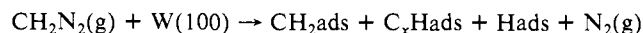


Through correlation with hydrogen desorption measurements and comparison with IR spectra of organometallic complexes, this species is usually attributed to surface methylidyne or to an acetylide species in the case where a $\nu(\text{CC})$ mode at approximately 1300 cm^{-1} is detected. For the system Ru(001), for example, CH is characterized by a stretching mode at $3010\text{--}3030\text{ cm}^{-1}$ and a bending mode at $800\text{--}840\text{ cm}^{-1}$.^{1a} The corresponding modes for $(\text{CO})_4\text{Co}_3\text{--}(\mu_3\text{-CH})^{20}$ appear at 3041 and 850 cm^{-1} , respectively. The $\nu(\text{CC})$ mode for acetylide on Ru(001) appears at 1290 cm^{-1} .^{1a} On the basis of the above fingerprinting considerations we assign the observed losses at 780 , 1230 , and 3050 cm^{-1} to a mixture of adsorbed CH and C_2H . Adsorbed acetylide is a common decomposition product of C_2 molecules, such as ethylene or acetylene, on metal surfaces. However, if acetylide is indeed present on the W(100) surface, following CH_2N_2 adsorption, then it most likely results from the coupling of C_1 species. Another possible route to CCH is the interaction of an adsorbed C_1 unit with a molecule of CH_2N_2 . The remaining two losses at 2950 and 1440 cm^{-1} are typical for a CH_2 species. The $\delta(\text{CH}_2)$ and the $\nu_s(\text{CH}_2)$ modes for CH_2 on Fe(110) appear at 1420 and 2970 cm^{-1} , respectively.⁸ The corresponding modes for $\text{Fe}_2(\text{CO})_6(\mu\text{-CO}_2)(\mu\text{-CH}_2)$ appear at 1379 and 2910 cm^{-1} , respectively.²¹ The interpretation of the interaction of diazirine with W(100) at 100 K , as given above, leads to the following simple decomposition scheme:



We anticipate that on less reactive metals than tungsten we may be able to use diazirine to vary the surface concentration of selected C_1 units. With this in mind, we are in the process of studying the interaction of diazirine- d_2 and diazirine with the Pd(110) surface as a function of temperature.

Acknowledgment. We gratefully acknowledge support from NSERC and the Fonds FCAR and (P.Mc B.) a University Research Grant from Imperial Oil Ltd.

(20) Howard, M. W.; Kettle, S. F.; Oxtun, I. A.; Powell, D. B.; Sheppard, N.; Skinner, P. J. *Chem. Soc., Faraday Trans. 2* **1981**, *77*, 397.

(21) Chan, S. C.; Kafafi, Z. H.; Huage, R. H.; Whitmire, K. H.; Billups, W. E.; Margrave, J. L. *Inorg. Chem.* **1986**, *25*, 4530.

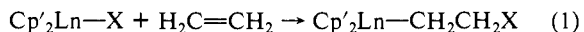
Organolanthanide-Catalyzed Hydroamination. Facile, Regiospecific Cyclization of Unprotected Amino Olefins

Michel R. Gagné and Tobin J. Marks*

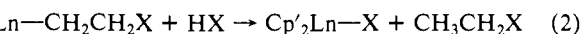
Department of Chemistry, Northwestern University
Evanston, Illinois 60208

Received December 22, 1988

The remarkable facility with which early lanthanide-alkyl bonds undergo olefin insertion within bis(pentamethylcyclopentadienyl)metal coordination spheres¹ (e.g., eq 1; N_1 (1 atm ethylene; $25\text{ }^\circ\text{C}$) $\geq 1800\text{ s}^{-1}$ when X = primary alkyl or hydride and Ln = La^{1a}) suggests that, in this environment, thermody-



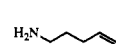
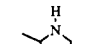

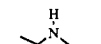
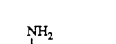
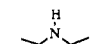
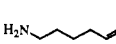
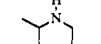
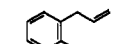
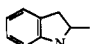
namically feasible but normally unobserved insertion processes involving other metal-X bonds may also be rapid. Coupling to proton-transfer processes (e.g., eq 2) would then constitute a



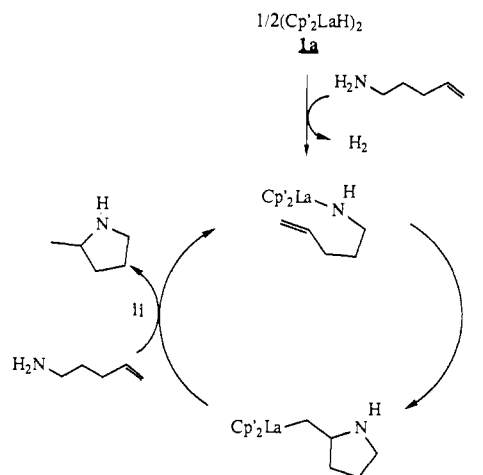
catalytic cycle for HX addition to olefins. For lanthanide amides

(1) (a) Mauermann, H.; Marks, T. J. *Organometallics* **1985**, *4*, 200-202. (b) Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8091-8103. (c) Jeske, G.; Schock, L. E.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8103-8110. (d) Jeske, G.; Lauke, H.; Mauermann, H.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8111-8118. (e) Watson, P. L.; Parshall, G. W. *Acc. Chem. Res.* **1985**, *18*, 51-55.

Table I

entry	substrate (ref)	product (ref)	N_1 (h^{-1} , $^\circ\text{C}$)	catalyst
1	 2 ⁹	 2 ⁹	13 (25) 140 (60)	1a 1a
2	 3 ^{6a}	 3 ⁹	125 (25) 75 (80) <1 (80)	1a 1b 1c
3	 4 ⁹	 4 ^{9,13}	84 (25)	1a
4	 5 ⁹	 5 ^{9,13}	5 (60)	1a
5	 6 ¹⁴	 6 ¹³	13 (80)	1a

Scheme I



(X = NR_2), we estimate eq 1 to be approximately thermoneutral,^{2,3} while eq 2 should be both rapid^{4a} and exothermic.^{2a-d,4b,c} As the first embodiment of such a strategy, we report here the facile and regiospecific organolanthanide-catalyzed hydroamination/cyclization of N-unprotected amino olefins,⁵ heretofore difficult homogeneous transformations proceeding (e.g., with Pd^{2+} catalysts) via distinctly different mechanistic pathways.⁶⁻⁸

(2) $\Delta H_{\text{calcd}} \approx -5$ to 0 kcal/mol using existing Th,^{2a} Zr,^{2b} and Sm^{2c,d} data. (a) Bruno, J. W.; Marks, T. J.; Morss, L. R. *J. Am. Chem. Soc.* **1983**, *105*, 6824-6832. (b) Schock, L. E.; Marks, T. J. *J. Am. Chem. Soc.* **1988**, *110*, 7701-7715. (c) Nolan, S. P.; Stern, D.; Marks, T. J. *Abstracts of Papers*, 196th National Meeting of the American Chemical Society, Los Angeles, CA: American Chemical Society: Washington, DC, Sept 25-30, 1988; INOR 378. (d) Nolan, S. P.; Stern, D.; Marks, T. J. *J. Am. Chem. Soc.*, in press.

(3) $\text{Cp}'_2\text{LaNMe}_2$ catalyzes ethylene polymerization (Hedden, D.; Marks, T. J., unpublished results).

(4) (a) Fagan, P. J.; Manriquez, J. M.; Vollmer, C. H.; Day, C. S.; Day, V. W.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 2206-2220. (b) For the addition of NH_3 to $\text{H}_2\text{C}=\text{CH}_2$, $\Delta G^\circ \approx -4\text{ kcal/mol}$.^{4c} (c) Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*, 2nd ed.; Chapman and Hall: London, 1986; Appendix Table 1.2.

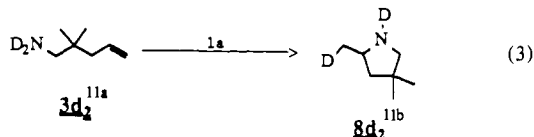
(5) Communicated in part at the Sixth International Symposium on Homogeneous Catalysis, Vancouver, British Columbia, Canada, August 21-26 1988.

(6) (a) Tamaru, Y.; Hojo, M.; Higashima, H.; Yoshida, Z. *J. Am. Chem. Soc.* **1988**, *110*, 3994-4002, and references therein. These authors summarize the strengths and weaknesses of platinum metal-catalyzed transformations. (b) Collman, J. P.; Hegedus, L. G.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987, Chapters 7.4, 17.1. (c) Hegedus, L. S.; Akermark, B.; Zetterburg, K.; Olsson, L. F. *J. Am. Chem. Soc.* **1984**, *106*, 7122-7126. (d) Hegedus, L. S.; McKearin, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 2444-2451. (e) Pugin, B.; Venanzi, L. M. *J. Organometal. Chem.* **1981**, *214*, 125-133, and references therein. (f) Hegedus, L. S.; Allen, G. F.; Bozell, J. J.; Waterman, E. L. *J. Am. Chem. Soc.* **1978**, *100*, 5800-5807.

(7) (a) Casalnuovo, A. L.; Calabrese, J. C.; Milstein, D. *J. Am. Chem. Soc.* **1988**, *110*, 6738-6744. (b) Cowan, R. L.; Troglor, W. *Organometallics* **1987**, *6*, 2451-2453. (c) Pez, G.; Galle, J. E. *Pure Appl. Chem.* **1985**, *57*, 1917-1926. (d) Gasc, M. B.; Lattes, A.; Perie, J. J. *Tetrahedron* **1983**, *39*, 703-731.

The anaerobic^{1a,b} catalytic reaction of $(\text{Cp}'_2\text{LaH})_2$ (**1a**)^{1b} with a variety of dry, degassed amino olefins (typically in 100–20-fold stoichiometric excess) proceeds to completion in hydrocarbon solvents (toluene, cyclohexane, pentane) as shown in Table I. Reactions are conveniently monitored by NMR spectroscopy, and products are identified by comparison with literature spectral data⁹ and/or with those of authentic samples. Several features of this hydroamination reaction are especially noteworthy. These include the formation of a six-membered heterocycle (**5** \rightarrow **10**), the cyclization of internal amines (**4** \rightarrow **9**, **6** \rightarrow **11**), and the rapidity of the *gem*-dimethyl transformation (**3** \rightarrow **8**). The latter observation strongly suggests that ring formation is turnover-limiting.¹⁰ The present reactions are found to be $\geq 99\%$ regioselective by NMR spectroscopy, with the exception of **6** \rightarrow **11**, where ca. 10% of the product is another species, the identity of which is currently under investigation.

Preliminary mechanistic observations, in addition to the aforementioned *gem*-dimethyl effect, are in accord with the scenario of Scheme I where olefin insertion/cyclization (i, eq 1) is, under all conditions so far investigated, turnover-limiting. Kinetically, we find the hydroaminations in Table I entries 1, 2, and 4 to be first-order in organolanthanide and zero-order in amino olefin within experimental error. That is, the turnover frequency (equiv of olefin transformed/equiv of Ln/time) is independent of olefin concentration over the entire course of the reaction and independent of organolanthanide concentration over a 5-fold range. These observations argue that protonolysis (ii, eq 2) is the rapid step (as expected^{4a}). Also in accord with this picture is the relative ordering of catalyst activities for **3** \rightarrow **8**: $(\text{Cp}'_2\text{LaH})_2$ (**1a**) > $[\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)_2\text{LuH}]_2$ (**1b**) > $(\text{Cp}'_2\text{LuH})_2$ (**1c**) (Table I)—identical with the previously reported ordering for catalytic propylene oligomerization activity.^{1b,c} The outcome of the isotopic labeling experiment **3-d**₂^{11a} \rightarrow **8-d**₂^{11b} (eq 3) further supports the



proposed mechanism, revealing the atom transposition pattern expected for Scheme I. The observation that hydroamination/cyclization rates are depressed when THF is the solvent¹² also supports a turnover-limiting k_i process. Such effects are common in $\text{Cp}'_2\text{Ln}$ -centered olefin transformations¹ and reflect Lewis base competition for the empty coordination site within the $\text{Cp}'_2\text{LnX}$ coordination sphere, which is a prerequisite for the insertion process.

These results demonstrate that organolanthanide centers can facilitate unusual types of olefin insertion processes and that such transformations can be readily incorporated into efficient and novel catalytic cycles. The scope of such chemistry is presently under investigation.

Acknowledgment. We are grateful to NSF for support of this research under Grant CHE8800813. M.R.G. thanks Rhône-Poulenc Corp. for a graduate fellowship. We thank W. R. Grace for gifts of dessicants.

(8) Solid acids are reported to catalyze the heterogeneous amination of several simple olefins at high temperatures and pressures: (a) Deeba, M.; Ford, M. E. *J. Org. Chem.* **1988**, *53*, 4594–4596. (b) Deeba, M.; Ford, M. E.; Johnson, T. A. *J. Chem. Soc., Chem. Commun.* **1987**, 562–563.

(9) (a) Ambuehl, J.; Pregosin, P. S.; Venanzi, L. M.; Consiglio, C.; Bachech, B.; Zambonelli, L. *J. Organomet. Chem.* **1979**, *181*, 255–269. (b) Ambuehl, J.; Pregosin, P. S.; Vananzi, L. M.; Ughetto, G.; Zambonelli, L. *J. Organomet. Chem.* **1978**, *160*, 329–335.

(10) Kirby, A. J. *Adv. Phys. Org. Chem.* **1980**, *17*, 183–278.

(11) (a) Prepared by exchange of **3** with D_2O . (b) Identified by IR, ¹H, and ¹³C NMR spectroscopy.

(12) For example, $N_t = 17 \text{ h}^{-1}$ for **3** \rightarrow **8** in THF- d_6 at 25 °C using **1a** as the catalyst.

(13) (a) Confirmed with spectroscopic data from an authentic sample. (b) In entry 3, compound **9**^{13c} is obtained as a 5:1 trans:cis mixture (8:1 at 0 °C). (c) Harding, K. E.; Burks, S. R. *J. Org. Chem.* **1981**, *46*, 3920–3922.

(14) Prepared by the $\text{BF}_3\text{Et}_2\text{O}$ -catalyzed rearrangement of *N*-allylaniline (We thank Prof. A. G. M. Barrett for suggesting this procedure).

Interactions between Eight Centers Are Required for Chiral Recognition

Sid Topiol* and Michael Sabio

Department of Medicinal Chemistry
Berlex Laboratories, Inc.
110 East Hanover Avenue
Cedar Knolls, New Jersey 07927

Received August 8, 1988

A recent analysis of the interactions of chiral molecules¹ concluded that six-center forces ("chirality forces"¹) suffice for chiral recognition. We demonstrate² that chiral recognition requires at least eight centers.

Salem et al. analyzed the interaction energies of homochiral (*RR'*) and heterochiral (*RS'*) complexes (between tetrahedra having different centers on their vertices) as a sum of *n*-center terms ($n = 2$ –8) between these centers; for example, four-center forces involve a pair of points on each monomer. The analysis is performed "in the limit of free relative molecular rotation (high-temperature limit, interactions small relative to kT)".¹ They claim, after rotational sampling of all possible interactions, "six-center forces, occurring simultaneously between triplets of atoms, one triplet on each molecule, are responsible for the discrimination".¹ They state "this is the first phenomenon where six-center forces are found to play an important role",¹ and "chiral discrimination depends on six-center forces alone and is purely a 'face-to-face' phenomenon for the two tetrahedra".¹

By simply considering that the terms in their analysis correspond to interactions of points, lines, planes, and solids, it follows that, just as with four-centers, six-center interactions must cancel as well. Only eight-center (or higher-order) terms represent interactions between solids and do not cancel. As chirality requires three dimensions, "chirality forces" cannot be represented by the interactions of zero-, one-, or two-dimensional objects.

Figure 1 illustrates such common six-center interactions by conversion of an *RR'* complex (top row) to an *RS'* complex by the interchange of *C'* and *D'* of *R'* to give *S'* (center) followed by a 180° rotation of *S'* about the line connecting *A'* with the midpoint of *C'D'* (i.e., "flip" the *A'C'D'* face; bottom), causing the three centers *A'C'D'* of *S'* and *R'* to coincide. Thus, the corresponding six-center forces will be equal. This was not evident in Salem's analysis where interaction energies of the *RR'* and *RS'* complexes were compared only for rotations which used the same distance (*OO'*) between central atoms (see Tables I and II of ref 1).³ There, the orientation of *S'* in the lower portion of Figure 1 corresponds to a different distance between the central atoms. In the high-temperature limit considered by Salem et al., both translations and rotations must be considered.⁴ Also, for any arbitrary structure, an analogous analysis can be made with every pair of triplets of centers on *R* and *R'* or *S'*. Because a term-(six-center on *RR'*)-by-term (six-center of *RS'*) equivalence can be generated for any arbitrary structure, it follows immediately that sampling all configurations will result in a complete cancellation of terms.

While Salem et al. suggest that the six-center forces model bears "some analogy with the three-center attachment theory of Ogston"^{1,5} (or, more generally, the three-contact-point⁶ model), the Ogston or three-contact-point model is based on eight-center interactions. Consider the example in Figure 2. While the six-center interactions of *ABC* with *A'B'C'* are identical for the *RS'*

(1) Salem, L.; Chapuisat, X.; Segal, G.; Hiberty, P. C.; Minot, C.; Leforestier, C.; Sautet, P. *J. Am. Chem. Soc.* **1987**, *109*, 2887.

(2) A quantitative demonstration is available as Supplementary Material.

(3) Thus, within the framework of fixed relative origins, six-center forces are discriminatory but, as real molecules do not have fixed origins, eight-center forces are responsible for chiral recognition.

(4) Alternatively, using arguments analogous to those of Salem et al., one could limit the angular sampling space (due to some physically justified constraints) and conclude that two- or four-center forces lead to chiral discrimination.

(5) Ogston, A. G. *Nature* **1948**, *162*, 963.

(6) Topiol, S. *Chirality* **1989**, *1*, 69.