Non-classical Organometallic Chemistry and Catalysis at Actinide Centers*

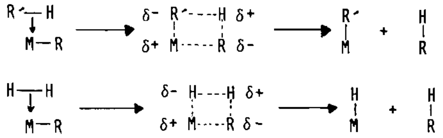
TOBIN J. MARKS

Department of Chemistry, Northwestern University, Evanston, Ill. 60201, U.S.A.

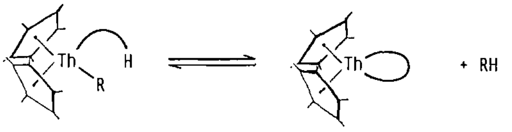
Abstract

In an appropriately tuned coordination environment, f-element ions can exhibit high coordinative unsaturation, kinetic lability and electrophilicity. In addition, oxidation state shuttling tendencies, π-bonding abilities, and metal–ligand bond enthalpy orderings differ markedly from those of most middle and late transition metals. One consequence of these non-classical features is a marked propensity for the activation of 2-center 2-electron fragments such as H–H and C–H functionalities. This lecture will focus primarily upon two closely related aspects of saturated hydrocarbon activation at actinide centers: (i) intramolecular cyclometalation chemistry involving C–H scission on saturated hydrocarbon ligands; (ii) activation of exogenous saturated and aromatic hydrocarbon molecules and organometallic molecules by an enthalpy-rich, entropy-poor actinacycle. Important ancillary information is provided by studies of H–H and olefin activation. Of central importance in all areas are those structural, electronic and bond enthalpy relationships that control reactivity and selectivity.

Processes by which C–H and H–H bonds are cleaved at metal centers are important in a wide range of catalytic processes. Pathways for such transformations at electron-deficient metals not readily capable of oxidative addition/reductive elimination sequences are not, in general, mechanistically well-understood. This lecture focuses on two aspects of this problem. In the first, the kinetic and thermodynamic aspects of thorium-centered cyclometalation processes involving saturated hydrocarbon ligands are discussed. In the second, a kinetic and mechanistic study of lanthanide-to-carbon and actinide-to-carbon sigma bond hydrogenolysis is presented. A major goal in both areas is to better understand the constraints under which ‘heterolytic’ ‘four-center’ C–H/H–H cleavage processes take place.



Bis(pentamethylcyclopentadienyl)thorium dialkyls undergo clean, highly regiospecific cyclometalation to yield the corresponding thoracyclobutanes [1].



The favored site of metalation is at a γ-CH_3 group with C–H scission as an important component of the rate-determining step, no evidence of homolytic free-radical processes, and relatively minor competing $(CH_3)_5C_5$ attack. Thermodynamically, the cyclometalation is endothermic (entropically driven) [2, 3], while kinetically the intramolecular C–H functionalization enjoys an entropic ($\Delta S^{\ddagger}$) advantage but an enthalpic ($\Delta H^{\ddagger}$) disadvantage relative to the intermolecular microscopic reverse [3]. This latter process also involves non-homolytic, rate-limiting C–H activation. As evidenced by a wide range in RH reactivities, such processes proceed with high selectivity [4]. Relative rates appear to reflect, among other factors, the susceptiblity of RH to electrophilic attack. Organometallic substrates can be employed in the ring-opening chemistry to prepare unusual heterobimetallic μ-methylene complexes [4, 5].

For a series of bis(pentamethylcyclopentadienyl)-lanthanide alkyls [6], hydrogenolysis is first-order in lanthanide complex and first-order in H_2. Rates are approximately inversely proportional to the lanthanide ionic radius, suggesting that the metal charge-to-radius ratio is a significant, electrophilicity-determining factor in the transition state. The rates

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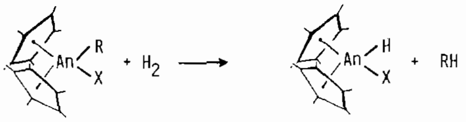
of hydrogenolysis are depressed by THF, suggesting inhibitory saturation of the Ln coordination sphere.

In a series of bis(pentamethylcyclopentadienyl)-thorium and uranium alkyls, hydrogenolysis is found to be first-order in metal complex and first-order in H_2 [7]. There is a significant kinetic isotope effect ($k_{H_2}/k_{D_2} = 2.5(4)$) and a slight rate increase with solvent polarity ($k_{THF}/k_{toluene} = 2.0(3)$). For a range of R and X, hydrogenolysis rates span a range of *ca.* 10^5. There is an approximate inverse correlation of $\Delta G^{\ddagger}$ for these reactions with the corresponding An–R bond disruption enthalpies (An = actinide). Ancillary ligands, X which can function as π-donors (e.g., alkoxides) effect a marked decrease in hydrogenolysis rates. As in the case of actinide-centered C–H functionalization processes, the hydrogenolysis reactions exhibit large, negative entropies of activation. A rough correlation also exists between $\Delta G^{\ddagger}$ values for An–R hydrogenolysis and for migratory CO insertion into the same bond.



References

1 J. W. Bruno, G. M. Smith, T. J. Marks, C. K. Fair, A. J. Schutz and J. M. Williams, *J. Am. Chem. Soc., 108,* 40 (1986).

2 J. W. Bruno, T. J. Marks and L. R. Morss, *J. Am. Chem. So., 105,* 6824 (1983).

3 G. M. Smith, J. D. Carpenter and T. J. Marks, *J. Am. Chem. Soc., 108,* 6805 (1986)..

4 C. M. Fendrick and T. J. Marks, *J. Am. Chem. Soc., 108,* 425 (1986).

5 (a) G. M. Smith, M. Sabat and T. J. Marks, *J. Am. Chem. Soc., 109,* 1854 (1987); (b) G. M. Smith and T. J. Marks, manuscript in preparation.

6 G. Jeske, H. Lauke, H. Mauermann, H. Schumann and T. J. Marks, *J. Am. Chem. Soc., 107,* 8111 (1985).

7 Z. Lin and T. J. Marks, *J. Am. Chem. Soc.,* in press.