Conditions of Award, if an award is approved.

Name and Position of Authorized Officer Paul Hamill

Signature of Authorized Officer _____ Date _____

Name of Chief Executive Officer and Title _____
(President or Chancellor); *signature not required*

Signature of Principal Investigator _____ Date _____

ENDORSEMENT PAGE

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Name and Position of Authorized Officer Paul Hamill, Ph.D., Director, Academic Funding

Signature of Authorized Officer  Date 11/10/05

Name of Chief Executive Officer and Title Peggy R. Williams, President
(President or Chancellor); signature not required

Signature of Principal Investigator  Date 11/11/05

IMPORTANT: DO NOT RETURN COPY – RETURN ONLY ORIGINAL WITH APPLICATION

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