Hydrocarbon Activation by Imido and Alkylidene Complexes

Stephen M. Contakes Literature Seminar September 19, 1996

Hydrocarbons are relatively abundant and inexpensive. However, conventional processes for the conversion of C-H bonds to other functionalities are poorly understood, difficult to control, and exhibit poor to moderate product selectivity. Consequently, there is an intense amount of research devoted to devising novel strategies for selective C-H bond functionalization. The most promising technologies involve the use of transition metal complexes.[1] These metal based C-H activation processes can roughly be divided into two categories: radical processes and concerted processes.[1,2] Radical processes involve the catalytic or initiated generation of hydrocarbon radicals by metal centers.[2,3] Concerted processes involve bonding between the hydrocarbon and metal center.[2,4] Concerted processes offer superior selectivity as well as the ability to influence product selectivity by engineering the steric bulk of the ligands around the metal center.[4] Of the latter, the activation of C-H bonds by 1,2 addition across metal imido and alkylidene double bonds has recently been the subject of intense interest.[2,5-10] The reasons for this are several: First, the nature of the complexes involved,[2,6-10] kinetic studies,[2] and theoretical calculations[5] suggest that the electrophillicity of the metal center plays an important role in C-H bond breakage.[2] Secondly, compounds containing isoelectronic oxo groups do not undergo this reaction and are known to activate C-H bonds only by radical processes.[3b,c] Finally, this process may possess greater selectivity than other C-H activations.[2,6d]

The general features of the 1,2-elimination/addition process for amide complexes are given in Scheme I. 1,2 R-H elimination occurs from a precursor L_nMR_2 or $L_nM(NHR)R$ (n=2, L=Cp, $^tBu_3SiO$, $^tBu_3SiNH$, ArO) complex to give a three-coordinate imido or alkylidene intermediate, which then adds a second hydrocarbon, R'-H, across the metal-heteroatom bond. R'-H addition is regiospecific with the carbon attaching to the metal center in all known cases. In the absence of sterically unhindered hydrocarbon, reaction of the intermediate with ligand C-H bonds to give metallacycles is a complicating side reaction.[2,6]

Scheme I

The types of complexes that exhibit the 1,2-addition/elimination reaction are shown in Figure 1. Note that all of the complexes except **complex e** are four-coordinate d^0 early metal complexes. Thus, three-coordinate imido and alkylidene complexes are generated on R-H elimination. Such intermediates are only stable when sterically demanding, electron donating ligands are present to stabilize the low coordinate d^0 metal center.[2,6] The combination of low coordination number and high oxidation state results in the presence of empty directional $d_{z}2/p_{z}$ hybrid orbitals on the metal center.[2,5,6] It is believed that C-H activation occurs by donation of C-H σ-bonding electrons into these orbitals, as shown in Figure 2a. Electron density on the alkylidene carbon or imido nitrogen atom may also facilitate this reaction by

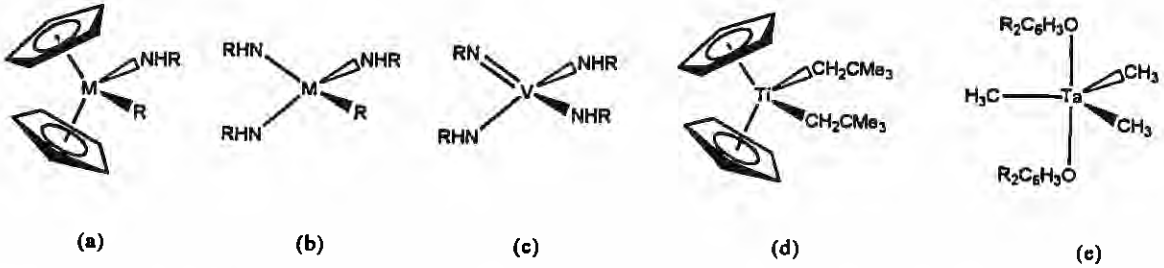

Figure 1. The major classes of compounds that activate C-H bonds through 1,2-elimination/addition: (a) $Cp_2M(NHR)R$ (M=Ti, Zr),[9] (b) $(^tBu_3SiNH)_3MR$ (M=Ti, Zr),[2,6] (c) $(^tBu_3SiNH)_3VR{=}NSi^tBu_3$,[10] (d) $Cp_2Ti(CH_2CMe_3)_2$,[8] and (e) (2,6-$R_2C_6H_3O)TaMe_3$ (R=^{t}Bu, ^{i}Pr).[7] Compounds of type e may exhibit 1,2 R-H elimination only under photochemical conditions.[7a-c]

electron donation into the C-H σ* orbital, as shown in Figure 2b. In an apparent exception to the above generalities, five coordinate $(ArO)_2TaR_3$ complexes of the type shown in Figure 1e are known to undergo 1,2 R-H elimination under photochemical conditions to give four-coordinate alkylidene complexes.[7a-c] However, many details regarding C-H activation by these complexes are not yet fully understood.[7a-c]

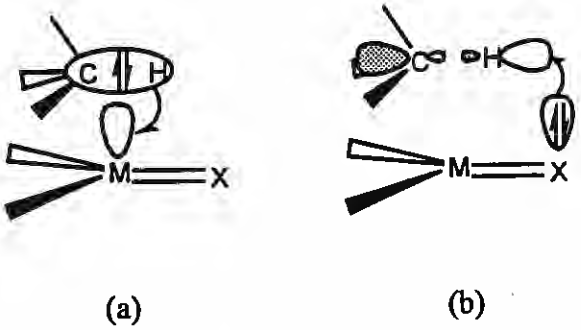

Figure 2. Orbital interactions during C-H bond activation by 1,2-addition. (a) electrons are donated from a C-H σ orbital into the empty d_{z^2}/p_z hybrid orbital on the metal center.[5] (b) electrons are donated from the heteroatom into an empty C-H σ* orbital.

A number of mechanistic investigations of 1,2-elimination/addition of C-H bonds across metal-heteroatom bonds have been undertaken.[2,6a-f,7a,b,d,10] Kinetic studies on hydrocarbon exchange reactions (i.e. R'H + MR-XH → MR'-XH + RH X = CR_2 or NR) show that the elimination/addition reaction is first order in metal complex and zero order in hydrocarbon.[2,6a-f,7a,b,d,10] Isotope labelling studies using deuterated hydrocarbons show incorporation of deuterium on the heteroatom in the product alkyl complex (i.e. R'D + MR-XH → RH + MR'-XD, X = CR_2 or NR).[2, 7a] This behavior indicates that elimination of RH precedes addition of R'H and is the rate determining step. There has been some discussion in the literature regarding the nature of the metal-hydrocarbon interactions along the reaction coordinate and the structure of the R-H addition/elimination transition state. Ab-initio RHF calculations indicate that metal to RH bonding precedes C-H bond cleavage and that there is appreciable M-CH bonding in the transition state.[5] Hydrocarbon exchange studies using the complex $(^tBu_3SiNH)_3ZrMe$ show a correlation between the rate of reaction (expressed as $\Delta G^\ddagger$) and the proton affinity of the hydrocarbon C-H bond as shown in Figure 3.[2] Because R-H elimination is the microscopic reverse of R-H addition, this correlation is consistent with the orbital based description of electron donation from the C-H bond to empty directed orbitals on the metal as discussed previously.

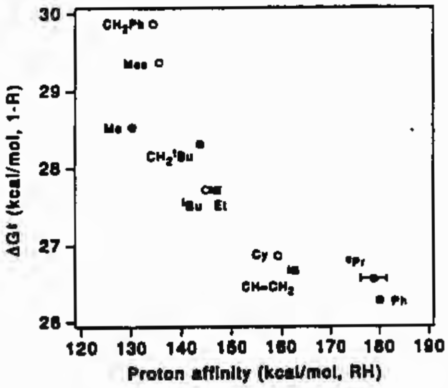

Figure 3. Correlation between $\Delta G^\ddagger$ for 1,2 R-H elimination from $(Bu_3SiNH)_3ZrR$ and the proton affinity of R. Filled circles indicate experimental proton affinity data. Open circles indicate calculated proton affinity data. See Ref. 2 for details.

Competition experiments involving reaction of the intermediate $(^tBu_3SiNH)_2Zr{=}NSi^tBu_3$ with various hydrocarbons indicates that C-H bond activation selectivity follows the order cyclopropyl-H ~ Ar-H > Me-H > $PhCH_2$-H > cyclometallation > Et-H > $^tBuCH_2$-H > Cyclohexyl-H.[2] This trend is consistent with similar trends observed for C-H activation by σ-bond metathesis (at Cp^*_2ScMe)[2,4a] and oxidative addition (to $[HB(2,3\text{-}Me_2\text{-}pyrazoyl)_2]Rh(CNCH_2{}^tBu)$) ,[2,4i] however, the selectivities for 1,2-elimination/addition are greater.[2, 6d] The origin of the greater selectivity is not presently understood but may be related to greater steric congestion at the Zr center.

Functionalization of the metal alkyl complexes that result on activation of hydrocarbons has not been reported, presumably because the steric congestion at the metal hinders functionalization. Consequently, these complexes are presently more useful as model systems for examining the fundamental chemistry of C-H cleavage at early transition metal centers (including surfaces) than as practical C-H functionalizing agents.

References

1. For a recent review see (a) Arndtsen, B. A.; Bergman, R. G.; Mobley, T. A.; Peterson, T. H. *Acc. Chem. Res.* 1995, *28*, 154. The best books are (b) *Activation and Functionalization of Alkanes*, Hill, C. L. Ed.; John Wiley and Sons: New York, 1989. (c) Shilov, A. E. *Activation of Saturated Hydrocarbons by Transition Metal Complexes*; Reidel: Dordrecht, 1984, Chapter V. A good review of industrial processes is given in Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis, 2nd ed.*; Wiley: New York, 1992, Chapter 10.

2. Schaller, C. P.; Cummins, C. C.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1996**, 118, 591.

3. (a) Taylor, H. S.; Hill, D. G. *J. Am. Chem. Soc.* **1929**, *51*, 2922. (b) Priestly, N. D.; Floss, H. G.; Froland, W. A.; J. D. Lipscomb; Williniams, P. G.; Morimoto, H *J. Am. Chem. Soc.* **1992**, *114*, 7561. (c) Green, J.; Dalton, H. *J. Biol. Chem.* **1989**, *264*, 17698.

4. (a) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 203. (b) Burger, P.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 10462. (c) Sen, A.; Lin, M. *Nature* **1994**, *368*, 613. (d) Labinger, J. A.; Herring, A. M.; Lyon, D. K.; Luinstra, G. A.; Bercaw, J. E. *Organometallics* **1993**, *12*, 895. (e) Luinstra, G. A.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1993**, *115*, 3004. (f) Trost, B. M.; Shi, Y. *J. Am. Chem. Soc.* **1991**, *113*, 701. (g) Sen, A.; Gretz, E.; Oliver, T. F.; Jiang, Z. *New J. Chem.* **1989**, *13*, 755. (h) Periana, R. A.; Taube, D. J.; Evitt, E. R.; Loffler, D. G.; Wentrcek, P. R.; Voss, G.; Masuda, T. *Science* **1993**, *259*, 340. (i) Jones, W. D.; Hessell, E. T. *J. Am. Chem. Soc.* **1993**, *115*, 554. (j) Fendrick, C. M.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 425.

5. (a) Cundari, T. R. *J. Am. Chem. Soc.* **1992**, *114*, 10557. (b) Cundari, T. R. *Organometallics* **1993**, *12*, 1998.

6. (a) Cummins, C. C.; Van Duyne, G. D.; Schaller, C. P.; Wolczanski, P. T. *Organometallics* **1991**, *10*, 164. (b) Schaller, C. P.; Bonnano, J. B.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1994**, *116*, 4133. (c) Cummins, C. C.; Baxter, S. M.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1988**, *110*, 8731. (d) Cummins, C. C; Schaller, C. P.; Van Duyne, G. D.; Wolczanski, P. T.; Chan, A. W. E.; Hoffman, R. *J. Am. Chem. Soc.* **1991**, *113*, 2985. (e) Bennett, J. L.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1994**, *116*, 2179. (f) Schaller, C. P.; Wolczanski, P. T. *Inorg. Chem.* **1993**, *32*, 131. (g) Wolczanski, P. T. *Polyhedron* **1995**, *14*, 3335.

7. (a) Chamberlain, L. R.; Rothwell, I. P.; Huffman, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 1502. (b) Chamberlain, L. R.; Rothwell, A. P.; Rothwell, I. P. *J. Am. Chem. Soc.* **1984**, *106*, 1847. (c) Chamberlain, L. R.; Rothwell, I. P. *J. Chem. Soc. Dalton Trans.* **1987**, 163. (d) Latesky, S. L.; McMullen, A. K.; Rothwell, I. P.; Huffman, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 5981. (e) Lockwood, M. A.; Clark, J. R.; Parkin, B. C.; Rothwell, I. P.; *Chem. Commun.* **1996**, 1974. (f) Yu, J. S.; Fanwick, P. E..; Rothwell, I. P. *J. Am. Chem. Soc.* **1990**, *112*, 8171. (g) Smith, G. D.; Fanwick, P. E.; Rothwell, I. P. *J. Am. Chem. Soc.* **1989**, *111*, 750.

8. van der Heijden, H.; Hessen, B. *J. Chem. Soc., Chem. Commun.* **1995**, 145.

9. (a) Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *Organometallics* **1993**, *12*, 3705. (b) McDade, C.; Green, J. C.; Bercaw, J. E. *Organometallics* **1982**, *1*, 1629. (c) Guram, A. S.; Jordan, R. F.; Taylor, D. F. *J. Am. Chem. Soc.* **1991**, *113*, 1833. (d) Lee, S. Y.; Bergman, R. G. *J. Am. Chem. Soc.* 1995, *117*, 5877. (e) Lee, S. Y.; Bergman, R. G. *Tetrahedron* **1995**, *51*, 4255.

10. de With, J.; Horton, A. D. *Angew. Chem. Int. Ed. Engl.* **1993**, *105*, 903.