**Improved Modeling of Transition Metals.
Applications to Catalysis and Technetium Chemistry
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There is considerable impetus for identification of aqueous OM catalysts as water is the ultimate "green" solvent. In collaboration with researchers at Ames Lab, we investigated effective fragment and Monte Carlo techniques for aqueous-phase hydroformylation (HyF). The Rh of the HyF catalyst is weakly aquated, in contrast to the hydride of the Rh-H bond. As the insertion of the olefin C=C into Rh-H determines the linear-to-branched aldehyde ratio, it is reasonable to infer that solvent plays an important role in regiochemistry.

Studies on aqueous-phase organometallic catalysis were complemented in studies of the gas-phase reaction. A Rh-carbonyl-phosphine catalyst was investigated. Two of the most important implications of this research include (a) pseudorotation among five-coordinate intermediates is significant in HyF, and (b) CO insertion is the rate-determining step. The latter is in contrast to experimental deductions, highlighting the need for more accurate modeling. To this end, we undertook studies of (a) experimentally relevant PR₃ co-ligands (PMe₃, PPh₃, P(p-PhSO₃-)₃, etc.), and (b) HyF of propene. For the propylene research, simulations indicated that the linear:branched aldehyde ratio (linear is more desirable) is determined by thermodynamic discrimination of two distinct pathways.

Other projects include a theory-experiment study of C-H activation by early transition metal systems, which establishes that weakly-bound adducts play a key role in activity and selectivity. By extension, more selective catalysts for functionalization of methane (major component of natural gas) will require better understanding of these adducts, which are greatly affected by steric interactions with the ligands.

In the *de novo* design of Tc complexes, we constructed (and are now testing) a coupled quantum mechanics-molecular mechanics protocol. Initial research shows it to be capable of accurately predicting structure "from scratch." Challenges include conformational, geometric, coordination, spin, and particularly linkage (e.g., Tc-SCN versus Tc-NCS) isomerism. In general, our protocol can rapidly (<1 day with desktop software/hardware) predict the structure of diverse Tc complexes with an accuracy commensurate to organics.

Our *de novo* strategy is also being used to investigate tris-pyrazolyl borate (Tp) complexes. Data suggests a fundamental difference in methane activation between TpRe and related CpRe complexes. Furthermore, Tp is a more electronically "flexible" platform for catalysts modification than Cp.

DOE Patent Clearance Granted

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Participating Scientists (University of Memphis):

- Principal Investigator: Tom Cundari, Professor of Chemistry
- Postdoctoral Research Associate: Steve Decker
- Graduate Research Assistant: Tom Klinckman
- Visiting Graduate Research Assistant: Jorge Carbo

Overall Research Goals:

The major goals of this research were:

- develop reliable protocols for the more accurate modeling of catalytic processes, in particular inclusion of solvent effects,
- develop a comprehensive, *de novo* design and analysis scheme for the prediction of the molecular and electronic structure of transition metal inorganics and organometallics.
- apply the improved methodologies developed to chemical processes important to the DOE mission.

Potential Impact Areas

- "green" chemistry,
- nuclear waste identification and remediation, and
- economical utilization of petroleum-based hydrocarbon feedstocks.

Research Summary and Final Report for Work Done at University of Memphis

Progress was made on all research fronts, in particular modeling of organometallic catalysis, implementation of previously developed *de novo* design and analysis strategies for transition metal complexes, and probing the chemistry of tris-pyrazolyl-borate (Tp) complexes. Additionally, profitable outgrowths of this research in catalysis design were investigated.

I. Organometallic Catalysis

As part of one of our primary objectives to develop and apply improved strategies for modeling aqueous phase organometallic chemistry, we carried out in-depth surveys of hydroformylation (HyF) in the gas-phase and aqueous media. HyF is one of the most important industrial reactions, producing millions of tons of aldehyde annually. Aldehydes are used in industrial applications ranging from detergents to pharmaceuticals to plastics. There is considerable commercial interest in replacing organic solvents with "green" solvents such as water. Rhône-Poulenc and Ruhrchemie have commercialized technology to effect olefins hydroformylation, eq 1, using sulfonated phosphine catalysts.

Scheme 1 shows the consensus mechanism for Rh-catalyzed HyF. Despite a massive research effort, experimental and computational, major issues still remain vis-à-vis traditional HyF and aqueous-phase derivatives. Some of the more important questions involve the following.

- the rate-determining step,
- selectivity of linear over branched products,
- the role of phosphine (PR_3) R groups, and
- differences/similarities in mechanism upon going to aqueous media.

To address these issues, and to serve as a platform for aqueous HyF studies, postdoctoral associate Steve Decker undertook a series of projects. He was assisted in some of these by Jorge Carbo, a visitor to our lab who was sponsored by the Spanish government. This extremely productive team carried out what is, to our knowledge, the most complete survey of the reaction coordinate of hydroformylation. The most important conclusions are summarized below.

a. Gas-Phase Ethylene Hydroformylation by a $\text{HRh}(\text{PH}_3)_2(\text{CO})$ Catalyst

This research (SA Decker, TR Cundari *Organometallics* 2001, 20, 2827) is a baseline study as it takes place in the gas-phase, and incorporates the simplest olefin (ethylene) and phosphine (PH_3) models. These choices permit us to identify theories with maximum accuracy and minimum computational expense for further research (*vide infra*) on experimental systems.

Several important conclusions came from this research, although two are particularly novel and significant. First, our research indicates that pseudorotation may play an important role in shunting the various intermediates in Scheme 1 from one pathway to another. Pseudorotation involving the five-coordinate intermediates $\text{HRh}(\text{PR}_3)_2(\text{CO})(\text{olefin})$ and $\text{Rh}(\text{PR}_3)_2(\text{CO})_2(\text{CH}_2\text{CH}_2\text{R})$ are the most plausible candidates. The former results from olefin addition to the $\text{HRh}(\text{PR}_3)_2(\text{CO})$ active species, while the latter derives from addition of CO to the olefin insertion product $\text{Rh}(\text{PR}_3)_2(\text{CO})(\text{CH}_2\text{CH}_2\text{R})$. Pseudorotation of five-coordinate intermediates is competitive with alternative sequences, and hence it is reasonable to infer that this process can help maintain catalyst activity by reducing the concentration of intermediates in non-productive reaction channels. Since some of the side reactions also yield different regiochemistry (*i.e.*, linear versus branched aldehyde) one can also assume that pseudorotation impacts HyF catalyst selectivity.

The second major conclusion from this research is the theoretical prediction that the rate-determining step is CO insertion. This is consistent with

previous computational studies on other catalysts or with more restricted methodologies. It is, however, in contrast to experimental data, which has been interpreted in favor of rate-determining H_2 oxidative addition. It is amazing that all computational studies of which we are aware are in agreement with each other, but in disagreement with experiment. Clearly, one of two scenarios seems plausible. Either the computations are wrong, or the experiments are wrong. To address this dichotomy, our group sought to methodically increase the overlap between theory and experiment. This requires modeling of (a) solvent effects, (b) more realistic phosphine co-ligands (PR_3), and (c) α -olefins. We will address these points in the following sections.

(1)

Scheme 2

b. Effect of Phosphine (PR_3) Co-ligands.

In this study (SA Decker, TR Cundari *New. J. Chem.* **2002**, 26, 129) using hybrid QM/MM (quantum mechanics/molecular mechanics) techniques, we modeled more experimentally relevant phosphines, PR_3 ($R = \text{Me}$, $t\text{Bu}$, Ph , *meta*- PhSO_3^- , and *para*- PhSO_3^-). The metal inner coordination sphere is modeled using high-level density functional theory (DFT), while phosphine R groups are modeled with inexpensive MM methods. As such, important electronic and steric factors can be efficiently incorporated in the study of large complexes. Experimental evidence indicates that olefin insertion is non-reversible. Hence, this step determines the regiochemistry of the aldehyde, and is thus the most crucial step within the catalytic cycle (Scheme 1).

Our previous research showed that the $\text{HRh}(\text{PR}_3)_2(\text{CO})(\eta^2\text{-CH}_2=\text{CH}_2)$ intermediate exists in two geometric isomers depending on the relative disposition of the two phosphines. The

equatorial-equatorial (**ee**) isomer has C_s symmetry and hence there is one pathway for olefin insertion. The equatorial-axial (**ea**) isomer has no symmetry and thus two pathways for olefin insertion are possible, Scheme 2. For all phosphines studied, pathway (2) (**ea** $\rightarrow$ **ea**₁[†] $\rightarrow$ **trans**) is disfavored relative to pathways (1) and (3), Scheme 2. More interestingly, pathways (1) and (3) are competitive for a PMe_3 catalyst, while for tri-aryl phosphines there is a clear thermodynamic and kinetic preference for pathway (1), implying that tri-aryl phosphine catalysts will be more selective. The QM/MM calculations suggest that π -stacking interactions may be vital in determining the preferred catalytic pathways.

c. Propene Insertion in the Rh-H Bond of $\text{HRh}(\text{PPh}_3)_2(\text{CO})(\eta^2\text{-CH}_2=\text{CH-CH}_3)$.

Selectivity for linear over branched aldehydes in hydroformylation of α -olefins is extremely important as the former are more desirable. To investigate this we conducted research on the propylene hydroformylation by $\text{HRh}(\text{PPh}_3)_2(\text{CO})(\eta^2\text{-CH}_2=\text{CH-CH}_3)$ using QM/MM methods (SA Decker, TR Cundari *J. Organomet. Chem.* **2001**, 635, 132). Two scenarios immediately suggest themselves in terms of catalyst selectivity – kinetic (transition state) or thermodynamic (ground state) discrimination, Scheme 3. In scenario (a) there is a common intermediate (*i.e.*, olefin adduct), while in scenario (b) the linear:branched ratio results from energetic partitioning between two olefin adducts. After investigating all possible isomeric olefin adduct geometries (**ea** and **ee** isomers as well as different olefin conformations) and all isomeric olefin insertion transition states emanating from these, our data support scenario (b) – thermodynamic discrimination. The branched product is predicted to result from a minor, but more active propene adduct, while linear product evolves from the major, albeit less reactive propylene adduct.

d. Aqueous Phase Hydroformylation

HyF is one of the most important industrial reactions, producing millions of tons of aldehyde annually. Aldehydes are used in industrial applications ranging from detergents to pharmaceuticals to plastics. There is considerable commercial interest in replacing organic solvents with “green” solvents such as water. Rhône-Poulenc and Ruhrchemie have commercialized technology to effect olefins hydroformylation, eq 1, using sulfonated phosphine catalysts.

In collaboration with researchers at Ames Lab, we investigated effective fragment and Monte Carlo techniques for aqueous-phase hydroformylation (HyF). HyF was chosen for its industrial significance, and because the catalytic cycle contains fundamental OM reactions: oxidative addition/reductive elimination, ligand association/dissociation, etc. Suitable models were identified, which are applicable to other systems, *e.g.*, Shilov catalysts for hydrocarbon functionalization. Studies on aqueous-phase organometallic catalysis were complemented by parallel studies of the gas-phase reaction. To our knowledge, this represents the most complete computational survey of hydroformylation (HyF), one of the largest industrial catalytic processes. A Rh-carbonyl-phosphine catalyst was investigated. Two of the most important implications of this research include (a) pseudorotation among five-coordinate intermediates is significant in HyF, and (b) CO insertion is the rate-determining step. The latter is in contrast to experimental deductions, highlighting the need for more accurate modeling. To this end, we undertook studies of (a) experimentally relevant PR_3 co-ligands (PMe_3 , PPh_3 , $\text{P}(\text{p-PhSO}_3^-)_3$, *etc.*), and (b) HyF of propene. The former project showed tri-alkyl versus tri-aryl phosphines to proceed through different mechanisms. For the propylene research, simulations indicated the linear:branched aldehyde ratio (linear is more desirable) is determined by thermodynamic discrimination of two distinct pathways. Our research on aqueous HyF indicates that the catalyst is only weakly aquated, in contrast to the hydride of the Rh-H bond. As the insertion of the olefin $\text{C}=\text{C}$ into Rh-H determines the linear-to-branched aldehyde ratio, it is reasonable to infer that solvent plays an important role in regiochemistry.

2. *De Novo* Design and Analysis Strategies for Transition Metal Chemistry

Previous supported research led to the development of integrated schemes for the *de novo* (from scratch) design and analysis of transition metal (TMs) complexes. Unlike organic and biological molecules, *de novo* design and analysis of transition metal complexes engenders special challenges, including the correct prediction of geometric (*e.g.*, cis versus trans, fac versus mer, *etc.*), spin (*e.g.*, high- versus intermediate- versus low-spin), linkage (*e.g.*, SCN versus NCS, CN versus NC, η^2 -carboxylate versus η^1 -carboxylate), and coordination (*e.g.*, square pyramidal versus trigonal bipyramidal, axial versus equatorial or apical versus basal) isomerism in addition to conformational isomers resulting from rotation about bonds and different ring conformations. Recent advances in computational methods such as effective core potentials (which reduce the computational task to only valence electrons) and density functional theory (which efficiently incorporate electron correlation effects) have revolutionized the field of computational transition metal chemistry. However, these methods are still too expensive for routine study of large ($\approx 50 - 100$ atoms), conformationally complex TM complexes. To this end, the past several years has seen a concerted effort on our part (TR Cundari, J Deng, W Fu *Intern. J. Quantum Chem.* **2000**, *77*, 421; TR Cundari, W Fu *Inorg. Chem. Acta* **2000**, *300* - 302, 113.), generously supported by the U.S. Department of Energy, to develop very rapid and reliable modeling methods for transition metals. We have focused on molecular mechanics

(MM) and semiempirical quantum mechanics. Previous work focused on the development of these methodologies and their integration to *de novo* predict the geometry of metal complexes. Our primary motivation is that important materials such as catalytic intermediates often have limited geometric information; obviously, metric data is unavailable for not yet synthesized materials. Finally, even when an experimental geometry exists it is typically only for one conformer, which may be only more marginally stable than other isomers or may be the congener most susceptible to crystallization. Hence, since the prediction of geometry is the most important and first step in any computer-aided design and analysis scenario, there is great value in rapid methods for prediction of metal complexes for a wide range of applications from advanced materials to biology to catalysis.

Technetium is a radiometal of great importance in nuclear waste. Significant interest revolves around the identification of waste forms of Tc and the development of strategies for its removal. We developed a coupled quantum mechanics-molecular mechanics protocol for the *de novo* design of Tc complexes. Initial research shows it to be capable of accurately predicting the structure of metal complexes "from scratch," with limited *a priori* knowledge. Challenges in the structural prediction of metal complexes include conformational, geometric (e.g., *fac* versus *mer*), structural (e.g., trigonal bipyramid versus square pyramid for five coordination), coordination (axial versus equatorial for a trigonal bipyramid), spin (high versus intermediate versus low spin states), and linkage (e.g., Tc-SCN versus Tc-NCS) isomerism. In general, our protocol can rapidly (<1 day with desktop software/hardware) predict the structure of diverse Tc complexes with an accuracy commensurate to organics.

As a continuing test of this we undertook a joint theory-experiment study of Ru-bis(thietane) complexes, which are relevant to hydrodesulfurization of petroleum feedstocks (PM Nave, M Draganjac, B Ward, AW Cordes, TM Barclay, TR Cundari, JJ Carbo, F Maseras *Inorg. Chim. Acta* 2001, 316, 13). Nave and Draganjac isolated a novel, cationic bis-thietane complex of ruthenium. This complex had simultaneously the most puckered and most planar thietane rings reported in the literature! We carried out *ab initio* calculations on the puckering motion of thietane and other sulfur heterocycles, and then followed this up with an extensive MM and SEQM study of the Ru complex without relying on the X-ray data. These calculations were then refined with QM/MM studies of the $[\text{CpRu}(\text{PPh}_3)(\text{S-thietane})_2]^+$ target molecule. The results of the predicted geometry are in excellent agreement with the crystal geometry with the exception that the thietane rings are both puckered by a normal amount, suggesting that there is an unresolved crystallographic disorder in this complex. These calculations do, however, indicate that ligation of the thietane to the cationic Ru makes it more susceptible to nucleophilic attack.

3. Tris-pyrazolyl Borate Complexes

An emerging theme in the dynamic field of C-H activation chemistry is the search for new supporting ligation to supplement the workhorses of the field, cyclopentadienyl and its derivatives. In this regard, tris(1-pyrazolyl)borate and related ligands have seen much interest following upon the pioneering work of Trofimenko.

Like Cp, Tp affords the potential for systematic manipulation of their steric and electronic profile through chemical modification. Tp ligands are generally envisaged as Cp equivalents. However,

more careful consideration of the experimental literature suggests that the situation may not be so straightforward.

Our main goals in the grant period in research carried out by Ph.D. student Thomas Klinckman were to (a) identify suitable levels of theory, (b) identify appropriate chemical models, and (c) provide a comparison of the potential energy surface for $\text{CpRe}(\text{CO})_2$ and $\text{TpRe}(\text{CO})_2$. Progress has been made with respect to these three goals. Specifically, the B3LYP hybrid functional combined with the Stevens effective core potential/valence basis set combination was found to provide the appropriate combination of computational efficiency and accuracy. Additionally, the model tris(pyrazolyl)borate ligand ($\text{Tp}^\# = [\text{H-B}(\text{N}=\text{NH})_3]$) is a suitable model for the full ligand. In addition to the benefits of providing a smaller, more computationally efficient model ligand for further research, this observation speaks to our third research goal. The similarity of the PESs for $\text{Tp}^\#\text{Re}(\text{CO})_2$ and $\text{TpRe}(\text{CO})_2$, Figure 1, is a clue to the chemistry behind the numbers. Tp and $\text{Tp}^\#$ differ primarily in the loss of resonance in the pyrazolyl arms for the latter model. The observation that the geometries and energetics of the potentials surfaces, Figure 1, for both the full complex (Tp) and the model ($\text{Tp}^\#$) thus suggests that the Tp ligand is acting as primarily a σ -donor through the pyrazolyl nitrogen, and that π effects are of less significance to its chemistry. This is decidedly unlike the Cp ligand, and suggests some Tp modifications that may yield enhanced reactivity, which we plan to study. The effect of the σ/π donor ability on the frontier orbitals is thus seemingly responsible for differences in the kinetics and thermodynamics each exhibits vis-à-vis carbon-hydrogen bond activation.

With respect to our third research goal, it is evident from Figure 1 that there are substantial differences in the reactivity of $\text{TpRe}(\text{CO})_2$ and $\text{CpRe}(\text{CO})_2$. This is a result that will be of great interest to experimentalists given the usual assumption in the literature that Tp and Cp can be freely interchanged.

Figure 1

4. Carbon-Hydrogen Bond Activation by Ti-Imido Complexes

Methane is the major component of natural gas, and hence its catalytic conversion to functionalized products is of great scientific and economic interest. However, other hydrocarbons are also found in natural gas so that both *activity* and *selectivity* are important for an industrial catalyst. Recent experiments and computations suggest that alkane adducts play a pivotal role in metal-mediated hydrocarbon activation. Given the evanescent nature of alkane adducts, computation is useful for probing these catalytic intermediates. Furthermore, it is of interest to compare adducts of larger hydrocarbons with methane as this may yield insight into selective catalysts for methane conversion. This research addresses selectivity issues in C-H bond activation ("Carbon-Hydrogen Bond Activation by Titanium Imidos. Computational Evidence for the Role of Alkane Adducts in Selective C-H Activation;" T. R. Cundari, T. R. Klinckman, P. T. Wolczanski *J. Am. Chem. Soc.*- in press), an issue that has been little addressed due to the importance of methane as a substrate, and also due to size considerations involved in modeling larger alkanes.

Wolczanski and co-workers have scrutinized the kinetics, thermodynamics and mechanism of both 1,2-RH-elimination from $(\text{silox})_2(\text{Bu}_3\text{SiNH})\text{TiR}$ and its microscopic reverse 1,2-RH-addition to $(\text{silox})_2\text{Ti}=\text{NSi}^t\text{Bu}_3$, $\text{silox} = \text{OSi}^t\text{Bu}_3$. This group has also studied related C-H activation by transient $\text{Zr}(=\text{NSi}^t\text{Bu}_3)(\text{N}(\text{H})\text{Si}^t\text{Bu}_3)_2$, $\text{Ta}(=\text{NSi}^t\text{Bu}_3)_2(\text{N}(\text{H})\text{Si}^t\text{Bu}_3)$, and $\text{W}(=\text{NSi}^t\text{Bu}_3)_3$. Their experiments suggested that 1,2-RH-elimination occurred via a four-center transition state (TS), involving concerted bond breaking and bond making. Previous computational studies from our lab on 1,2-RH-elimination from d^0 -amido complexes, and 1,2-RH-activation by d^0 -imidos, supported a planar, four-centered TS in which the major atomic motion corresponded to bond making and breaking for CH and NH bonds. Calculated RH elimination barriers as a function of metal and R are in very good agreement with experimental data for Zr-amido/Zr-imido systems. The titanium imido $(\text{silox})_2\text{Ti}=\text{NSi}^t\text{Bu}_3$ is somewhat less selective than $(\text{N}(\text{H})\text{Si}^t\text{Bu}_3)_2\text{Zr}=\text{NSi}^t\text{Bu}_3$. Selectivity differences between titanium and zirconium imidos may arise from greater substrate access to the $\text{M}=\text{N}$ active site for the former. Geometry optimizations employing high-level calculations yield, near linear Ti-O-Si and Ti=N-Si angles for the putative three-coordinate imido active species. Hence, despite its smaller covalent radius the Ti system is expected to be fairly accessible due to the large Ti-O-Si and Ti=N-Si angles.

This research investigated hydrocarbon adducts of TM complexes with effective core

potential (ECP) methods using the parallel-GAMESS program. Hydrocarbon adducts of high-valent (d^0) titanium imidos, $(OR')_2Ti=NR'$ ($R' = H, SiH_3, SiMe_3$), are studied; substrates ($R = Me, Et, Vy, cPr, Cy, Ph, Bz, cubyl$) are chosen to complement experimental research by the Wolczanski group. The role of chemical environment was analyzed as a function of hydrocarbon and the Ti-imido. Subsequently, reaction coordinates for carbon-hydrogen bond activation, Scheme 5, were studied with quantum methods to address issues related to selectivity. The most important results are summarized here.

- There is little variability in the molecular structure of the reactants, products, and perhaps most interestingly, transition states as R and R' are changed. Structural flexibility is greatest in the hydrocarbon adducts, $Ti(OR')_2(=NR')\cdots HR$.
- Despite the small structural changes observed for $Ti(OR')_2(=NR')$ with different R' , significant changes are manifested in calculated electronic properties - the Mulliken charge on Ti becomes more positive with larger R' (ligand substituents) and the $Ti=N$ bond orders decreases with larger ligand substituents - changes that should facilitate C-H activation. Indeed, it is observed that the $\Delta G_{add}(MeH)$ decreases as the ligand substituent gets larger ($R' = H, silyl, TMS$).
- A reduced variational space analysis of adduct binding energies suggests that differences in the polarization of RH by the Ti-imido differentiate one hydrocarbon adduct from another for a given complex. However, a substantial steric modification of the alkane-complex is expected from $R-R'$ interactions, given the magnitude of ΔG_{add} and the conformational flexibility of the adduct.
- Molecular mechanics simulations of isomeric $Ti(OSi^tBu_3)_2(=NSi^tBu_3)\cdots$ isopentane adducts yield an energy ordering as a function of the rank of the C-H bond coordinated to Ti that is consistent with experimental selectivity patterns. Specifically, 1° C-H bonds are preferentially coordinated versus 2° C-H bonds, which are in turn coordinated in preference to 3° C-H bonds.
- Calculated elimination barriers compare very favorably with experimental results. Larger SiH_3 and TMS ligand substituents generally yield better agreement with experiment. The level of agreement is evidence that the quantum modeling of the major contributions to the elimination barrier (N-H and C-H bond making) is ostensibly correct.
- The calculations indicate that weakening the C-H bond of the hydrocarbon yields a more strongly bound adduct.

Combining these conclusions, the present research points to the adduct, specifically the structure and energetics of the substrate/Ti-imido interaction, as the main factor in determining the selectivity of hydrocarbons (R).

Publications from University of Memphis Acknowledging Grant No. DE-FG02-97ER14811

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