previous notion about the key interactions responsible for the formation of specific mitomycin C-DNA monoadducts.[3b] These results may provide a molecular basis for future drug design. Currently studies are in progress to determine the specific site of drug modification and the consensus bonding sequences for **1b-f** and to model the binding process for select mitomycins to aid in identifying the specific interactions responsible for the sequence selectivity.

Acknowledgment. We thank Dr. M. Nazimiec and Ms. A. Pao for UVR protein purification and Dr. A. Sancar (University of North Carolina) for providing *E. coli* strains containing UVR gene plasmids. We also thank Drs. A. M. Casazza and W. Rose and the Bristol-Myers Squibb Co. for a gift of **1a**. This work was supported by NIH Grants RO1CA29756 (H.K.) and ES03124 (M.-s.T.), the Robert A. Welch Foundation (E607, H.K.), and the American Cancer Society (CH-485, M.-s.T.).

Supplementary Material Available: Copies of ^1H and ^{13}C NMR and mass spectra for **1c**, autoradiograms of UVRABC nuclease cutting of the **1b-d**-modified 3'-end-labeled 129 base pair fragment from pBR322 plasmid (Figure S1), and full histograms depicting the relative intensities of UVRABC nuclease incision sites for **1a-f**-DNA adducts in the 3'-end-labeled 129 base pair fragment from pBR322 plasmid (Figure S2) (7 pages). Ordering information is given on any current masthead page.

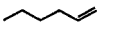
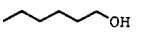
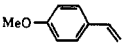
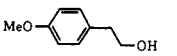
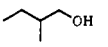
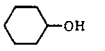
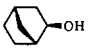
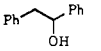
Organolanthanide-Catalyzed Hydroboration of Olefins

Karl N. Harrison and Tobin J. Marks*

Department of Chemistry
Northwestern University
Evanston, Illinois 60208-3113
Received July 21, 1992

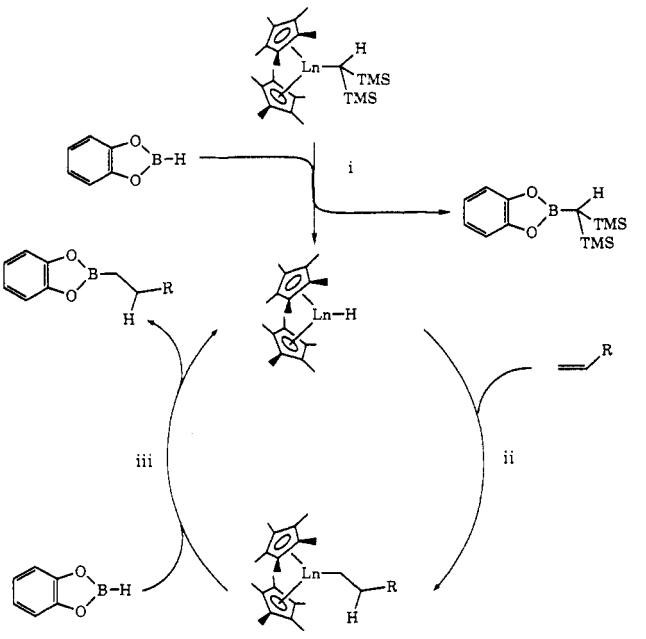
The great utility of hydroboration in organic synthesis[1] has recently been enhanced by transition-metal-catalyzed processes which afford increased rates and substantially modified regio- and enantioselectivities.[2,3] Mechanistic results have identified the central role of oxidative addition/reductive elimination sequences at the electron-rich group 9 metal centers in mediating R_2B-H/olefin addition.[2,3] Distinctive reactivity patterns at organolanthanide centers include facile olefin insertion, σ-bond metathesis, and hydrocarbyl protonolysis. Combinations of these transformations have recently been shown to effect the efficient and selective catalysis of a variety of olefin transformations including hydrogenation,[4] oligomerization/polymerization/cyclization,[5] hydroamination,[6] hydrosilylation,[7] and hydrophosphination,[8] via unconventional electrophilic pathways (not involving change in metal formal oxidation state). We now report that organolanthanides are effective homogeneous catalysts for olefin hydroboration and disclose initial observations on scope, selectivity, and mechanism.

Table I. Organolanthanide-Catalyzed Olefin Hydroboration with Catecholborane[a]

Entry	Substrate	Product	Isolated Yield [%]
1			78
2			89
3			71
4			95
5			71
6			61
7			79
8			73

[a] Procedures given in ref 12.

Scheme I. Proposed Mechanism of Homogeneous Organolanthanide-Catalyzed Olefin Hydroboration



(1) Pelter, A.; Smith, K.; Brown, H. C. *Borane Reagents*; Academic Press: New York, 1988.

(2) (a) Burgess, K.; Ohlmeyer, M. J. *Chem. Rev.* **1991**, *91*, 1179-1191 and references therein. (b) Zhang, J.; Luo, B.; Guo, G.; Dai, L. *J. Org. Chem.* **1991**, *56*, 1670-1672. (c) Hayashi, T.; Matsumoto, Y.; Ito, T. *J. Am. Chem. Soc.* **1989**, *111*, 3426-3428. (d) Burgess, K.; Ohlmeyer, M. J. *J. Org. Chem.* **1988**, *53*, 5179-5181. (e) Mannig, D.; Nöth, H. *Angew. Chem., Int. Ed. Engl.* **1985**, *25*, 878-879. (f) Hewes, J. D.; Kreimendahl, C. W.; Marder, T. B.; Hawthorne, M. F. *J. Am. Chem. Soc.*, **1984**, *106*, 5757-5759.

(3) (a) Evans, D. A.; Fu, G. C.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1992**, *114*, 6671-6679. (b) Evans, D. A.; Fu, G. C.; Anderson, B. A. *J. Am. Chem. Soc.* **1992**, *114*, 6679-6685. (c) Westcott, S. A.; Taylor, N. J.; Marder, T. B.; Baker, R. T.; Jones, N. J.; Calabrese, J. C. *J. Chem. Soc., Chem. Commun.* **1991**, 304-305. (d) Knorr, J. R.; Merola, J. S. *Organometallics* **1990**, *9*, 3008-3010. (e) Baker, R. T.; Overnall, D. W.; Calabrese, J. C.; Wescott, S. A.; Taylor, N. J.; Williams, I. D.; Marder, T. B. *J. Am. Chem. Soc.* **1990**, *112*, 9399-9400.

(4) (a) Conticello, V. P.; Brard, L.; Giardello, M. A.; Tsujii, Y.; Sabat, M.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 2761-2762. (b) Molander, G. A.; Hobert, J. O. *J. Org. Chem.* **1992**, *57*, 3326-3268. (c) Jeske, G.; Lauke, H.; Mauermann, H.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8111-8118. (d) Mauermann, H.; Sweptson, P. N.; Marks, T. J. *Organometallics* **1985**, *4*, 200-202.

(5) (a) Molander, G. A.; Hoberg, J. O. *J. Am. Chem. Soc.* **1992**, *114*, 3123-3125. (b) Jeske, G.; Lauke, H.; Mauermann, H.; Sweptson, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8091-8103. (c) Jeske, G.; Schock, L. E.; Sweptson, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8103-8110. (d) Watson, P. L.; Parshall, G. W. *Acc. Chem. Res.* **1985**, *18*, 51-55.

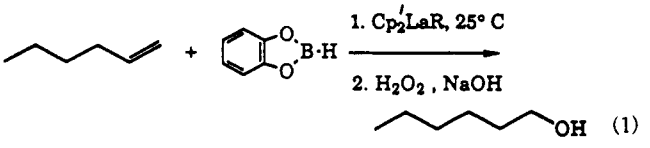
(6) (a) Gagné, M. R.; Brard, L.; Conticello, V. P.; Giardello, M. A.; Stern, C. L.; Marks, T. J. *Organometallics* **1992**, *11*, 2003-2005. (b) Gagné, M. R.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 275-294. (c) Gagné, M. R.; Nolan, S. P.; Marks, T. J. *Organometallics* **1990**, *9*, 1716-1718. (d) Gagné, M. R.; Marks, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 4108-4109.

(7) (a) Nolan, S. P.; Porchia, M.; Marks, T. J. *Organometallics* **1991**, *10*, 1450-1457. (b) Sakakura, T.; Lautenschlager, H.-J.; Tanaka, M. *J. Chem. Soc., Chem. Commun.* **1991**, 40-41. (c) Brard, L.; Forsyth, C. M.; Nolan, S. P.; Marks, T. J. Manuscript in preparation.

(8) Giardello, M. A.; King, W. A.; Nolan, S. P.; Porchia, M.; Sishta, C.; Marks, T. J. In *Energetics of Organometallic Species*; Martinho Simoes, J. A., Ed.; Kuwer: Dordrecht, 1992; pp 35-51.

0002-7863/92/1514-9220$03.00/0

As monitored by NMR, Cp'_2LnR ($Cp' = \eta^5$ - Me_5C_5; Ln = La, Sm; R = H, $CH(SiMe_3)_2$),[4b] $Me_2SiCp''_2LnR$ ($Cp'' = \eta^5$-Me_4C_5; Ln = Sm; R = $CH(SiMe_3)_2$),[5b] and $Cp'_2Sm(THF)$[9] complexes catalyze the room temperature hydroboration of a variety of dry, degassed olefins (25-100-fold stoichiometric excess) with catecholborane at efficient rates (e.g., Cp'_2LaR: $N_t \approx 200$ h^{-1} for 1-hexene, eq 1; ≈ 50 h^{-1} for cyclohexene; ≈ 10 h^{-1} for 1-methcyclohexene).[10,11] As deduced from these and preparative scale experiments (Table I)[12] the reaction encompasses a significant range of olefinic substrates, including terminal (entries 1 and 2), terminal or internal disubstituted (entry 3 and entries

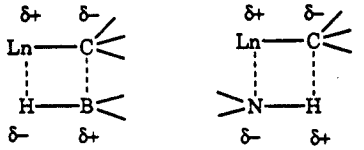


(1)

4-6, respectively), and trisubstituted (entry 7 and 8). No reaction is observed for tetrasubstituted 2,3-dimethyl-2-butene at 25 °C. All of these organolanthanide-catalyzed transformations exhibit high regioselectivity (>98% by NMR) with negligible concomitant substrate hydrogenation. Labeling studies with catecholborane-d_1 show that entries 1, 2, 4, and 5 proceed with exclusive (by NMR) delivery of the deuteron to the C2 position (β to B). Both substrate hydrogenation and D label scrambling (presumably via reversible olefin insertion-extrusion) are undesirable accompanying features of many Rh(I)-catalyzed hydroborations.[2,3b,c] The present regiochemistries are exclusively anti-Markovnikov, which for entry 2 contrasts the general pattern observed for the Rh(I)-catalyzed hydroboration of styrenes.[2b-d,3a]

Regarding mechanistic details, the substrate dependence of rates (for constant Ln complex) follows the ordering terminal ≥ terminal disubstituted > internal disubstituted > trisubstituted, likely reflecting steric demands at the metal center. In accord with this and paralleling a number of other organolanthanide-catalyzed transformations,[4,5b,c,6] both larger metal ions ($N_t(La) \approx 10\ N_t(Sm)$) and more open ancillary ligation ($N_t(Me_2SiCp''_2Ln) \approx 4\ N_t$-$(Cp'_2Ln)$) increase the rate of hydroboration. In common with other organolanthanide-mediated processes, R = H and = $CH(SiMe_3)_2$-based catalysts exhibit indistinguishable turnover frequencies. For the latter substituent, NMR reveals that catalytic turnover is preceded by elimination of (catechol)$BCH(SiMe_3)_2$.[13] This result contrasts other organolanthanide-catalyzed catalytic processes (e.g., hydroamination[6]) in which the Ln-C moieties instead undergo facile protonolysis (e.g., eliminating $CH_2(SiMe_3)_2$). That conveniently prepared $Cp'_2Sm(THF)$ is an efficient precatalyst argues that binuclear substrate C-H activation,[14] to yield Sm(III) hydrocarbyls and hydrides, provides access to the catalytic manifold, as found previously for organosamarium-catalyzed hydroamination.[6c]

The present results can be accommodated by tentative Scheme I, in which Ln-H[15] → Ln-alkyl and B-H + Ln-alkyl → B-alkyl + Ln-H are key transformations. The former (ii) is typically rapid, exothermic,[4,5b,c,8,14] and well-documented in other organolanthanide catalytic sequences. Its importance moreover suggests that hydroboration may be subject to the stereocontrol, functional group tolerance, and follow-up chemistry operative in other Ln-C bond-forming reactions.[4-6] Transpositions (i) and (iii)[16] are estimated[17] to be slightly exothermic (~ -3 kcal/mol) and can be understood vis-à-vis contrasting hydroamination chemistry[6] on the basis of bond polarity arguments (**A** vs **B**).



A B

In summary, these results show that facile catalytic olefin hydroboration can be mediated by organolanthanides and via rather unconventional pathways. Further investigation of this and related catalytic reactions is continuing.

Acknowledgment. We thank N.S.F. (Grant CHE9104112) for generous support of this research. K.N.H. thanks NATO/SERC for a postdoctoral fellowship.

(9) Evans, W. J.; Ulibarri, T. A. *Inorg. Synth.* **1990**, *28*, 297-300.

(10) Uncatalyzed hydroborations using catecholborane typically require temperatures in excess of 100 °C: Brown, H. C.; Gupta, S. K. *J. Am. Chem. Soc.* **1975**, *97*, 5249-5253.

(11) Typical NMR-scale reaction: Under inert atmosphere, a 5-mm NMR tube with a J. Young valve was charged with 0.60 mmol of olefin, 1.2 mmol of catecholborane, 0.30 mL of C_6D_6, and 10 μmol of catalyst. Progress of the hydroboration was monitored via the olefinic ^1H resonances. The alkylborane ester product was identified by ^1H, $^{13}C\{^1H\}$, and $^{11}B\{^1H\}$ spectra.

(12) Typical preparative-scale reaction: Under inert atmosphere, 6.0 mmol of olefin, 20 mmol of catecholborane, and 0.1 mmoL $Cp'_2Sm(THF)$ were stirred in 1.0 mL of benzene at 20 °C. Upon addition of the catecholborane, the reaction solution gradually changed from the characteristic purple of the Sm(II) complex to dark orange-red. Oxidative workup after 14 h with $NaOH/H_2O_2$,[1] followed by diethyl ether extraction, drying, and concentration afforded the product alcohol.

(13) Identified by ^1H, $^{13}C\{^1H\}$, $^{11}B\{^1H\}$ NMR, and mass spectroscopy.

(14) (a) Stern, D.; Sabat, M.; Marks, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 9558-9575. (b) Nolan, S. P.; Marks, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 7844-7853.

(15) (a) We cannot exclude the possibility that the Lewis acidic hydride is present as a hydroborate complex[15b] (e.g., $Cp'_2Ln(\mu\text{-}H)_2B(catechol)$). Efforts to isolate such a complex have so far been unsuccessful. In the absence of olefin, the organolanthanides form complex mixtures of insoluble products (consistent with known catecholborane-metal hydride chemistry).[15c,d] (b) Marks, T. J.; Kolb, J. R. *Chem. Rev.* **1977**, *77*, 263-293. (c) Manning, D.; Nöth, H. *J. Organomet. Chem.* **1984**, *275*, 169-171. (d) Manning, D.; Nöth, H. *J. Chem. Soc., Dalton Trans.* **1985**, 1689-1692.

(16) Analogous transpositions: (a) Rh-Me + thexylborane → Rh-H + thexylmethylborane: Baker, R. T.; Ovenall, D. W.; Harlow, R. L.; Westcott, S. A.; Taylor, N. J.; Marder, T. B. *Organometallics* **1990**, *9*, 3028-3030. (b) Zr-C(H)=C(H)R + *B*-chlorocatecholborane → Zr-Cl + alkenylcatecholborane: Cole, T. E.; Quintanilla, R.; Rodewald, S. *Organometallics* **1991**, *10*, 3777-3781.

(17) Data from ref 14b and (a) Pilcher, G.; Skinner, H. A. In *The Chemistry of the Metal-Carbon Bond*; Hartley, F. R., Patai, S., Eds.; Wiley: New York, 1982; pp 42-90. (b) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon: Oxford, 1984; p 185.

Organo-f-Element Bonding Energetics. Large Magnitudes of Metal-Arene Bond Enthalpies in Zero-Valent Lanthanide Sandwich Complexes

Wayne A. King and Tobin J. Marks*

Department of Chemistry, Northwestern University Evanston, Illinois 60208-3113

David M. Anderson, David J. Duncalf, and F. Geoffrey N. Cloke

School of Chemistry and Molecular Sciences University of Sussex, Brighton BN1 9QJ, U.K.

Received June 29, 1992
Revised Manuscript Received August 25, 1992

The traditional description of metal-ligand bonding in organolanthanides[1] has been one of largely electrostatic interactions necessarily involving metals in relatively high formal oxidation states coordinated to anionic hydrocarbyl/polyene ligands.[1,2]

(1) (a) Schumann, H. In *Fundamental and Technological Aspects of Organo-f-Element Chemistry*; Marks, T. J., Fragalà, I., Eds.; D. Reidel: Dordrecht, Holland, 1985; Chapter 1. (b) Evans, W. J. *Adv. Organomet. Chem.* **1985**, *24*, 131-177. (c) Kagan, H. B.; Namy, J. L. In *Handbook on the Physics and Chemistry of Rare Earths*; Gschneider, K. A., Eyring, L., Eds.; Elsevier: Amsterdam, 1984; Chapter 50. (d) Forsberg, J. H.; Moeller, T. In *Gmelin Handbook of Inorganic Chemistry, Sc, Y, La-Lu Rare Earth Elements, Part D6*; Moeller, T., Krüerke, U., Schleitzer-Rust, E., Eds.; Springer-Verlag: Berlin, 1983; pp 137-303. (e) Marks, T. J.; Ernst, R. D. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Chapter 21.

0002-7863/92/1514-9221$03.00/0