

## What can metal–ligand bonding energetics teach us about stoichiometric and catalytic organometallic chemistry?

Tobin J. Marks, Michel R. Gagne, Steven P. Nolan, Laurel E. Schock, Afif M. Seyam and David Stern

Department of Chemistry, Northwestern University, Evanston, IL 60208, USA

**Abstract**—This contribution surveys recent progress in the thermochemistry of lanthanide, actinide, and early transition element organometallic compounds. General trends in metal–ligand bond enthalpy patterns across the transition series can be understood largely on the basis of straightforward electronegativity concepts. Metal–ligand bonding energetics in such unusual species as metallacycles, early transition element carbonyls and benzyne, as well as in actinide carbonyls are also quantified. Such data furthermore provide a deeper insight into  $d^0, f^0$ -centered  $\beta$ -hydride/ $\beta$ -alkyl elimination, cyclometalation, and hydrocarbon functionalization processes, as well as into U(IV)-centered elimination reactions. New reactions which are examined in the light of metal–ligand bond enthalpy data include binuclear organolanthanide-centered hydrocarbon activation and organo-lanthanide-catalyzed hydroamination of olefins.

### INTRODUCTION

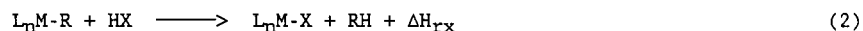
As organometallic chemistry reaches higher levels of sophistication and we strive to "engineer" increasingly complex reaction sequences, it is reasonable to inquire more deeply about the strengths of the metal–ligand bonds being made and broken in key transformations. Indeed, metal–ligand bond enthalpies can provide valuable information on metal–ligand bonding, can offer a deeper insight into known reaction pathways, and can aid in designing new transformations (refs.1-4). In this Laboratory, interest in metal–ligand bonding energetics grew out of a progression of unusual organometallic reactions discovered at actinide, lanthanide, and early transition metal centers which suggested marked differences in metal–ligand bonding patterns *vis-à-vis* middle and late transition elements. In the present article, we survey our recent research in this area, focusing on trends in bond enthalpies, on analyzing known transformations, and on developing new reactions.

In this contribution, homolytic bond disruption enthalpies are defined as in eq.(1). *Relative*  $D(L_nM-R)$  values have been determined using protonolytic (refs.5-8) or halogenolytic (refs. 9-10) titration calorimetry (eqs.(2)-(5)) and are, of

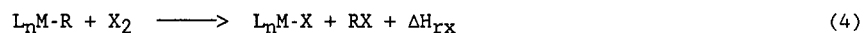
$$D(L_nM-R) = \Delta H_f^\circ(L_nM) + \Delta H_f^\circ(R\cdot) - \Delta H_f^\circ(L_nM-R) \quad (1)$$

$L_n$  = ancillary ligands

course, "anchored" to the corresponding  $D(L_nM-X)$  values. While relative  $D$  values



$$\Delta H_{RX} = D(L_nM-R) + D(H-X) - D(L_nM-X) - D(R-H) \quad (3)$$

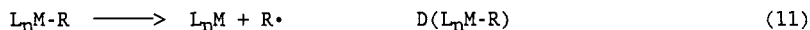
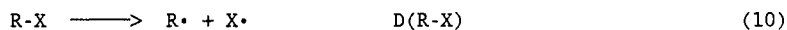
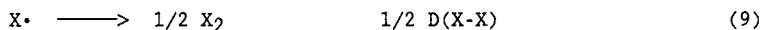


$$\Delta H_{RX} = D(L_nM-R) + D(X_2) - D(L_nM-X) - D(R-X) \quad (5)$$

suffice to analyze numerous  $L_nM-R \rightarrow L_nM-R'$  transformations, they can be placed on a more absolute footing by approximating  $D(L_nM-X)$  with the homoleptic  $D(M-X)$  value for  $M$  in the same formal oxidation state (eq.(6), refs, 5,8).

$$D(L_nM-X) \approx D_1(MX_y) \text{ or } \bar{D}(MX_y) \quad (6)$$

Especially for X = halogen, M = lanthanide, actinide, or early transition metal, this appears to be a reasonable approximation (*vide infra*). For appropriate  $L_nM/L_nMR/L_nMX$  ensembles, it is also possible to derive absolute  $D(L_nM-R)$  values via the reaction sequence of eqs.(7)-(11) (ref. 9). The validity of eq.(6) is



supported by this approach in that derived values of  $D[(Me_3SiC_5H_4)_3U-I] = 62.4(4)$  kcal/mol (ref. 9) and  $D(Cp_2Sm-I) = 69.4(3.0)$  kcal/mol ( $Cp = \eta^5-Me_5C_5$ ) (ref. 10) agree well with the corresponding  $\bar{D}(UI_4)$  and  $\bar{D}(SmI_3)$  parameters of 66(8) and 68(3) kcal/mol, respectively. The close parallels between  $\bar{D}(ZrX_4)$  and  $D(Cp_2Zr(X)-X)$  data also argue that differential effects of  $Cp$  ancillary ligands are small in this part of the Periodic Table (ref. 8).

### TRENDS IN METAL-LIGAND BOND ENTHALPIES

The thermochemical data now available for actinides and early transition elements allow, in combination with literature data (refs. 11-16), comparisons of metal-ligand bond enthalpy trends across the transition series. Two sensitive and chemically important parameters,  $D(M-H)-D(M-CH_3)$  and  $D(M-I)-D(M-CH_3)$ , are surveyed in Figures 1 and 2, respectively. It can be seen that there is a general increase in  $D(M-H)-D(M-CH_3)$  and a general decrease in  $D(M-I)-D(M-CH_3)$  as the transition series is transversed to the right. Some insight into the origins of these trends is provided by a variant (ref. 8) of the bond enthalpy-electronegativity relationship proposed by Matcha (ref. 17), eq.(12).

$$D(A-B) = 1/2[D(A_2)+D(B_2)] + 105(1-e^{-0.219(\chi_A-\chi_B)^2}) \quad (12)$$

This relationship employs Pauling electronegativities and gives far better agreement with experiment for diatomics than the original Pauling formulation. Calculation of  $D(M-I)-D(M-CH_3)$  as a function of  $\chi_M$  (eq.(13), Figure 3) yields

$$D(M-I)-D(M-Me) = 1/2[D(I_2)-D(Me_2)] + 105(e^{-0.219(\chi_M-\chi_{Me})^2} - e^{-0.219(\chi_M-\chi_I)^2}) \quad (13)$$

results in favorable accord with Figure 2 (ref. 18). It is of course recognized here that ancillary ligand effects on  $\chi_M$  are assumed to be approximately constant (cf., the  $D(Sm-I)$  and  $D(U-I)$  results above). Application of eq.(12) to  $D(M-H)-D(M-CH_3)$  values is also possible, however the near equality of  $\chi_H$  and  $\chi_{Me}$  in many tabulations (ref. 19) renders such a treatment more approximate.

Another potentially informative bond enthalpy trend is the simple linear relationship between corresponding  $D(M-X)$  and  $D(H-X)$  parameters (for constant M), recently reported for Pt and Ru complexes (ref. 20). It is not obvious *a priori* why such a relationship should obtain, and indeed, results in the  $Cp_2ThX_2$  (ref. 9) and  $Cp_2ZrX_2$  series (Figure 4) reveal serious deviations. Reference to eq.(14), derived from

$$D(M-X) = D(H-X) + 1/2[D(M_2)-D(H_2)] + 105(e^{-0.219(\chi_H-\chi_X)^2} - e^{-0.219(\chi_M-\chi_X)^2}) \quad (14)$$

eq.(12), reveals that for constant M, the X-dependence of  $D(M-X)$  arises solely from the exponential terms. Importantly, for middle and late transition elements where  $\chi_M \approx \chi_H \approx 2.2$ , the exponential terms will approximately cancel and  $D(M-X) \approx D(H-X) +$  a constant. This result is in agreement with the aforementioned Pt and Ru data. However, as  $\chi_M$  falls below  $\chi_H$  (lanthanides, actinides, early transition elements), there will be a deviation from linear behavior, with  $D(M-X)$  progressively displaced to the right in the  $D(M-X)$  vs.  $D(H-X)$  plot as  $\chi_X$  increases. This effect can be seen in Figure 4 and in more detailed numerical analyses (ref. 8). It should be noted that this treatment does not explicitly exclude descriptions involving metal-ligand orbital repulsion (ref. 21), polarization (ref. 22), or ligand-to-metal  $\pi$  donation (ref. 20). Such effects are doubtless incorporated to a significant degree in the experimental electronegativity parameters.

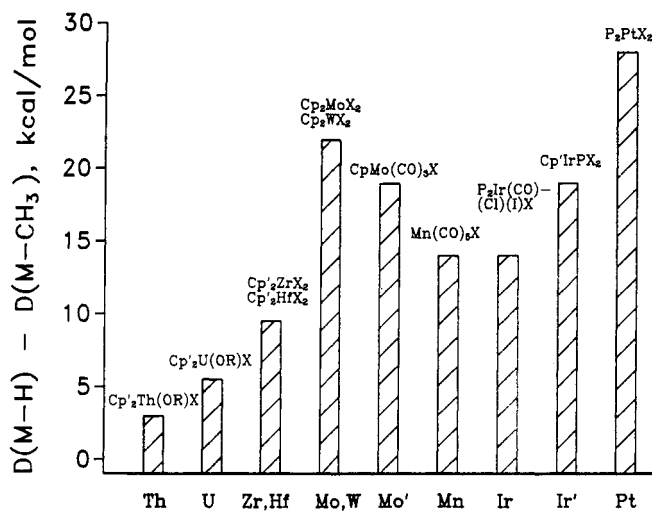


Fig. 1

Fig. 1. Comparison of  $D(M-H) - D(M-CH_3)$  for various transition metal complexes. Key:  $Cp_2Th(OR)X$  (refs.5,7);  $Cp_2U(OR)X$  (ref.7); average  $Cp_2MX_2$  (ref.8);  $Cp_2MX_2$  (ref.11);  $CpMo(CO)_3X$  (ref.12);  $Mn(CO)_5X$  (ref.13);  $Ir(PMe_3)_2(Cl)(I)(CO)X$  (ref.14);  $Cp'Ir(PMe_3)X_2$  (ref.15);  $Pt(PtEt_3)_2X_2$  (ref.16, adjusted assuming  $D(Pt-Me) - D(Pt-Et) \approx 5$  kcal/mol).

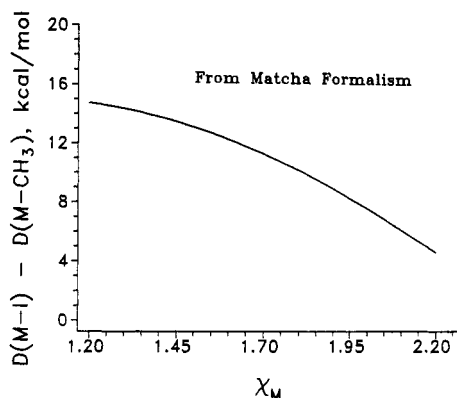


Fig. 3

Fig. 3. Correlation between  $D(M-I) - D(M-CH_3)$  calculated via eq.(13) (with the nonexponential term set equal to zero—see footnote 18) and metal Pauling electronegativity.

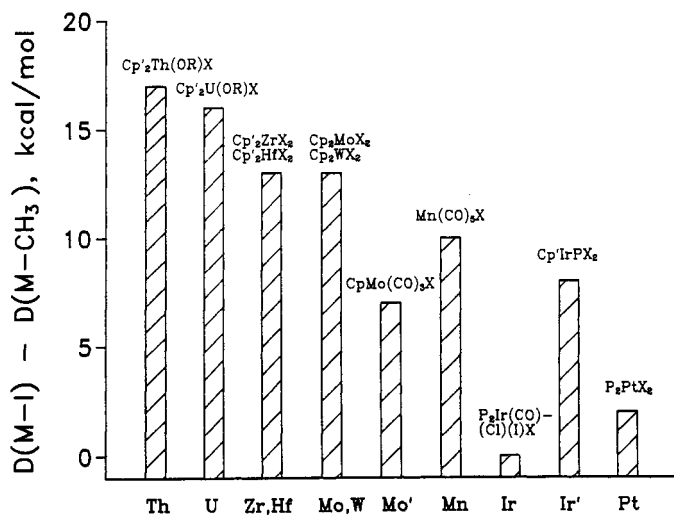


Fig. 2

Fig. 2. Comparison of  $D(M-I) - D(M-CH_3)$  for various transition metal complexes. Key:  $Cp_2ThX_2$  (ref.5) assuming  $D(Th-I) = \bar{D}(ThI_4)$ ;  $Cp_3UX$  (ref.9); average  $Cp_2MX_2$  (ref.8); average  $Cp_2MX_2$  (ref.11);  $CpMo(CO)_3X$  (ref.12);  $Mn(CO)_5X$  (ref.13);  $Ir(PMe_3)_2(Cl)(I)(CO)X$  (ref.14);  $Cp'Ir(PMe_3)X_2$  (ref.15);  $Pt(PPh_3)_2(I)X$  (ref.14).

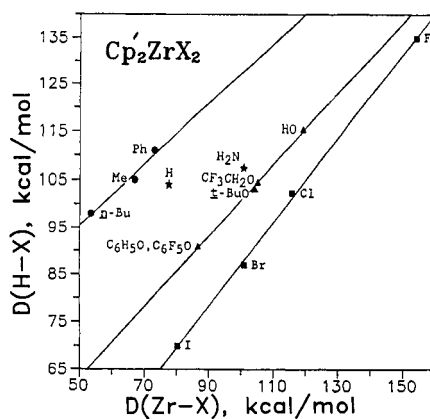
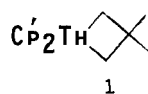


Fig. 4

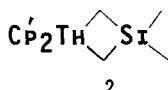
Fig. 4. Correlations between  $D(H-X)$  values and the corresponding average  $D(Zr-X)$  values for  $Cp_2ZrX_2$  complexes (ref. 8). Ligands of the same type are indicated by separate symbols, and the lines represent least-squares fits to these data points.

### SOME UNUSUAL BOND ENTHALPIES

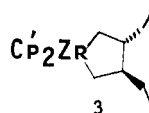
Thermochemical studies of actinide and group 4 complexes provide metal-ligand bond enthalpy parameters for a variety of unusual environments. Metallacycles are important intermediates in a number of catalytic processes, and there has been considerable discussion as to whether or not ring strain is an important factor in their chemistry. The strain enthalpy is defined as the diminution in the first  $D(M-R)$  *vis-à-vis* a sterically/electronically reasonable acyclic model. As can be seen from the strain enthalpies below, such effects are significant for thoracyclobutanes. The difference in strain enthalpy between 1 and the zirconacyclopentane 3 is approximately the same as that between cyclobutane and cyclopentane (ref. 23). Metal  $\eta^1:\eta^5$ - $CH_2C_5Me_4$  species are ubiquitous intermediates in  $d^0$  chemistry, and



~15 KCAL/MOL

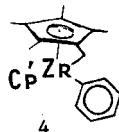


~ 8 KCAL/MOL

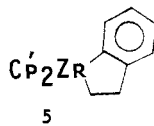


~ 0 KCAL/MOL

the present results for 4 evidence non-negligible strain. Interestingly, the strain enthalpy in the aryl-metallated species 5 is estimated to be negative in that the measured Zr- $CH_2CH_2$  bond enthalpy is greater than that predicted from the  $Cp_2Zr(\eta\text{-Bu})_2$  model. The reason likely resides in the tightly constrained chelation of the metallacyclic geometry and in reduced nonbonded repulsions.



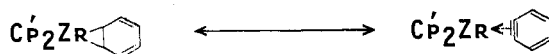
~ 5 KCAL/MOL



~-10 KCAL/MOL

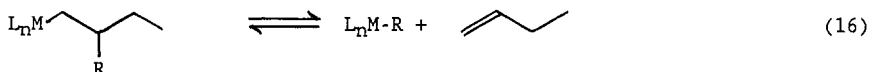
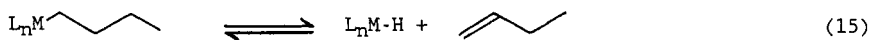
Metal carbonyls of early transition and f-elements are unusual species and little is known about the strength of M-CO bonding. For  $Cp_2Zr(CO)_2$ ,  $\bar{D}(Zr-CO)$  is found to be 39.7(9) kcal/mol, in the range of that for typical homoleptic middle transition metal carbonyls (ref. 3). This value also compares favorably with that recently reported for  $Cp_2Ti(CO)_2$ , 41.1(1.9) kcal/mol (ref. 24). In contrast,  $\bar{D}(U-CO)$  in  $(Me_3SiC_5H_4)_3UCO$  is found to be only 10.3(2) kcal/mol (ref. 9).

Benzynes/ $\sigma$ -phenylene species are widespread intermediates in early transition element and actinide chemistry. The intermediate below is formed by thermal elimination of benzene from  $Cp_2Zr(C_6H_5)_2$  (ref. 25). Knowing  $\bar{D}(Cp_2Zr(C_6H_5)-C_6H_5)$  as well as  $\Delta H^\ddagger$  for the elimination process allows a minimum value of ca. 120 kcal/mol to be assigned to  $\bar{D}(Cp_2Zr\text{-benzynes})$  (ref. 8).



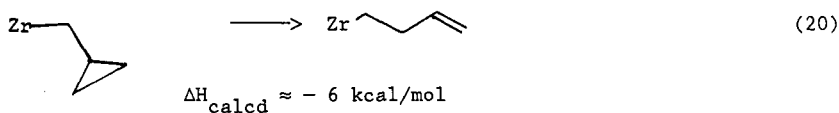
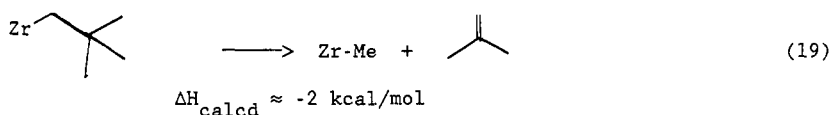
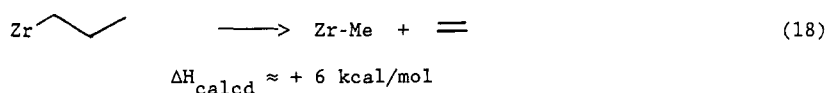
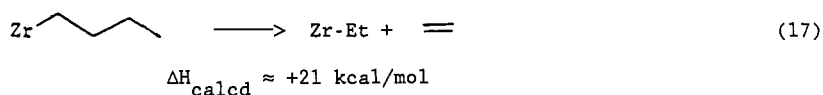
### ANALYZING KNOWN TRANSFORMATIONS

Thermochemical data also provide a unique perspective on fundamental organometallic reaction patterns such as  $\beta$ -hydride and  $\beta$ -alkyl elimination (e.g., eqs.(15),(16)). Extrapolating the trends of Figure 2 to eq.(15) predicts, in the absence of large, differential steric



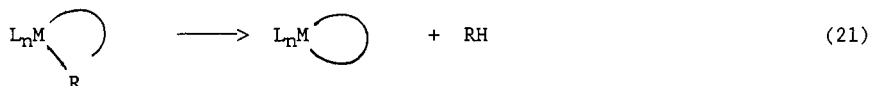
effects, that the tendency for  $\beta$ -hydride elimination should be least for actinides, lanthanides, and early transition elements. This observation offers a thermodynamic (but not kinetic) reason for the efficacy of these elements in olefin polymerization catalysis (refs. 5,7). Elimination processes involving  $\beta$ -alkyl substituents are less common (refs. 26-29), but an analysis based upon group 4 data

(ref. 9, eqs.(17)-(20)) indicates that they

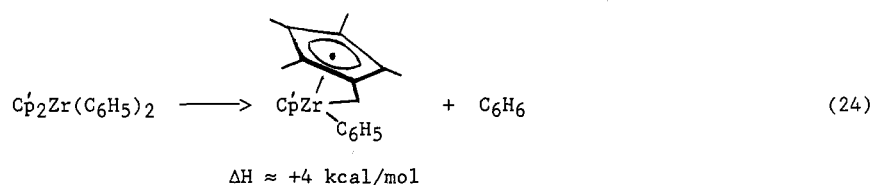
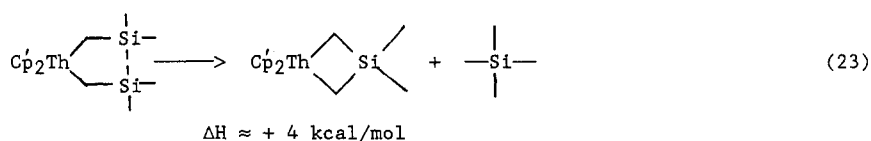
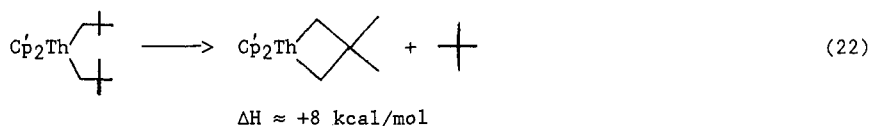


become more favorable if a stronger Zr-C bond is formed (eq.(18) vs.(17)), when weak Zr-C and C-C bonds are broken (eq.(19), refs. 26-28), or when a strained ring is opened (eq.(20), ref. 29). It is estimated that the  $-T\Delta S$  contribution to  $\Delta G$  in processes where one particle becomes two is on the order of ca. -6 - -12 kcal/mol for processes as in eqs.(17)-(19) (refs. 30,31).

Although cyclometalation processes (eq.(21)) are common in organometallic



chemistry, little is known about the driving force for such reactions (are they exothermic? if so, why?). Thermochemical data (refs. 5,8,30) for the processes in eqs.(22)-(24) indicate that all are slightly endothermic.



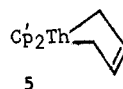
Enthalpically, it appears that severe steric crowding in the starting complexes (ref. 32) partly offsets the metallacyclic ring strain (refs. 5,8,30).

The functionalization of exogenous hydrocarbon molecules by driving eq.(21) significantly in the reverse direction (eq.(25)) involves a subtle interplay of the

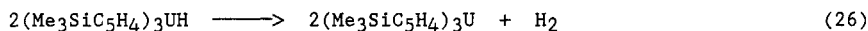


same types (*vide supra*) of reagent and product bond enthalpies. Thus, the relatively weak Th-C bonds of 1 and the strong C-H bonds which will be formed render 1 an effective C-H activation reagent for cases in which the new Th-C bond

is relatively strong (refs. 33,34). The stronger Th-C bonds of 2 decrease the exothermicity of such processes (ref. 30), while the weaker ("benzylic") Me<sub>4</sub>C<sub>5</sub>CH<sub>2</sub>-H bond which would be formed in "ring opening" reactions of 4 is likely to be an inhibiting factor in C-H activation. Although the Th-C bonds of butadiene complex 5 are also weak, the weakness the C-H bonds which would be formed upon ring opening again hinders hydrocarbon activation (ref. 35).

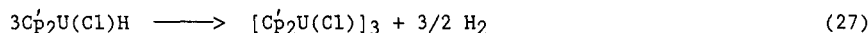


The properties of certain U(IV) hydrides are also explicable on the basis of metal-ligand bonding energetics. Thus, neither Cp<sub>3</sub>UH nor Cp<sub>2</sub>U(Cl)H (ref. 36) have been prepared despite numerous attempts. Thermochemical data (ref. 9) argue that H<sub>2</sub> elimination (eq.(26)) from Cp<sub>3</sub>UH should be sufficiently close to thermoneutrality



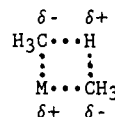
$$\Delta H_{\text{calcd}} \approx +5 \text{ kcal/mol H}_2$$

as to be entropically driven (as well as driven by typical preparative *in vacuo* isolation procedures). The apparent instability of Cp<sub>2</sub>U(Cl)H can be explained in a similar manner (ref. 36, eq.(27)).

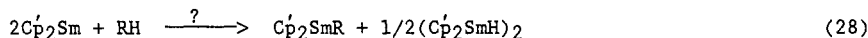


### ANALYSIS OF INTERESTING HYPOTHETICAL TRANSFORMATIONS

To date, solution phase thermal C-H functionalization processes at lanthanide and actinide centers have involved electrophilic, four-center pathways (e.g., transition state 6) (refs. 28,30,33), while oxidative addition/reductive elimination pathways have typified the corresponding chemistry at electron-rich transition metal centers (refs. 37,38). In principle, the unsaturated, highly reactive low-valent organolanthanide Cp<sub>2</sub>Sm (refs. 39,40) might be an ideal candidate for lanthanide-centered, dinuclear oxidative C-H activation processes (eq.(28)).



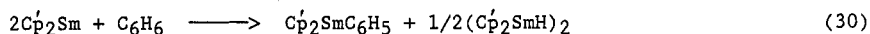
However, a consideration of the thermochemistry (ref. 10) indicates



that such processes will only be exothermic if the R-H bond is rather weak and/or the new Sm-R bond is rather strong, and/or the reaction is coupled to an exothermic follow-up process. Thus, H<sub>2</sub> activation is not predicted to easily overcome entropic constraints (eq.(29)), and benzene activation (eq.(30)) is predicted to be

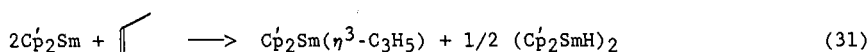


$$\Delta H_{\text{calcd}} \approx -5 \text{ kcal/mol H}_2$$

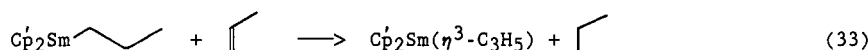
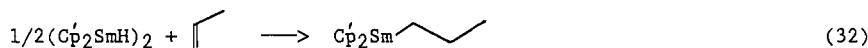


$$\Delta H_{\text{calcd}} \approx +10 \text{ kcal/mol C}_6\text{H}_6$$

endothermic. Both predictions are in accord with experimental observations (refs. 10,39,41,42). However, the allylic C-H bond of propylene and the relatively strong η<sup>3</sup>-allyl bonding of the product render propylene activation more promising (eq.(31)). Furthermore, the known (ref. 41) propylene hydrogenation sequence of eqs.(32),(33)



$$\Delta H_{\text{calcd}} \approx -12 \text{ kcal/mol CH}_2=\text{CH}-\text{CH}_3$$



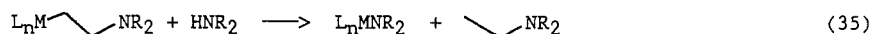
should substantially (by ca. -38 kcal/mol Sm) enhance the driving force.

Experimentally, the reaction of  $\text{Cp}_2\text{Sm}$  and propylene is found to be rapid with  $\text{Cp}_2\text{Sm}(\eta^3\text{-C}_3\text{H}_5)$  and propane as the only detectable products (ref. 10).

The existing thermochemical data also provide a means to test ideas about new types of  $d^0$ -centered insertion processes. The insertion of ethylene into a metal alkyl bond (the reverse of eq.(17)) is calculated to be equally exothermic for any metal center. However, lanthanide, actinide, and early transition metal centers are atypical in that such processes can also be kinetically very facile (e.g.,  $N_t$  for  $\text{Cp}_2\text{La}^-$  centers exceeds  $1500 \text{ s}^{-1}$  at 1 atm ethylene pressure,  $25^\circ\text{C}$ ). Given this kinetic leverage, it is intriguing to inquire about the thermodynamics of other insertion processes. The insertion of ethylene into a lanthanide amide bond is estimated to be approximately thermoneutral (eq.(34)). Coupling this to the known, rapid (ref. 43), protonolytic process of eq.(35) yields a plausible cycle



$$\Delta H_{\text{calcd}} \approx 0 \text{ kcal/mol}$$



$$\Delta H_{\text{calcd}} \approx -11 \text{ kcal/mol}$$

for catalytic hydroamination. To date, efficient transformations of this type have not been possible for nonfunctionalized amines (refs. 44-46).

Initial organolanthanide studies (refs. 47,48) have focused principally upon intramolecular olefin insertion processes (ref. 48). As shown in Figure 5 and in

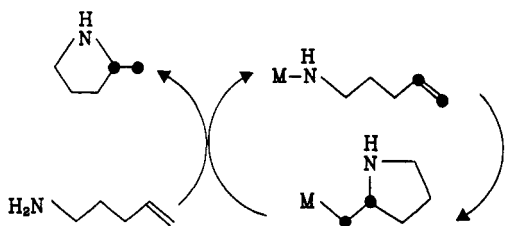


Fig. 5. Representative catalytic cycle for organolanthanide-catalyzed hydroamination of unsaturated amines.

Table I. Rate data for  $(\text{Cp}_2\text{LaH})_2$ -catalyzed hydroamination of several unsaturated amines.

Substrate	Product	$N_t$ ( $h^{-1}$ )
		70 ( $60^\circ\text{C}$ )
		5 ( $60^\circ\text{C}$ )
		120 ( $23^\circ\text{C}$ )

Table I, such catalytic processes are highly chemoselective and can be carried out with relatively good rates. As a function of metal and ancillary ligation, rates qualitatively parallel those for propylene oligomeration ( $\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)_2\text{Sm} > \text{Cp}_2\text{La} >> \text{Cp}_2\text{Lu}$ , refs. 41,49), arguing that olefin insertion is the turnover-limiting step.

## CONCLUSIONS

This short review has emphasized the importance of metal-ligand bond enthalpy data for better understanding metal-ligand bonding, for better understanding known reaction pathways, and for aiding in the design of new types of reactions. While the emphasis here has been on lanthanide, actinide, and early transition element chemistry, the broad generality of the approaches discussed should be evident.

**Acknowledgments** We thank the National Science Foundation for generous support under grants CHE8306255 and CHE8800813. L.E.S. and D.S. thank Dow Chemical Co. and Rhône-Poulenc, respectively, for fellowship support.

## REFERENCES

1. T.J. Marks, ed. Metal-Ligand Bonding Energetics in Organotransition Metal Compounds, Polyhedron symposium-in-print, in press.
2. G. Pilcher and H.A. Skinner in The Chemistry of the Metal-Carbon Bond, pp. 43-90, Wiley, New York (1982), F.R. Hartley and S. Patai, eds.
3. J.A. Connor, Top. Curr. Chem. **71**, 71-110 (1977).
4. J. Halpern, Acc. Chem. Res. **15**, 238-244 (1982).
5. J.W. Bruno, T.J. Marks, and L.R. Morss, J. Am. Chem. Soc. **105**, 6824-6832 (1983).

6. D.C. Sonnenberger, L.R. Morss, and T.J. Marks, Organometallics **4**, 352-355 (1985).
7. J.W. Bruno, H.A. Stecher, L.R. Morss, D.C. Sonnenberger, and T.J. Marks, J. Am. Chem. Soc. **108**, 7275-7280 (1986).
8. L.E. Schock and T.J. Marks, J. Am. Chem. Soc., in press.
9. L.E. Schock, A.M. Seyam, M. Sabat, and T.J. Marks, in ref. 1, in press.
10. S.P. Nolan, D. Stern, and T.J. Marks, submitted for publication.
11. A.R. Dias, M.S. Salema, and J.A. Simoes, J. Organometal. Chem. **222**, 69-78 (1981).
12. S.P. Nolan, R. Lopez de la Vega, S.L. Mukerjee, A.A. Gonzalez, K. Zhang, and C.D. Hoff, ref. 1. We thank these authors for permission to quote their data.
13. J.A. Connor, M.T. Zarafani-Moattar, J. Bickerton, M. L. El Saied, S. Suradi, E. Caron, G. Al-Takhin, and H.A. Skinner, Organometallics **1**, 1166-1174 (1982), and references therein.
14. J.U. Mondal and D.M. Blake, Coord. Chem. Rev. **47**, 205-238 (1982).
15. P.O. Stoutland, R.G. Bergman, S.P. Nolan, C.D. Hoff, ref. 1. We thank these authors for permission to quote their data.
16. R.L. Brainard and G.M. Whitesides, Organometallics **4**, 1550-1557 (1985).
17. R. L. Matcha, J. Am. Chem. Soc. **105**, 4859-4862 (1983). We employ the formulation using an arithmetic mean expression for D(A-B) since this leads more straightforwardly to useful relationships as eq.(12). Both arithmetic and geometric mean approaches have been employed in the Pauling formulation, with the latter preferred in cases of sign ambiguities.
18. Because  $D(I_2)-D(Me_2)$  is negative (a common artifact when the arithmetic mean is used in eq.(12)), we arbitrarily set it equal to zero in eq.(13). This in no way affects the  $\chi_M$  dependence of the function.
19. J. Mullay, Struct. Bond (Berlin) **66**, 1-25 (1987), and references therein.
20. H.E. Bryndza, L.K. Fong, R.A. Paciello, W. Tam, J.E. Bercaw, J. Am. Chem. Soc. **109**, 1444-1456 (1987).
21. T. Ziegler, V. Tschinke, A. Becke, J. Am. Chem. Soc. **107**, 1351-1358 (1987).
22. J.W. Bruno, M.R. Duttera, C.M. Fendrick, G.M. Smith, T.J. Marks, Inorg. Chim. Acta **94**, 271-277 (1984).
23. S.W. Benson, Thermochemical Kinetics, 2nd ed., pp. 60-63, 273, Wiley, New York (1976).
24. M.J. Calhorda, A.R. Dias, M.E. Minas da Piedade, M.S. Salema, and J.A. Martinho Simoes, Organometallics **6**, 734-738 (1987), and references therein.
25. L.E. Schock, C.P. Brock, and T.J. Marks, Organometallics **6**, 232-241 (1987).
26. K. Ziegler, K. Nagel, W. Pfohl, Ann. **629**, 210-221 (1960) (aluminum).
27. J.J. Eisch and W.C. Kaska, J. Am. Chem. Soc. **85**, 2165-2166 (1963) (aluminum).
28. P.J. Watson and G.W. Parshall, Acc. Chem. Res. **18**, 51-56 (1985) (lutetium).
29. G. Parkin, E. Bunel, B.J. Burger, M.S. Trimmer, Z. Van Asselt, and J.E. Bercaw, J. Mol. Cat. **41**, 21-39 (1987) (scandium).
30. G.M. Smith, J.D. Carpernter, and T.J. Marks, J. Am. Chem. Soc. **108**, 6805-6807 (1986).
31. M.I. Page in The Chemistry of Enzyme Action, M.I. Page, ed., pp 1-65, Elsevier, New York (1984).
32. J.W. Bruno, G.M. Smith, T.J. Marks, C.K. Fair, A.J. Schultz, and J.M. Williams, J. Am. Chem. Soc. **108**, 40-56 (1986).
33. C.M. Fendrick and T.J. Marks, J. Am. Chem. Soc. **108**, 425-437 (1986).
34. G.M. Smith, M. Sabat, and T.J. Marks, J. Am. Chem. Soc. **109**, 1854-1856 (1987).
35. G.M. Smith, H. Suzuki, D.C. Sonnenberger, V.C. Day, and T.J. Marks, Organometallics **5**, 549-561 (1986).
36. P.J. Fagan, J.M. Manriquez, T.J. Marks, C.S. Day, S.H. Vollmer, and V.W. Day, Organometallics **1**, 170-180 (1982).
37. R.H. Crabtree, Chem. Rev. **85**, 245-269 (1985).
38. J. Halpern, Inorg. Chim. Acta **100**, 41-48 (1985).
39. W.J. Evans, Polyhedron **6**, 803-835 (1987).
40. R.G. Finke, S.R. Keenan, D.A. Schiraldi, and P.L. Watson, Organometallics **6**, 1356-1358 (1987).
41. G. Jeske, H. Lauke, H. Mauermann, P.N. Sweptston, H. Schumann, and T.J. Marks, J. Am. Chem. Soc. **107**, 8091-8103 (1985).
42. G. Jeske, H. Lauke, H. Mauermann, H. Schumann, and T.J. Marks, J. Am. Chem. Soc. **107**, 8111-8118 (1985).
43. P.J. Fagan, J.M. Manriquez, S.H. Vollmer, C.S. Day, V.W. Day, and T.J. Marks, J. Am. Chem. Soc. **103**, 2206-2220 (1981).
44. Y. Tamaru, M. Hojo, H. Higashimura, and Z. Yoshida, J. Am. Chem. Soc. **110**, 3994-4002, (1988), and references therein.
45. G. Pez and J.E. Galle, Pure Appl. Chem. **57**, 1917-1926 (1985), and references therein.
46. B. Pugin and L.M. Venanzi, J. Organometal. Chem. **214**, 125-133 (1981), and references therein.
47. D. Hedden and T.J. Marks, unpublished results showing that  $Cp_2^*LaNMe_2$  catalyzes ethylene polymerization.
48. M.R. Gagne and T.J. Marks, submitted for publication.
49. G. Jeske, L.E. Schock, P.N. Sweptson, H. Schumann, and T.J. Marks, J. Am. Chem. Soc. **107**, 8103-8110 (1985).