

FINAL TECHNICAL REPORT DE-FG02-93ER14353 1993-2007
“Carbon-Hydrogen Bond Functionalization Catalyzed by Transition Metal Systems”

Principal Investigator: Alan S. Goldman, Rutgers University

Summary

Alkanes are our most abundant organic resource but are highly resistant to selective chemical transformations. Alkenes (olefins) by contrast are the single most versatile class of molecules for selective transformations, and are intermediates in virtually every petrochemical process as well as a vast range of commodity and fine chemical processes. Over the course of this project we have developed the most efficient catalysts to date for the selective conversion of alkanes to give olefins, and have applied these catalysts to other dehydrogenation reactions. We have also developed some of the first efficient catalysts for carbonylation of alkanes and arenes to give aldehydes. The development of these catalysts has been accompanied by elucidation of the mechanism of their operation and the factors controlling the kinetics and thermodynamics of C-H bond activation and other individual steps of the catalytic cycles. This fundamental understanding will allow the further improvement of these catalysts, as well as the development of the next generation of catalysts for the functionalization of alkanes and other molecules containing C-H bonds.

Introduction

The C-H bond is the most common linkage in organic chemistry. Alkanes, our most abundant organic resource, have only C-H bonds and (other than the very important exception of methane) C-C bonds. Development of catalysts for the conversion of C-H bonds to higher value fuels and chemicals is accordingly one of the most important and attractive challenges in modern organic chemistry, and in fuel-related chemistry in particular.

In stark contrast to alkanes, alkenes (olefins) are considered to be the most versatile intermediates in organic chemistry. Olefins are key intermediates in virtually every process in the petrochemical industry, as well as the majority of commodity chemical processes and a wide range of fine chemical syntheses. The dehydrogenation of alkane to give alkenes, and more generally, alkyl groups to give olefins, is thus a reaction with vast potential applicability.

Results and Discussion

Preliminary work in our labs and others¹⁻³ showed that *trans*-Rh(PMe₃)₂(CO)Cl acted as a remarkably efficient catalyst for photochemical dehydrogenation of alkanes. Photochemical conversions, however, are assumed to be impractical for large-scale reactions. It was therefore particularly noteworthy that our mechanistic studies of this system revealed that the critical catalytic steps were all thermochemical.³ Under the auspices of DOE funding we therefore endeavored to develop a fully thermochemical catalytic system based on the same fragment, Rh(PMe₃)₂Cl, which was found to be active in the photochemical system. We successfully developed the first efficient thermochemical systems for catalytic alkane transfer-dehydrogenation (transfer of hydrogen to a sacrificial olefinic acceptor).^{4,5} Remarkably, the system required the presence of a hydrogen atmosphere to effect this dehydrogenation. Although fundamentally quite

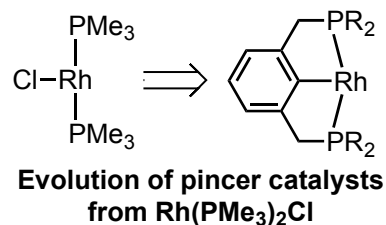
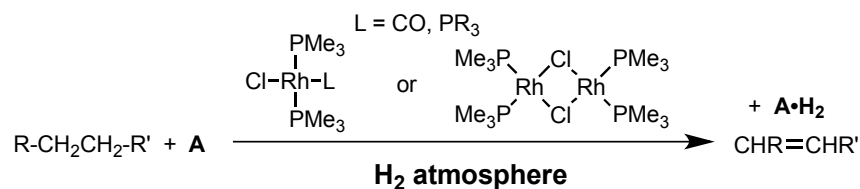
intriguing, the presence of a hydrogen atmosphere led to several moles of acceptor being hydrogenated per mol

dehydrogenated product, precluding practical viability of this system.

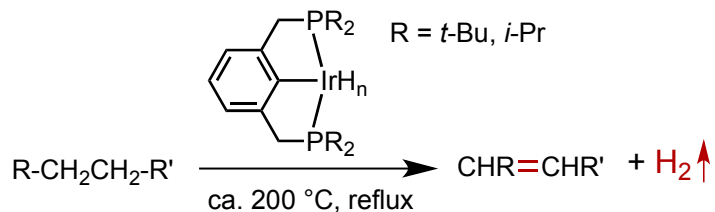
Mechanistic studies of the Rh(PMe₃)₂Cl-based systems indicated that the role of hydrogen atmosphere was to provide access to the catalytic cycle via Rh(PMe₃)₂ClH₂, from either Rh(PMe₃)₂ClL (L = CO, PR₃) or, in the absence of L, from [Rh(PMe₃)₂Cl]₂.⁴⁻⁷ This led to the hypothesis that the need for hydrogen might be obviated by synthesis of “pincer” analogues of Rh(PMe₃)₂Cl which would be incapable of the μ -chloride or similar bridging motifs. To this end we synthesized rhodium-based pincer complexes but these were not found to be very active for transfer-dehydrogenation.⁸

Independently, however, Jensen and Kaska reported that the analogous iridium-based pincers were indeed active,⁹ although requiring somewhat higher temperatures than the rhodium analogues.

Computational studies indicated that addition of H-H or C-H bonds to pincer-ligated fragments (^RPCP)Ir (^RPCP = κ^3 -2,6-C₆H₃(CH₂PR₂)₂) was thermodynamically quite similar to



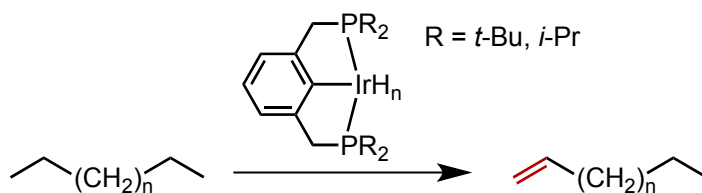
additions to $\text{Rh}(\text{PMe}_3)_2\text{Cl}$, much more similar than addition to the pincer fragments $(\text{PCP})\text{Rh}$ which we initially investigated.¹⁰ Additionally, we realized that the high temperatures tolerated by the $(\text{PCP})\text{Ir}$ complexes might permit dehydrogenation without the use of sacrificial acceptor. Indeed, allowing H_2 to escape from a refluxed solution of alkanes and $(^R\text{PCP})\text{IrH}_n$ ($R = t\text{-Bu}$ or $i\text{-Pr}$; $n = 2$ or 4) resulted in the first examples of efficient acceptorless dehydrogenation of alkanes by a molecular catalyst.^{10,11}



Acceptorless dehydrogenation of alkanes by $(\text{PCP})\text{IrH}_n$

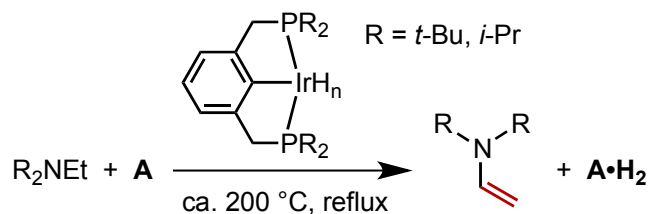
Mechanistic study of the pincer catalysts led to a remarkable observation: dehydrogenation could be regioselective for the terminal position of n -alkanes, thereby affording α -olefins.¹² Such regioselectivity was unanticipated (and unprecedented) as it requires cleavage of the strongest C-H bond in the n -alkane (the primary position) to produce the thermodynamically least stable double bond isomer. It is also highly desirable since α -olefins are used for a variety of large-scale applications (surfactants, co-polymers) and potentially as intermediates in others (*vide infra*).

Accordingly, our initial report of this work¹² has been cited nearly 200 times according to *Web of Science* as of May 2012, and the pace of citation has actually increased somewhat over time (23 citations in 2011).



Terminus-selective dehydrogenation of n -alkanes by $(\text{PCP})\text{IrH}_n$ to give α -olefin

The mechanisms of the dehydrogenation reactions, both transfer¹³⁻¹⁵ and acceptorless,^{16,17} have been elucidated. This has led to (and will continue to inform) rational development of improved dehydrogenation catalysts based on iridium¹⁸, and hopefully it will facilitate development of catalysts based on metals that are more earth-abundant. Mechanistically a particularly important (and controversial) conclusion was that loss of H_2 in the acceptorless systems proceeds dissociatively; therefore particularly strong binding of H_2 to the metal center, although favoring the alkane dehydrogenation step, will disfavor the kinetics of acceptorless dehydrogenation.



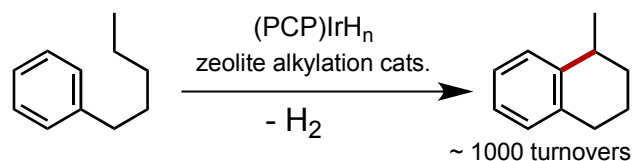
Dehydrogenation of amine to give an enamine

Under the auspices of this program, we have exploited the pincer-iridium catalysts for the dehydrogenation of substrates other than alkanes. For example, enamines are highly valuable and versatile organic synthons. Highlighting the compatibility of the catalysts with coordinating functional group and their applicability toward organic synthesis, in collaboration with Prof. Spencer Knapp (Rutgers) we have effected, with high yield, the very atom-economical dehydrogenation of amines to give enamines. In some cases we were able to obtain elementary enamines that are highly reactive and had not previously been successfully synthesized by any method.¹⁹ In another example, in collaboration with Prof. Geoff Coates (Cornell) we have shown that polyolefins can be dehydrogenated to give functionalized polymers, with good regioselectivity.^{20,21}

The key steps in the dehydrogenation cycles are oxidative addition of the C-H bond, β -hydride elimination, and in the case of acceptorless dehydrogenation, reductive elimination of H_2 . Oxidative addition of C-H bonds is of course generally critical to C-H bond functionalization reactions that might be catalyzed by late-metal complexes, while the importance of addition/elimination of H_2 extends to a wide range of reactions including many practiced on an industrial scale. In general, oxidative addition and reductive elimination play a key role in many, even the majority, of reactions catalyzed by transition-metal complexes. In this context we have conducted in depth studies of both the kinetics and thermodynamics of C-H and H-H addition/elimination. Our approach has been to integrate, in a highly synergistic fashion, computational and experimental methods, with the computational component being led by Prof. Karsten Krogh-Jespersen (Rutgers). Our results have led to a reevaluation within the organometallic/catalysis community of underlying assumptions concerning these fundamental reactions.²²⁻²⁵ Moreover, we believe that the success of our approach of tightly integrating calculations and experiments has had a general influence on the way the theoretical and organometallic communities interact, extending well beyond the specific reactions that we have studied.

Given the great chemical versatility of olefins, the combination of dehydrogenation with a secondary reaction is quite attractive. For example, with the support of this program and in

collaboration with ChevronTexaco, we have investigated dehydrogenation coupled with alkylation of arenes. Intramolecular alkyl-aryl coupling has been particularly successful by this



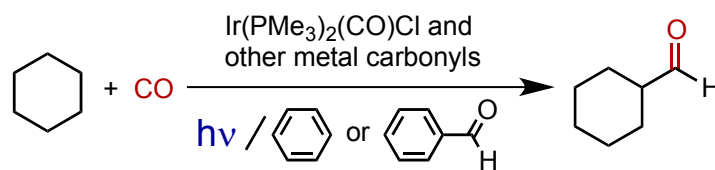
Intramolecular alkyl aryl coupling catalyzed by tandem dehydrogenation (pincer-Ir) / alkylation (zeolite) catalysts

route.²⁶ In collaboration with Maurice Brookhart (under the auspices of the Center for Enabling New Technologies through Catalysis), we have also applied the dehydrogenation catalysts developed in

this work to tandem dehydrogenation/olefin-metathesis, resulting in the metathesis of *n*-alkanes^{27,28}, and toward the dehydroaromatization of *n*-alkanes to give *n*-alkyl arenes²⁹.

Another alkane functionalization studied under the auspices of this program has been carbonylation, the net insertion of CO into a C-H bond to give an aldehyde.

We discovered an efficient iridium-catalyzed photochemical system for carbonylation of cyclohexane in the presence of benzene, and elucidated a completely unanticipated mechanism.³⁰ We found that the initial C-H activation step was



Photochemical alkane carbonylation co-catalyzed by metal carbonyls and benzaldehyde (produced from benzene carbonylation)

hydrogen radical abstraction by photoexcited benzaldehyde (which had been formed via a non-radical iridium catalyzed path). The resulting cyclohexyl radical then added to an iridium carbonyl to give an iridium acyl complex, which ultimately led to the formation of the aldehyde. Quite surprisingly, under sufficiently high pressures of CO, the radical would add to free CO and the transition metal catalyst was not required,³¹ although yields and selectivity were much higher with the iridium catalyst, and only 1 atm CO was required. This novel reaction of an alkyl radical with a metal carbonyl has been the subject of computational study by Prof. Faraj Hasanayn (who obtained his Ph.D. from our lab, and is now faculty at American University in Beirut) both in collaboration with us³² and independently³³.

This project has also yielded numerous spin-off studies.³⁴⁻⁴² For example, a key question in the design of catalysts is the degree of “electron-richness” at the metal center. The C-O stretching frequency of carbonyl ligands is typically assumed to reliably reflect this property through the degree of π -backbonding. We showed that the electrostatic charge at and around the metal center, independent of the degree of either covalent sigma bonding or pi-backbonding, can

strongly influence ν_{CO} .³⁴ (The report of this work has been cited approximately 150 times.) We have also found that the (PCP)Ir fragment is not only active with respect to oxidative addition of C-H bonds. In collaboration with John Hartwig we showed that it could also undergo the very rare oxidative addition of N-H bonds (aniline³⁹ or even ammonia⁴³) to give simple monomeric amido hydrides.

References

(# indicates work performed under the auspices of this project and acknowledging funding accordingly)

- (1) Nomura, K.; Saito, Y. "*n*-Alkene and H₂ Formation from *n*-Alkanes by Photocatalysis using RhCl(CO)(PR₃)₂" *J. Chem. Soc., Chem. Commun.* **1988**, 161.
- (2) Sakakura, T.; Sodeyama, T.; Tokunaga, Y.; Tanaka, M. "Highly catalytic dehydrogenation of alkanes to olefins via carbon-hydrogen activation in the presence of rhodium phosphine catalyst [RhCl(CO)(PMe₃)₂] under irradiation" *Chem. Lett.* **1988**, 263-264.
- (3) (a) Maguire, J. A.; Boese, W. T.; Goldman, A. S. "Photochemical Dehydrogenation of Alkanes Catalyzed by *trans*-Carbonylchlorobis(trimethylphosphine)rhodium: Aspects of Mechanism and Selectivity" *J. Am. Chem. Soc.* **1989**, *111*, 7088-7093. (b) Maguire, J. A.; Boese, W. T.; Goldman, M. E.; Goldman, A. S. "Mechanism of the Photochemical Dehydrogenation and Transfer-Dehydrogenation of Alkanes Catalyzed by *trans*-Rh(PMe₃)₂(CO)Cl" *Coord. Chem. Rev.* **1990**, *97*, 179-192.
- (4) # Maguire, J. A.; Goldman, A. S. "Efficient Low-Temperature Thermal Functionalization of Alkanes. Transfer-Dehydrogenation Catalyzed by Rh(PMe₃)₂(CO)Cl in Solution Under High Pressure Dihydrogen Atmosphere" *J. Am. Chem. Soc.* **1991**, *113*, 6706-6708.
- (5) # Maguire, J. A.; Petrillo, A.; Goldman, A. S. "Efficient Transfer-Dehydrogenation of Alkanes Catalyzed by Rhodium Trimethylphosphine Complexes Under Dihydrogen Atmosphere" *J. Am. Chem. Soc.* **1992**, *114*, 9492-9498.
- (6) # Shih, K.; Goldman, A. S. "Alkane Dehydrogenation Catalyzed by Rhodium(I) Phosphine Complexes: Observation of the Stoichiometric Alkane-to-Rhodium Hydrogen Transfer Step" *Organometallics* **1993**, *9*, 3390-3392.
- (7) # Rosini, G. P.; Soubra, S.; Wang, S.; Vixamar, M.; Goldman, A. S. "Kinetics of Photochemical Alkane Dehydrogenation Catalyzed by Rh(PMe₃)₂(CO)Cl: Implications Concerning the C-H Bond Activation Step" *J. Organomet. Chem.* **1998**, *554*, 41-47.
- (8) # Wang, K.; Goldman, M. E.; Emge, T. J.; Goldman, A. S. "Transfer-Dehydrogenation of Alkanes Catalyzed by Rhodium(I) Phosphine Complexes" *J. Organomet. Chem.* **1996**, *518*, 55-68.
- (9) (a) "A highly active alkane dehydrogenation catalyst: stabilization of dihydrido Rh and Ir complexes by a P-C-P pincer ligand" Gupta, M., Hagen, C., Flesher, R. J., Kaska, W. C. and Jensen, C. M. *Chem. Commun.* **1996**, 2083-2084. (b) "Catalytic Dehydrogenation of Cycloalkanes to Arenes by a Dihydrido Iridium P-C-P Pincer Complex" Gupta, M., Hagen, C., Kaska, W. C., Cramer, R. E. and Jensen, C. M. *J. Am. Chem. Soc.* **1997**, *119*, 840-841.
- (10) # Xu, W.; Rosini, G. P.; Gupta, M.; Jensen, C. M.; Kaska, W. C.; Krogh-Jespersen, K.; Goldman, A. S. "Thermochemical Alkane Dehydrogenation Catalyzed in Solution Without the Use of a Hydrogen Acceptor" *Chem. Commun.* **1997**, 2273-2274.
- (11) # Liu, F.; Goldman, A. S. "Efficient thermochemical alkane dehydrogenation and isomerization catalyzed by an iridium pincer complex" *Chem. Commun.* **1999**, 655-656.
- (12) # Liu, F.; Pak, E. B.; Singh, B.; Jensen, C. M.; Goldman, A. S. "Dehydrogenation of *n*-Alkanes Catalyzed by Iridium "Pincer" Complexes. Regioselective Formation of Alpha-Olefins" *J. Am. Chem. Soc.* **1999**, *121*, 4086-4087.
- (13) # Krogh-Jespersen, K.; Czerw, M.; Summa, N.; Renkema, K. B.; Achord, P. D.; Goldman, A. S. "On the Mechanism of (PCP)Ir-catalyzed Acceptorless Dehydrogenation of Alkanes: a Combined Computational and Experimental Study" *J. Am. Chem. Soc.* **2002**, *124*, 11404-11416.

- (14) # Goldman, A. S.; Renkema, K. B.; Czerw, M.; Krogh-Jespersen, K. In *Activation and Functionalization of C-H Bonds*; Goldberg, K. I., Goldman, A. S., Eds. Washington, DC, 2004; Vol. ACS Symposium Series 885, p 198-215.
- (15) # Renkema, K. B.; Kissin, Y. V.; Goldman, A. S. "The Mechanism of Alkane Transfer-Dehydrogenation Catalyzed by a Pincer-Ligated Iridium Complex" *J. Am. Chem. Soc.* **2003**, *125*, 7770-7771.
- (16) # Krogh-Jespersen, K.; Czerw, M.; Goldman, A. S. "Computational and Experimental Studies of the Mechanism of (PCP)Ir-catalyzed Acceptorless Dehydrogenation of Alkanes" *J. Mol. Cat., A* **2002**, *189*, 95-110.
- (17) # Krogh-Jespersen, K.; Czerw, M.; Goldman, A. S. In *Activation and Functionalization of C-H Bonds*; Goldberg, K. I., Goldman, A. S., Eds. Washington, DC, 2004; Vol. ACS Symposium Series 885, p 216-233.
- (18) # Zhu, K.; Achord, P. D.; Zhang, X.; Krogh-Jespersen, K.; Goldman, A. S. "Highly Effective Pincer-Ligated Iridium Catalysts for Alkane Dehydrogenation. DFT Calculations of Relevant Thermodynamic, Kinetic, and Spectroscopic Properties" *J. Am. Chem. Soc.* **2004**, *126*, 13044-13053.
- (19) # Zhang, X.; Fried, A.; Knapp, S.; Goldman, A. S. "Novel synthesis of enamines by iridium-catalyzed dehydrogenation of tertiary amines" *Chem. Commun.* **2003**, 2060-2061.
- (20) # Ray, A.; Kissin, Y. V.; Zhu, K.; Goldman, A. S.; Cherian, A. E.; Coates, G. W. "Catalytic post-modification of alkene polymers" *J. Mol. Cat. A* **2006**, *256*, 200-207.
- (21) # Ray, A.; Zhu, K.; Kissin, Y. V.; Cherian, A. E.; Coates, G. W.; Goldman, A. S. "Dehydrogenation of aliphatic polyolefins catalyzed by pincer-ligated iridium complexes" *Chem. Commun.* **2005**, 3388-3390.
- (22) # Abu-Hasanayn, F.; Goldman, A. S.; Krogh-Jespersen, K. "Computational Study of the Transition State for H₂ Addition to Vaska-Type Complexes (trans-IrL₂(CO)X): Substituent Effects on the Energy Barrier and the Origin of the Small H₂/D₂ Kinetic Isotope Effect" *J. Phys. Chem.* **1993**, *97*, 5890-5896.
- (23) # Abu-Hasanayn, F.; Krogh-Jespersen, K.; Goldman, A. S. "Theoretical Study of Primary and Secondary Deuterium Equilibrium Isotope Effects for H₂ and CH₄ Addition to trans-Ir(PR₃)₂(CO)X." *J. Am. Chem. Soc.* **1993**, *115*, 8019-8023.
- (24) # Abu-Hasanayn, F.; Krogh-Jespersen, K.; Goldman, A. S. "Factors influencing the thermodynamics of molecular hydrogen oxidation addition to Vaska-type complexes (trans-Ir(PR₃)₂(CO)X): predictions from ab initio calculations and experimental verification" *Inorg. Chem.* **1993**, *32*, 495-496.
- (25) # Abu-Hasanayn, F.; Goldman, A. S.; Krogh-Jespersen, K. "Ab Initio Molecular Orbital Study of Substituent Effects in Vaska Type Complexes (trans-IrL₂(CO)X): Electron Affinities, Ionization Potentials, Carbonyl Stretch Frequencies and the Thermodynamics of H₂ Dissociative Addition" *Inorg. Chem.* **1994**, *33*, 5122-5130.
- (26) # Van Dinh, L.; Schinski, W.; Goldman, A. S. "Preparation of Alkyl Aromatic Compounds" filed November 8, 2011 as provisional patent; to be submitted for publication.
- (27) Goldman, A. S.; Roy, A. H.; Huang, Z.; Ahuja, R.; Schinski, W.; Brookhart, M. "Catalytic Alkane Metathesis by Tandem Alkane Dehydrogenation-Olefin Metathesis" *Science* **2006**, *312*, 257-261.
- (28) Huang, Z.; Rolfe, E.; Carson, E. C.; Brookhart, M.; Goldman, A. S.; El-Khalafy, S. H.; MacArthur, A. H. R. "Efficient Heterogeneous Dual Catalyst Systems for Alkane Metathesis" *Adv. Synth. Catal.* **2010**, *352*, 125-135.
- (29) Ahuja, R.; Punji, B.; Findlater, M.; Supplee, C.; Schinski, W.; Brookhart, M.; Goldman, A. S. "Catalytic dehydroaromatization of n-alkanes by pincer-ligated iridium complexes" *Nature Chem.* **2011**, *3*, 167-171.
- (30) # Boese, W. T.; Goldman, A. S. "Photochemical Cyclohexane Carbonylation Cocatalyzed by d⁸ Transition Metal Carbonyls and Aromatic Ketones and Aldehydes" *J. Am. Chem. Soc.* **1992**, *114*, 350-1.
- (31) # Boese, W. T.; Goldman, A. S. "Alkane Carbonylation Photocatalyzed by Aromatic Ketones Under High CO Pressure" *Tetrahedron Lett.* **1992**, *33*, 2119-2122.
- (32) # Hasanayn, F.; Nsouli, N. H.; Al-Ayoubi, A.; Goldman, A. S. "Addition of Alkyl Radicals to Transition-Metal-Coordinated CO: Calculation of the Reaction of [Ru(CO)₅] and Related Complexes and Relevance to Alkane Carbonylation" *J. Am. Chem. Soc.* **2008**, *130*, 511-521.
- (33) (a) Nsouli, N. H.; Mouawad, I.; Hasanayn, F. "DFT study of the products, potential energy surface, and substituent effects for methyl radical addition to [Rh(PMe₃)₂(CO)X] (X = halogen or CN)" *Organometallics* **2008**, *27*, 2004-2012. (b) Hasanayn, F.; Abu-El-Ez, D. "Calculation of Dramatic Differences in the Activation Energy of Phenyl Migratory Insertion in the Isomers of

[Rh(PMe₃)₂Cl(CO)(Ph)H]: Important Effects from Both the Ligand trans to Ph and the Ligand trans to CO" *Inorg. Chem.* **2010**, *49*, 9162-9168.

(34) # Goldman, A. S.; Krogh-Jespersen, K. "Why do Cationic Carbonyl Complexes Have High C-O Stretching Force Constants and Short C-O Bonds? Electrostatic Effects" *J. Am. Chem. Soc.* **1996**, *118*, 12159-12166.

(35) # Wang, K.; Emge, T. J.; Goldman, A. S. "Crystal and Molecular Structure of a Novel Coordinatively Unsaturated Rhodium(II) Dimer" *Inorg. Chim. Acta.* **1997**, *255*, 395-398.

(36) # Kelly, A.; Rosini, G. P.; Goldman, A. S. "Oxygen Transfer from Organoelement Oxides to Carbon Monoxide Catalyzed by Transition Metal Carbonyls" *J. Am. Chem. Soc.* **1997**, *119*, 6115-6125.

(37) # Wang, K.; Emge, T. J.; Goldman, A. S. "Synthesis and Structure of a Diphosphoxanerhodium(I) Complex. Novel Reaction with CO to Liberate a Phosphinidene Oxide" *Organometallics* **1994**, *13*, 2135-7.

(38) # Zhang, X.; Emge, T. J.; Goldman, A. S. "Synthesis and crystal structure of a coordinatively unsaturated organomercury iridium complex (PCP)Ir(HgPh) Cl (PCP = η^3 -2,6-(CH₂P^tBu₂)₂C₆H₃)" *J. Chem. Cryst.* **2003**, *33*, 613-617.

(39) # Kanzelberger, M.; Zhang, X.; Emge, T. J.; Goldman, A. S.; Zhao, J.; Incarvito, C.; Hartwig, J. F. "Distinct Thermodynamics for the Formation and Cleavage of N-H Bonds in Aniline and Ammonia. Directly-Observed Reductive Elimination of Ammonia from an Isolated Amido Hydride Complex" *J. Am. Chem. Soc.* **2003**, *125*, 13644-13645.

(40) # Ghosh, R.; Kanzelberger, M.; Emge, T. J.; Hall, G. S.; Goldman, A. S. "Dinitrogen Complexes of Pincer-Ligated Iridium" *Organometallics* **2006**, *25*, 5668-5671.

(41) # Pelczar, E. M.; Emge, T. J.; Goldman, A. S. "A mixed-valence chloride-bridged (pincer)Ir(III)-(diene)Ir(I) complex" *Acta Cryst., C* **2007**, *63*, m323-m326.

(42) # Pelczar, E. M.; Emge, T. J.; Krogh-Jespersen, K.; Goldman, A. S. "Unusual Structural and Spectroscopic Features of Some PNP-Pincer Complexes of Iron" *Organometallics* **2008**, *27*, 5759-5767.

(43) Zhao, J.; Goldman, A. S.; Hartwig, J. F. "Oxidative Addition of Ammonia to Form a Stable Monomeric Amido Hydride Complex" *Science* **2005**, *307*, 1080-1082.