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I. Final Report (DOE-FG05-94ER14460)

Research in the initial grant period focused on computational studies relevant to the selective activation of methane, the prime component of natural gas. Reaction coordinates for methane activation by experimental models were delineated, as well as the bonding and structure of complexes that effect this important reaction. This research, highlighted in the following sections, also provided the impetus for further development, and application of methods for modeling metal-containing catalysts. This work resulted in ten published papers in refereed scientific journals.[1-10] Our DOE research was also highlighted in an invited review,[11] and an invited conference proceeding.[12] DOE funds supported the research of two Masters,[13,14] and two Ph.D.[15,16] researchers. Additionally, four undergraduate students contributed to DOE-funded research whose name appears on these publications (S Curtiss, ML Lutz, LC Saunders, DL Tippett). Finally, the principal investigator gave 30 invited seminars at national and international conferences which discussed and acknowledged research funded through DOE-FG05-94ER14460.[17]

A. Methane Activation by Multiply Bonded Transition Metal Complexes

Imidos ($L_nM{=}NZ$) are known to effect methane CH activation.[18] We studied π-loading as a route to more potent methane activators.[3,19,20] Briefly, coordination of strong π-bonding ligands should increase competition for M dπ - N pπ bonding and reduce MN π-bond strengths. As methane is activated by $[2_\sigma + 2_\pi]$ addition of CH across the MN π-bond, experimentalists have proposed that π-loading may yield greater driving force and lower CH activation barriers.[18a]

Our early studies of methane activation by imido[19] and bis(imido)[20] complexes suggested that further π-loading (by coordination of a third imido) would be of interest. We thus initiated a systematic analysis of tris(imido) complexes as a prelude to study of their methane activating ability, eq 1.[1,3] We sought to rigorously confirm the accuracy of the computations by extensive

$$M(=NH)_3 \quad + \quad Me\text{-}H \quad \dashrightarrow \quad M(=NH)_2(NH_2)(Me) \qquad (1)$$

comparison with experiment. We initiated a theory-experiment collaboration with Bryan (Oak Ridge) on tris(imido) complexes, $MX(=NZ)_3$.[1,7] This work convincingly shows the computational methods to be applicable to tris(imido) complexes, and yielded valuable insight into how X changes the bonding of the tris(imido) fragment in $MX(=NZ)_3$. Three-coordinate, d^0-tris(imido) complexes are highly reactive and transient; this research suggests routes to $MX(=NZ)_3$ as metastable precursors to $M(=NZ)_3$ methane-activators which we will explore in the future.

Methane activation by experimentally relevant tris(imido) complexes, eq 1, permits a probe of the π-loading strategy, and the effect of charge, geometry, d orbital occupation and transition metal (TM).[3] Methane activation by tris(imido) complexes[3] is more exothermic than bis(imido)[20] and mono(imido)[19] analogues, consistent with the π-loading thesis. However, contrary to experimental predictions, greater driving force does not yield lower CH activation barriers.[3]

Considerable attention has focused on weakly-bound, alkane adducts in CH activation.[21,22] Although the best experimental data is for low-valent complexes,[21a] our calculations suggest that methane adducts are also plausible for high-valent complexes.[22] Subsequent experiments[21b,c] support our calculations, but more research is needed. Thus, we have sought to identify complexes which can form adducts amenable to experimental study and further elucidation of their role in CH activation. One of the most exciting results from DOE-supported research involves identification of tris(imido) complexes, $M(=NZ)_3$, as targets for characterization of stable or metastable methane adducts of d^0 complexes.[3] For an isoelectronic tris(imido) series a positive charge makes methane bind more tightly to the complex, and also increases the barrier to CH activation. Thus, a methane adduct of $[Tc(=NZ)_3]^+$ (and its Re analogue) are worthy experimental targets. Experiments are underway by Burrell to test our assertion.[23] Also, kinetic evidence by Wolczanski is consistent with tightly-bound alkane adducts of neutral, W-tris(imido) complexes.[22c]

The preceding research marks our first use of molecular mechanics (MM) for modeling inorganic systems.[3,12] MM is fast and applicable to very large complexes, and has been widely used in organic chemistry, but much less so for metal complexes.[24,25] Through a combination of quantum mechanical (QM) and MM calculations we can efficiently probe both steric and electronic factors. For example, QM calculations show an electronic driving force for methane coordination to the complexes $W(=NH)_3$ and $[Tc(=NH)_3]^+$.[3,22] However, one must question whether this preference can be realized when NH is replaced by more realistic and sterically demanding ligands such as NAr (Ar = $2,6\text{-}C_6H_3{}^iPr_2$) or NSi' (Si' = ${}^tBu_3Si$)? We used QM methods to develop an MM force field for Zr[11,26] and Tc[3] organometallics, and applied it to the question of whether methane can coordinate to $[Tc(=NAr)_3]^+$ and $Zr(=NSi')(N(H)Si')_2$. MM calculations indicate that methane can coordinate to these methane activating imidos without steric hindrance.[3,26]

Our research on TM imidos seeks to understand how the components of eq 2 affect bond

$$L_nM{=}EZ \quad + \quad CH_4 \quad \text{-->} \quad L_nM(CH_3)\text{-}E(H)Z \qquad (2)$$

activation reaction coordinates, and provide insight with respect to modifying imidos for greater methane activating ability.[1,3,5,8,12,19,20,22,26] Earlier research focused on metal (M) and ancillary ligands (L_n). Thus, we studied the final component of eq 2: the role of imido substituent (Z) in methane activation.[5] Substituent effects (structural, electronic and enthalpic) are much less consequential in the imido ($L_nM{=}NZ$) and transition state (TS) than amido ($L_nM\text{-}NHZ$) product. Thus, for a given TM it will be difficult to tailor imido reactivity through electronic modification of Z and L_n since most ancillary ligands and substituents studied to date, experimentally and computationally, exert their influence primarily through inductive effects localized on the MN σ bond. Since the imido π-bond is more sensitive to conjugative effects arising from changing L_n or Z,[27] our research suggests profitable routes for greater imido reactivity and further research.

B. Computational Lanthanide Chemistry

Experimentalists have shown increased interest in the lanthanides in order to exploit their unique properties in advanced materials and catalysis.[28] The attributes, e.g. the contracted 4f orbitals, responsible for their attractive properties also lead to major challenges in computational lanthanide (Ln) chemistry. A major effort[2,11-13] involved development of better computational methods for lanthanides. In collaboration with Walt Stevens (NIST), we extended the effective core potential (ECP) scheme, employed with great success in our studies of transition metals (TMs),[11,29] to lanthanides.[30] We worked with the GAMESS[31] team at Iowa State/Ames Lab to implement our ECPs into this software package, to encourage their use by other researchers.

We embarked on a systematic evaluation of our ECPs for Ln chemistry.[2,11,12] This research is, to our knowledge, the first ECP study of polyatomics in which 4f electrons are explicitly included in the lanthanide valence space.[2] The high-spin $4f^4$ configuration of Ln(III) is described using multi-configuration (MC) and unrestricted Hartree-Fock (UHF) wavefunctions. Both methods display excellent structural prediction, although UHF is much faster with no evidence of extensive spin contamination. We predicted the geometry of all 56 lanthanide trihalides (LnX_3, Ln = Ce to Lu, X = F, Cl, Br, I) to an RMS error of ≈ 2%! There is no loss of accuracy from early to late members of the lanthanide series and from the lightest to heaviest halogen.[2]

As with transition metals, methane activation provides the impetus for development of improved methods for computational Ln chemistry. Two reactions, eqs 3 and 4, were studied.

$$Cl_2M\text{-}CH_3 \quad + \quad C^*H_4 \quad <\!\!-\!\!-\!\!> \quad Cl_2M\text{-}C^*H_3 \quad + \quad CH_4 \tag{3}$$

$$LnF_3 \quad + \quad CH_4 \quad -\!\!-\!\!-\!\!> \quad LnF_2CH_3 \quad + \quad HF \tag{4}$$

Early (La) and late (Lu) lanthanides were compared with transition metal (Sc, Y), and main group (Group 13) analogues, eq 4.[12] Study of metals from across the periodic table is only feasible with compact ECP schemes.[12] Since eq 3 is a degenerate reaction we can probe the metal's effect on the kinetics of methane activation without the complication of having different thermodynamic driving forces. We find a direct linear correlation between lower barrier heights and the metal's ability to stabilize both the carbon and hydrogen atoms of the CH bond being activated.[12] Also, although the p-, d- and f-block complexes are highly electrophilic at the metal, only the latter two form tightly bound methane adducts. This further supports the contention[22] that there is a critical covalent contribution to the bonding in adducts of high-valent metal complexes.

Molecular mechanics was applied to Ln coordination complexes.[4,12] The MM approach is very exciting and valuable for assessing steric consequences of bulky ligands. In the future we envision increased coupling of MM and ECP methods for the study of larger, more realistic d- and f-block complexes.

C. Methane Activation by Non-imido, Multiply Bonded Ligands

Although the imido continues to be of considerable importance, we expanded our research to other multiply bonded ligands. We compared a series of imidos with oxo ($L_nM{=}O$) and methylidene ($L_nM{=}CH_2$) models, eq 5.[32] The former are models of intermediates in industrial and biochemical oxidations.[33] Alkylidenes are important olefin polymerization catalysts.[34] While our research was in progress, that Ti-alkylidenes are potent methane activators.[35] Group IVB metals and their cationic Ta analogues were chosen to maximize experimental relevancy.[18,35,36]

$$Cl_2M{=}E \quad + \quad CH_4 \quad \text{-->} \quad Cl_2M(EH)(CH_3) \qquad (5)$$

By changing the multiply bonded ligand we can probe the nature of the activating ligand on methane activation.[32] The polarity of the ME π-bond decreases in the order MO > MN > MC. Experimentalists have focused on bond polarity as crucial in determining methane activating ability by high-valent complexes.[37,38] However, limited data available from theory or experiment for multiply bonded TM complexes suggests the ordering in eq 5 based on thermodynamic driving force will be MC > MN > MO.[32] Thus, its seems that there are conflicting chemical forces in eq 5. Having demonstrated the utility of the methods, it is possible to address the preceding debate. Our calculations show that for a given TM, lower CH activation barriers follow the order oxo > imido > alkylidene.[32] Computations show a strong linear correlation between lower activation barriers and more exothermic reactions. Our results apply to $[2_\sigma+2_\pi]$ mechanisms, and might explain why oxos, which are potent CH activators, generally activate through alternate pathways centered at the oxygen involving non-concerted, radical mechanisms;[33] imidos, on the other hand, effect CH activation through concerted pathways without evidence of radical pathways.[18]

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