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# Highly Reactive Organolanthanides. A Mechanistic Study of Catalytic Olefin Hydrogenation by Bis(pentamethylcyclopentadienyl) and Related 4f Complexes†

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**Abstract:** The organolanthanides $(Cp'_2MH)_2$, $Cp' = \eta^5\text{-}(CH_3)_5C_5$, M = La, Nd, Sm, and Lu, and $(Me_2SiCp''_2MH)_2$, $Cp'' = \eta^5\text{-}(CH_3)_4C_5$, M = Nd, Sm, and Lu are highly active catalysts for olefin hydrogenation. In the case of 1-hexene → *n*-hexane, activities decrease in the order $Cp'_2Lu > Cp'_2Sm > Cp'_2Nd > Me_2SiCp''_2Lu > Cp'_2La > Me_2SiCp''_2Sm > Me_2SiCp''_2Nd$, with $N_t$ for the most active catalyst exceeding 120 000 $h^{-1}$ at 25 °C and 1 atm of $H_2$. Under the conditions employed, the rate law is $\nu \propto [\text{olefin}]^0[\text{Lanthanide}][H_2]$ suggesting rapid, exothermic Lanthanide–H/olefin addition and rate-limiting M–C hydrogenolysis. When $D_2$ uptake is not mass-transport-limited, the predominant product is hexane-*1,2*-$d_2$. For all catalysts except $(Cp'_2LuH)_2$, cyclohexene hydrogenation (to yield predominantly cyclohexane-*1,2*-$d_2$ under $D_2$ in a non-mass-transport-limited regime) obeys the rate law $\nu \propto [\text{olefin}][\text{Lanthanide}]^{1/2}[H_2]^0$, suggesting rate-limiting Lanthanide–H/olefin addition. For $Cp'_2Lu$, the rate law is $\nu \propto [\text{olefin}][\text{lanthanide}][H_2]^0$, suggesting rate-limiting $(Lu\text{–}H)_2$/olefin addition or that the hydride dimer is largely dissociated under these conditions. The relative activities are less than for 1-hexene and follow the order $(Me_2SiCp''_2NdH)_2 > (Me_2SiCp''_2SmH)_2 > (Cp'_2LaH)_2 \geq (Cp'_2NdH)_2 > (Me_2SiCp''_2LuH)_2 \geq (Cp'_2SmH)_2$. Addition of THF significantly decreases the rate both of 1-hexene hydrogenation and (more so) cyclohexene hydrogenation. For all catalysts examined, 3-hexyne hydrogenation follows a two-stage rate law $\nu \propto [\text{alkyne}]^0[\text{Lanthanide}][H_2]$ (3-hexyne → *cis*-3-hexene) and $\nu \propto [\text{olefin}][\text{Lanthanide}]^{1/2}[H_2]^0$ (*cis*-3-hexane → *n*-hexane) except for $(Cp'_2LuH)_2$ where $\nu \propto [\text{olefin}][\text{Lanthanide}][H_2]^0$. The rate laws and relative activity trends for *trans*-2-hexene and *trans*-3-hexene hydrogenation parallel those for 1-hexene, while *cis*-2-hexene behaves like *cis*-3-hexene. While the present olefin and acetylene hydrogenation catalysis can be understood largely on the basis of established or reasonably extrapolated organo-f-element reactivity and bond enthalpy patterns, the steps in the catalytic cycles must proceed with remarkably low activation energies and must be coupled with high efficiency.

In the two preceding papers in this issue,[2,3] we describe general syntheses, chemical, and structural properties of broad classes of lanthanide $Cp'_2MCH(TMS)_2$, $(Cp'_2MH)_2$, $Me_2SiCp''_2MCH(TMS)_2$, and $(Me_2SiCp''_2MH)_2$ complexes ($Cp' = \eta^5\text{-}(CH_3)_5C_5$, $Cp'' = (CH_3)_4C_5$, TMS = $Si(CH_3)_3$). The hydrides, prepared by hydrogenolysis of the alkyls, were found to be highly reactive. For example, the lighter members of the series were found to be some of the most active "homogeneous" ethylene polymerization catalysts known. Survey experiments also indicated surprisingly high activity for olefin hydrogenation, which is the topic of the present contribution.

Mechanistically, homogeneous olefin hydrogenation catalysts[4] with early transition-metal,[5] lanthanide,[6] and actinide[7] catalysts is not well understood and offers a much different mechanistic situation than conventional group 8 or late transition-element catalysts.[4,8] In particular, the metal center may be in a relatively high (≥3) formal oxidation state, may not possess energetically accessible formal oxidation states for oxidative addition/reductive elimination processes, may be engaged in relatively polar metal–ligand bonding with a strong preference for "hard" ligands (not olefins), and may exhibit unusual M–H/M–C bond disruption enthalpy relationships vis-à-vis middle and late transition elements. Lanthanide ions represent the extreme cases of many of the above considerations and as such offer an opportunity to better understand hydrogenation catalysis in such environments. We present here a full account of our kinetic and mechanistic studies using bis(pentamethylcyclopentadienyl) and related organolanthanides as homogeneous olefin hydrogenation catalysts.[9] The investigation has been carried out as a function of lanthanide (La, Nd, Sm, and Lu), lanthanide supporting ligation ($Cp'_2M$ vs. $Me_2SiCp''_2M$), solvent, and olefin. It will be seen that the component transformations of the catalytic cycles can be largely understood on the basis of established f-element reactivity and thermodynamic relationships. What is surprising, however, is how efficiently the sequences of transformations can be coupled when in the proper coordination environment.

## Experimental Section

All operations were carried out under rigorously anhydrous and anaerobic conditions employing the procedures, methods, and precautions

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† In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

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(2) Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P. J.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.*, paper 1 of a series of three in this issue.

(3) Jeske, G.: Schock, L. E.; Swepston, P. J.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.*, preceding paper in this issue.

(4) (a) James, B. R. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Chapter 51. (b) Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, 1980; Chapter 6. (c) Parshall, G. W. "Homogeneous Catalysis"; Wiley-Interscience: New York, 1980; Chapter 3. (d) Crabtree, R. *Acc. Chem. Res.* **1979**, *12*, 331–338 and references therein. (e) James, B. R. "Homogeneous Hydrogenation"; Wiley: New York, 1973.

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(7) Fagan, P. J.; Manriquez, J. M.; Maatta, E. A.; Seyam, A. M.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 6650–6667.

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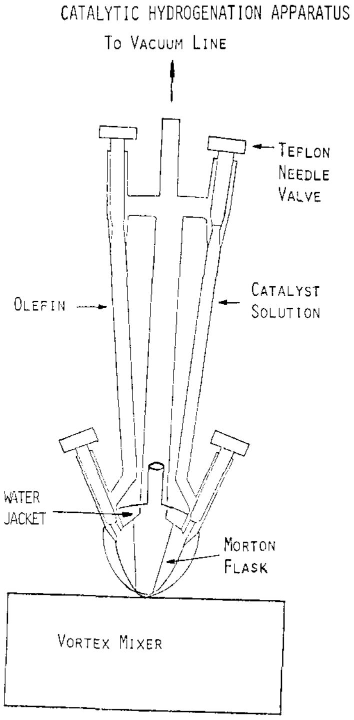

**Figure 1.** Reactor for catalytic hydrogenation experiments. A third buret is not shown.

described previously.[2,3] Solvents were purified and distilled as indicated[2,3] and were stored (with stirring) over Na/K. They were vacuum-transferred from Na/K immediately prior to use. The olefins 1-hexene (Aldrich Gold Label), cyclohexene (Aldrich Gold Label), *trans*-2-hexene (Aldrich Gold Label), *trans*-3-hexene (Aldrich), and *cis*-2-hexene (Fluka) were dried by stirring over Na/K for at least 6 h and were freshly vacuum-transferred. The acetylene, 3-hexyne (Albany International Chemicals), was dried by repeated vacuum transfer onto freshly activated Davison 4A molecular sieves followed by vacuum transferring onto Na/K stirring for ca. 1 h. Purity of the final fraction was verified by GC. Hydrogen (Matheson), argon (Matheson), and deuterium (Matheson) were purified by passing sequentially through regularly activated MnO[10a-c] and Davison 4A molecular sieve columns. Organolanthanide complexes were prepared as described previously.[2,3] Identical results were obtained if the various hydrides were employed from isolated batches or were generated from the alkyls in situ by hydrogenolysis. Instrumentation and analytical procedures were as described previously.[2,3] Positional analyses of D labels in hydrocarbons employed standard high-field $^{13}C$ NMR methods ($^{13}C$, $^{13}C\{^1H\}$, and $\Delta C(D)$).[2,10d-f]

**Catalytic Experiments.** Kinetic studies were carried out in an all glass, metal, and Teflon grease-free constant-volume, pseudo-constant-pressure gas-uptake apparatus. The glass reaction vessel (ca. 20 mL in volume, Figure 1) was fitted with Morton-type indentations and a high-speed vortex agitator (American Scientific MT-51 vortex mixer) to ensure efficient mixing, a water jacket connected to a recirculating pump and a Haake constant-temperature bath (25.0 ± 0.1 °C) for thermal regulation, calibrated burets for admitting reagents, and a large diameter flexible stainless steel connection to a high-vacuum line with an efficient diffusion pump. The gas handling system was of the Hussey-Burwell type[11a-c] with gas ballasts (all thermostated at 25.0 ± 0.1 °C except for a large, 21.0-L steel gas cylinder ballast employed for very rapid reactions[12]) and a Datametrics 1023 Barocel Differential Electronic Manometer to measure small pressure changes. In addition to the standard gas purification columns, $H_2$ (or $D_2$) was passed through an additional $MnO/SiO_2$[10a-c] column immediately prior to entering the gas handling manifold. Data (pressure in the system vs. an adjustable reference pressure as a function of time) were outputed to a Linear Systems strip chart recorder. Data analysis and plotting were carried out with a Hewlett-Packard HP-1000 F series minicomputer and interfaced graphics system.

In a typical experiment, the oven-dried reaction vessel was attached to the vacuum line while still hot, pumped down for at least 1 h, closed under vacuum, and taken into a Vacuum Atmospheres glovebox with a high-capacity recirculating system. The burets were then filled with catalyst solution (freshly prepared on the vacuum line using calibrated volumetric vessels) and olefin. The reaction vessel was then filled with a measured quantity of freshly distilled solvent (cyclohexane, toluene, or THF), closed, and transferred outside to the vacuum line. The reaction volume was evacuated and the solvent freeze–thaw-degassed, back-filling repeatedly with $H_2$. Next, the thermostated water circulating system was connected and actuated. After all parts of the system had appropriate time to reach thermal equilibrium and equilibrium with the reactor atmosphere, measured volumes of catalyst solution and olefin were added to the reaction vessel. High-speed vortex mixing was then initiated and the $H_2$ pressure recorded as a function of time. Appropriate corrections in data analysis were made for solvent and reactant/product vapor pressures. In general, conditions were adjusted such that all of the olefin was consumed in 0.13–10 min and the overall pressure drop in the system was always less than 2% (usually less than 1%). A number of control experiments were conducted to determine experimental boundary conditions beyond which the rate of $H_2$ uptake became mass-transport-limited;[11d,e] i.e., the regime in which the measured rate of gas uptake was limited by the rate at which hydrogen could be delivered (diffuse) to all parts of the reaction solution rather than by the actual rate of the chemical reaction being studied. Under such conditions, the concentration of $H_2$ in the liquid phase is no longer that corresponding to equilibrium with gas-phase $H_2$. This situation was evident when, for constant $P_{H_2}$, constant mixing rate, and constant concentrations of olefin and catalyst, plots of turnover frequency ($N_t$) vs. increasing overall quantity of reaction solution began to deviate from linearity (i.e., $N_t$ was no longer constant) or when, at very high rates of gas uptake, the measured reaction rate began to deviate (in a negative direction) from a well-behaved rate law for further increases in rate. Such effects were, of course, most evident at low mixing speeds, and conditions for optimum mixing (to ensure the maximum reaction solution surface area, the reaction solution should appear as a dense aerosol) as well as optimum reaction solution volume were carefully established. In all experiments employed for kinetic analyses, experimental $N_t$ values were at least 25% below the point where it was determined that mass-transport effects became significant. Reproducibility in $N_t$ values for the same reaction at the same $H_2$ pressure using different batches of olefin and catalyst solution was within 5–10%.

## Results

The goal of this investigation was to obtain mechanistic information on olefin hydrogenation catalysis by $Cp'_2$- and $Me_2SiCp''_2$-substituted lanthanide hydrides. Studies of the magnitudes and molecularities of reaction kinetics, selectivity

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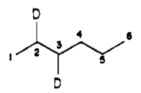
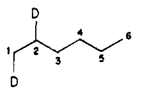
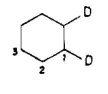
(10) (a) Moeseler, R.; Horvath, B.; Lindenau, D.; Horvath, E. G.; Krauss, H. L. *Z. Naturforsch., B* **1976**, *31B*, 892–893. (b) McIlwrick, C. R.; Phillips, C. S. G. *J. Chem. Phys. E* **1973**, *6*, 1208–1210. (c) He, M.-Y.; Xiong, G.; Toscano, P. J.; Burwell, R. L., Jr.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 641–652. (d) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. "Spectrometric Identification of Organic Compounds", 4th ed.; Wiley: New York, 1981; pp 259–261. (e) Hansen, P. E. *Annu. Rep. NMR Spectrosc.* **1983**, *15*, 108–160. (f) Levy, G. C.; Lichter, R. L.; Nelson, G. L "Carbon-13 Nuclear Magnetic Resonance Spectroscopy", 2nd ed.; Wiley: New York, 1980; pp 50–53. (g)



$\delta$ 14.10 (C1), 22.78 (C2, $J_{C-D} = 18.9$ Hz) 31.78 (C3, $J_{C-D} = 19.0$ Hz), 32.30 (C4), 23.26 (C5), 14.24 (C6). (h)



$\delta$ 13.86 (C1, $J_{C-D} = 19.30$ Hz), 22.82 ($J_{C-D} = 19.1$ Hz), 32.22 (C3), 32.33 (C4), 23.31 (C5), 14.28 (C6). (i)

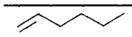
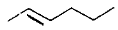
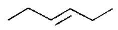
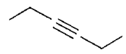
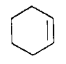


$\delta$ 26.77 (C1, $J_{C-D} = 19.2$ Hz), 27.12 (C2), 27.28 (C3).

(11) (a) Kung, H. H.; Pellet, R. J.; Burwell, R. L., Jr. *J. Am. Chem. Soc.* **1976**, *98*, 5603–5611. (b) Kung, H. H. Ph.D. Thesis, Northwestern University, 1974. (c) Hussey, A. S.; Keulks, G. W.; Nowack, G. P.; Baker, R. H. *J. Org. Chem.* **1968**, *33*, 610–616. (d) Yao, H.-C.; Emmett, P. H. *J. Am. Chem. Soc.* **1959**, *81*, 4125–4132. (e) Nagy, F.; Pethö, A'.; Möger, D. *J. Catal.* **1966**, *5*, 348–353.

(12) In this case, fluctuations in the room temperature were negligible over such a short time period. A control experiment using the same substrate with both vessels verified this.

**Table I.** Rate Constant Data for Catalytic Hydrogenation

| substrate | $(Cp'_2LaH)_2$ | $(Cp'_2NdH)_2$ | $(Cp'_2SmH)_2$ | $(Cp'_2LuH)_2$ | $(Me_2SiCp''_2NdH)_2$ | $(Me_2SiCp''_2SmH)_2$ | $(Me_2SiCp''_2LuH)_2$ |
|---|---|---|---|---|---|---|---|
|  | 6.2 (3)[a] | 21.6 (2.0)[a] | 23.8 (8)[a] | 34.5 (3.0)[a] | 0.8 (1)[a] | 3.1 (3)[a] | 11.8 (5)[a] |
|  | 1.7 (2)[a] | 7.1 (7)[a] | 7.9 (7)[a] | 9.0 (8)[a] | | | |
|  | 7.3[d] | 33.4[d,e] | 51[d,e] | 240 (160)[e,f] | | | |
|  | 0.20 (5)[a] | 0.46 (4)[a] | 0.82 (7)[a] | 2.3 (2)[a] | 0.11[a] | | |
|  | | 6.6 (8)[c] | | 13.4 (1.0)[b] | | | |
|  | | 2.2 (3)[c] | 3.8 (6)[c] | 8.1 (5)[b] | | | |
|  | 0.015 (2)[c] | 0.014 (2)[c] | 0.005 (2)[c] | 0.023 (2)[b] | 0.060 (4)[c] | 0.025 (3)[c] | 0.007 (1)[c] |

[a] Rate law $\nu = k[M][H_2]$, in units of $atm^{-1} s^{-1}$. Multiply by 224.0 to convert to $M^{-1} s^{-1}$. [b] Rate law $\nu = k[M][olefin]$, in units of $M^{-1} s^{-1}$. [c] Rate law $\nu = k[M]^{1/2}[olefin]$, in units of $M^{-1/2} s^{-1}$. [d] Rate law approximately $\nu = k[M][H_2]$, in units of $atm^{-1} s^{-1}$. [e] Accuracy limited by the rapidity of the process. [f] Rate law approximately $\nu = k[M][olefin]$, in units of $M^{-1} s^{-1}$.

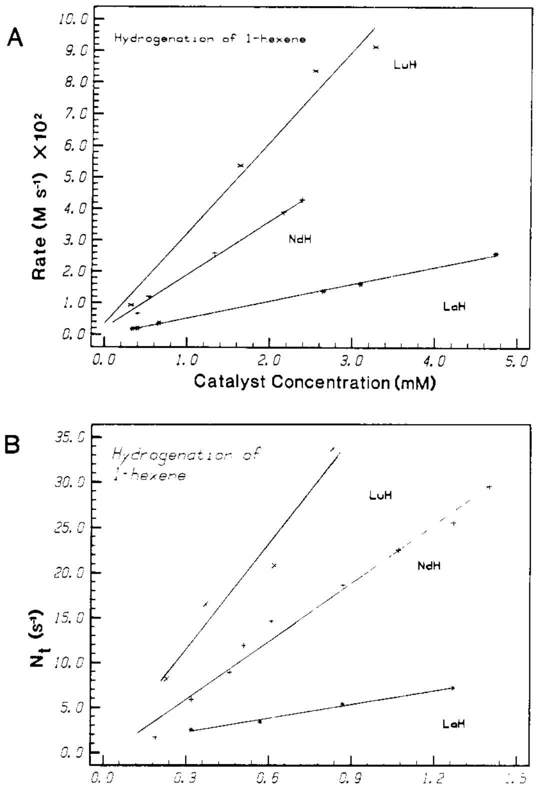


**Figure 2.** Hydrogenation of 1-hexene catalyzed by $(Cp'_2MH)_2$ complexes. (A) Hydrogenation rate as a function of catalyst concentration ($P_{H_2}$ = 0.87 atm). (B) Turnover frequency as a function of hydrogen pressure.

vis-â-vis various substrates, the disposition of deuterium labels, the effects of a coordinating solvent, and stoichiometric model reactions were carried out. Considerable attention was devoted to the scrupulous maintenance of anaerobic conditions and to the avoidance of mass-transport effects. In the ensuing discussion, it is implicitly assumed that the catalysts are homogeneous in nature. Indeed, it will be seen that all the mechanistic data and stoichiometric model reactions are readily interpreted in terms of the chemistry of soluble $(Cp'_2MH)_n$, $Cp'_2MR$, $(Me_2SiCp''_2MH)_n$, and $Me_2SiCp''_2MR$ species. Furthermore, neither the activities nor selectivities we observe are consistent with reported properties of lanthanide atom or binary lanthanide hydride-derived, or oxide-derived, presumably heterogeneous, catalysts.[13-15]

**Hydrogenation of 1-Hexene.** The hydrogenation of 1-hexene by the members of either organolanthanide series was found to be extremely rapid. In both series, the relative ordering of activities was found to be approximately inversely proportional to metal ionic radius: Lu > Sm > Nd > La. For constant M, the $Cp'_2M$ derivatives are more active than the corresponding $Me_2SiCp''_2$ complexes. To view the present activities in perspective, it is instructive to compare $N_t$ for $(Cp'_2LuH)_2$-catalyzed hydrogenation at 25 °C, 1 atm of $H_2$ pressure, $N_t$ = 120 000 $h^{-1}$, to reported values of $N_t$ = 650 $h^{-1}$ for $Rh(PPh_3)_3Cl$,[16a] 3000 $h^{-1}$ for $Ru(H)(Cl)(PPh_3)_3$,[16a] 4000 $h^{-1}$ for $Ru(COD)(PPh_3)_2PF_6$,[16a] and 6400 $h^{-1}$ for $Ir(COD)P(c\text{-hex})_3(py)^+PF_6^-$[16b] under essentially the same conditions.

Under the conditions of the present studies, 1-hexene hydrogenation in cyclohexane or toluene solutions was found to be zero-order in olefin (over ≥99% of the reaction), first-order in catalyst, and first-order in hydrogen pressure. The ranges of concentrations/pressures employed are given in the representative kinetic plots of Figure 2. These observations and those with other unsaturated substrates (vide infra) are most simply accomodated by the sequence shown in eq 1–3. Under the conditions in which

$$(LMH)_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2LMH \qquad K_1 \tag{1}$$

$$LMH + olefin \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \underset{\mathbf{A}}{LMR} \qquad K_2 \tag{2}$$

$$LMR + H_2 \xrightarrow[\text{slow}]{k_3} LMH + alkane \tag{3}$$

$$L = Cp'_2,\ Me_2SiCp''_2 \qquad M = \text{lanthanide}$$

olefin concentration is high and $k_2$ and $K_2$ are very large, virtually all the lanthanide will be present as hydrocarbyl **A** and the rate law reduces to eq 4.[17,18] Here metal–carbon bond hydrogenolysis

$$\nu_{1\text{-hexene}} = k_3[\text{Lanthanide}][H_2] \tag{4}$$

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(13) (a) Imamura, H.; Ohmura, A.; Tamura, T.; Tsuchiya, S. *J. Less-Common Met.* **1983**, *94*, 107–109. (b) Evans, W. J.; Bloom, I.; Engerer, S. C. *J. Catal.* **1983**, *84*, 468–476.

(14) (a) Konenko, I. R.; Gorshkova, L. S.; Klabunovskii, E. I.; Moreva, N. I. *Kinet. Katal.* **1977**, *18*, 1066–1069 and references therein. (b) Under the conditions of the present reactions, the lanthanide metals are not expected to be thermodynamically stable with respect to hydride formation. For example, $\Delta H_f°$ and $\Delta G_f°$ values for early lanthanide $MH_2$ compounds are on the order of −50 and −40 kcal/mol, respectively.[14c] (c) Moeller, T. H. In "Comprehensive Inorganic Chemistry"; Bailar, J. C., Emelêus, H. J., Nyholm, R., Trotman-Dickenson, A. F., Eds.; Pergamon Press: Oxford, 1973; Vol. 4, pp 83–84.

(15) (a) Minachev, Kh. M.; Khodakov, Yu. S.; Nakhshunov, V. S. *J. Catal.* **1977**, *49*, 207–215. (b) Khodakov, Yu. S.; Makarov, P. A.; Delzer, G.; Minachev, Kh. M. *J. Catal.* **1980**, *61*, 184–191.

(16) (a) Crabtree, R. *Acc. Chem. Res.* **1979**, *12*, 331–338 and references therein. (b) Data for the Ir complex were only reported at 0 °C.

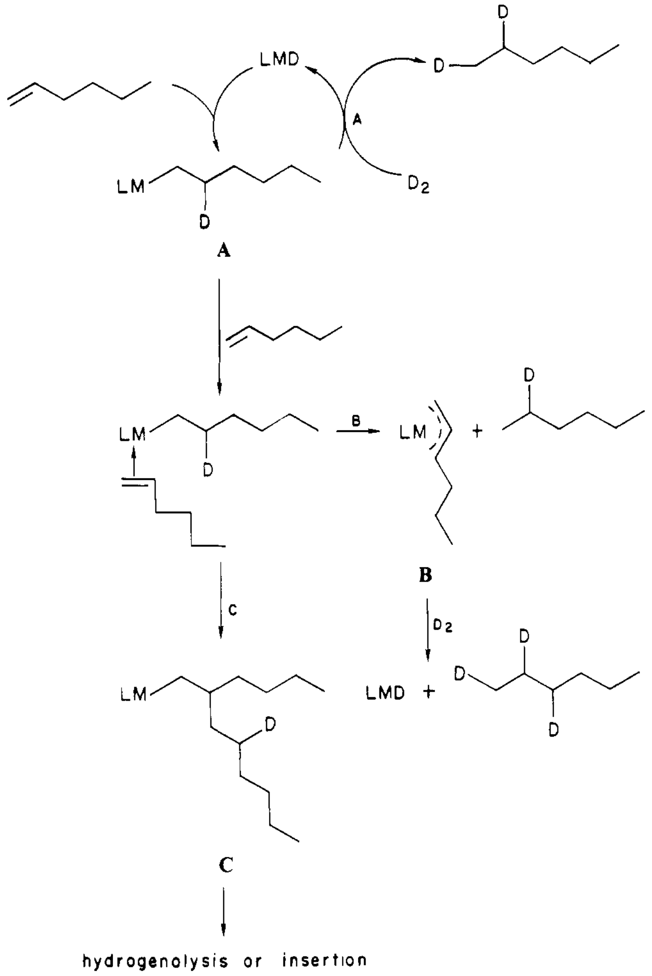
(17) The situtation is reminiscent of Langmuir–Hinshelwood,[17a] Michaelis–Menten[17b,c] kinetics (with a very large binding constant). In principle, information on the "binding constant" could be obtained via a Lineweaver–Burk treatment. (a) Satterfield, C. N. "Heterogeneous Catalysis in Practice"; McGraw-Hill: New York, 1980; Chapter 3. (b) Moore, J. W.; Pearson, R. G. "Kinetics and Mechanisms", 3rd eds.; Wiley: New York, 1981; pp 378–383. (c) Segel, I. H. "Enzyme Kinetics"; Wiley: New York, 1975; Chapter 2

(eq 3) is rate-limiting. For 1-hexene, the assertion that $K_2$ is large is borne out by both thermodynamic data[19] and numerous empirical observations relating to $\beta$-hydride elimination processes in organo-*f*-element systems.[20,21] Moreover, $^1$H NMR studies of eq 2 described in the first paper in this series[2] also indicate that $k_2$ (and probably $K_2$) are very large, since at millimolar concentrations, hydride is consumed by 1-hexene at a rate which is too rapid to measure by NMR at room temperature.

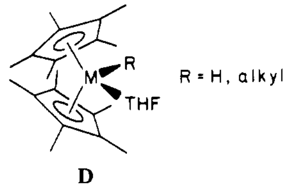
The best information on eq 1 comes from variable-temperature NMR studies of $Cp'_2Lu(\mu\text{-}H)Lu(H)Cp'_2$.[22] Here, $k_1$ and $k_{-1}$ are reported to be rapid on the NMR time scale and $\Delta G° < 2$ kcal/mol. Thus, at 25 °C, a 1 mM solution of this hydride will be greater than 10% dissociated. This conclusion is also in agreement with our cryoscopy results.[2] It is reasonable to expect that the behavior of the other lanthanide hydrides will be similar, although species with $M(\mu\text{-}H)_2M$ structures appear to be somewhat less dissociated[2] or reactive (vide infra). In regard to the irreversibility of eq 3, thermochemical estimates[19] place $\Delta H \approx -15$ kcal/mol. Kinetic data for 1-hexene hydrogenation are compiled in Table I. The highest $k_3$ value is for the M = Lu system, 7700 $M^{-1}\ s^{-1}$. For comparison, the rate-determining hydrogenolysis step in the catalytic hydrogenation of methyl (*Z*)-$\alpha$-acetamidocinnamate by $Rh(diphos)_2^+$ proceeds with $k$ = 100 $M^{-1}\ s^{-1}$ at 25 °C.[8b]

When the $(Cp'_2NdH)_2$-catalyzed hydrogenation of 1-hexene is carried out under $D_2$, the *n*-hexane obtained is ≥97% *n*-hexane-*1,2*-$d_2$ by GC/MS and $^{13}$C NMR.[10d-f,h] There are only traces of *n*-hexane-$d_3$ (~2%). Similar results are observed for M = La and Lu (the Lu-catalyzed reaction yields slightly more *n*-hexane-$d_3$). If the Nd-catalyzed reaction mixture is sampled at 33% conversion, 2.9% of the unreacted olefin is present as 2-hexene (approximately equal amounts of cis and trans isomers); under $D_2$, this 2-hexene is ca. 65% $d_1$ and 0% $d_2$. There is no deuterium detectable (≤1%) in the unreacted 1-hexene at 33% conversion, nor do control experiments evidence detectable exchange between *n*-hexane and $D_2$ under these conditions. On the other hand, carrying out the $(Cp'_2NdH)_2$-catalyzed reaction with a *deficiency* of hydrogen (i.e., slower stirring) results in a mixture of *n*-hexane and branched, saturated 1-hexene oligomers[2] (predominantly a dimer). For one such experiment under $D_2$, the *n*-hexane was found to be ca. 10% $d_3$, 72% $d_2$, and 14% $d_1$. Under approximately the same conditions, results for M = La were similar, while the $d_3$ and $d_1$ products are somewhat less abundant (ca. 6%) for M = Lu. A similar trend is observed for the $(Me_2SiCp''_2MH)_2$ series. Isotopic analysis by $^{13}$C NMR and GC/MS of the hexene oligomers reveals in all cases species which are largely $d_2$, with the dimer containing approximately equal quantities of $CH_2D$ and CHD functionalities.[2,10d-f] These results suggest that the lanthanide hexyl intermediate of eq 2 can suffer several competing fates, shown in Scheme I: hydrogenolysis (A), allylic hydrogen atom transfer (B), olefin insertion (C). At sufficiently high $D_2$ pressures, the reaction is predicted to predominantly cycle through pathway A to produce *n*-hexane-*1,2*-$d_2$ catalytically, as observed. Although the scheme is drawn for a 1-hexyl product, it is impossible to rule out a contribution from 2-hexyl regiochemistry, although such a product seems less likely on the basis of steric and thermodynamic[19] considerations as well as kinetic results with internal hexenes (vide infra). It is conceivable that the traces of partially deuterated 2-hexenes observed at partial conversion could result from $\beta$-hydride elimination of a 2-hexyl compound. At lower $D_2$ pressures, competing $\eta^3$-allyl formation[2] (pathway B) and insertion (pathway C) become significant. Reaction of **B** with $D_2$ should yield hexane-$d_3$[2] (presumably in a stepwise process). Scheme I also predicts that the allyl pathway should yield approximately equal amounts of hexane-$d_1$ and hexane-$d_3$, in accord with the isotopic analyses (vide supra). Pathway C will yield, after $D_2$ scission of **C**, saturated $(C_6)_n$-$d_2$ species. The spectroscopic information for $n$ = 2 is in good accord with Scheme I.[2]

Scheme I. $(Cp'_2MD)_2$ and $(Me_2SiCp''_2MD)_2$ Catalytic and Stoichiometric Chemistry with 1-Hexene



Experiments were also conducted to determine the effect of added THF on $(Me_2SiCp''_2NdH)_2$-catalyzed 1-hexene hydrogenation. When a solution in the molar ratio 220:220:1 1-hexene/THF/Nd was studied, it was found that the reaction was still zero-order in olefin but that $k \approx 0.045$ $atm^{-1}\ s^{-1}$—a factor of 16 lower. Thus, any effect the Lewis base might have in altering $k_2$ or $K_2$ in eq 2 (e.g., **D**)[21c,22] is obscured by the degree to which $k_3$ is altered. Further experiments would be required to place this conclusion on a more quantitative footing. That a Lewis base can also alter the kinetics of eq 2 is confirmed by experiments with cyclohexene (vide infra).



**D**

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(18) It is assumed that Henry's law is valid for hydrogen in cyclohexane or toluene. Solubility data are from: Stephen, H.; Stephen, T. "Solubilities of Inorganic and Organic Compounds"; Macmillan: New York, 1983; Vol. 1, Part 1, p 547.

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(22) Watson, P. L.; Roe, D. C. *J. Am. Chem. Soc.* **1982**, *104*, 6471–6473.

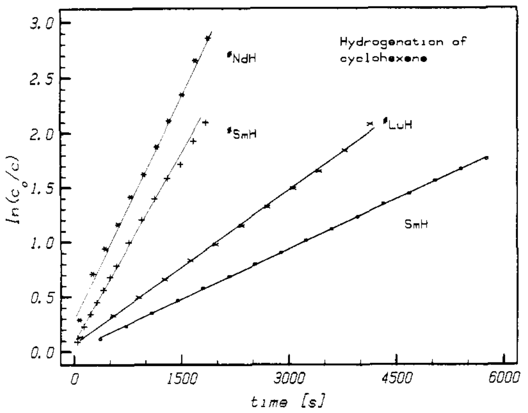


**Figure 3.** Olefin concentration as a function of time for the hydrogenation of cyclohexene by $(Me_2SiCp''_2MH)_2$ complexes (designated by a crosshatch) and by $(Cp'_2SmH)_2$.

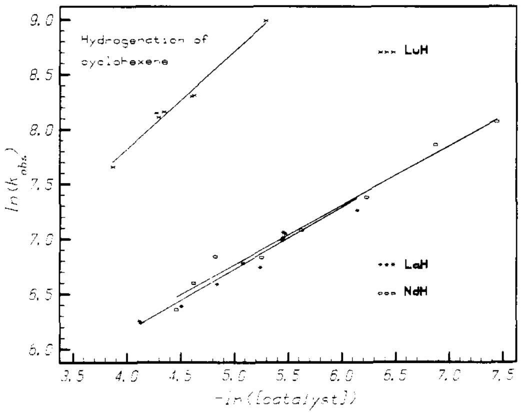


**Figure 4.** Hydrogenation of cyclohexene by $(Cp'_2MH)_2$ complexes. Plots to determine the reaction order in hydride.

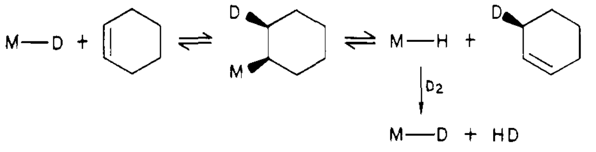
**Hydrogenation of Cyclohexene.** The kinetics of cyclohexene hydrogenation exhibit an interesting sensitivity to metal identity and supporting ligation. For all complexes, the rate law is first-order in olefin (e.g., Figure 3) and zero-order in $P_{H_2}$ (over a pressure range of 0.2–1.5 atm). In the $(Cp'_2MH)_2$ series under the conditions employed, the reaction is one-half-order in lanthanide for M = La, Nd, and Sm, while it is first-order in lanthanide for M = Lu. Figure 4 illustrates representative results, plotted according to the procedure of van't Hoff.[23] Least-squares analysis of these data yields orders of 0.57 (9) for La, 0.54 (9) for Nd, and 0.90 (15) for Lu. Rate constant data are set out in Table I. This kinetic behavior can be most simply interpreted if addition of the lanthanide hydride to the sterically shielded cyclohexene double bond is now rate-limiting. Previous $^1$H NMR studies[2] indicate that $(Cp'_2NdH)_2$ addition to cyclohexene is far slower than to 1-hexene under the same conditions. The kinetic order in the lanthanide complex most reasonably reflects the dissociation characteristics of the dimer. Thus, La, Nd, and Sm possess $M(\mu\text{-}H)_2M$ structures,[2] and application of an equilibrium treatment to eq 1–3 would yield rate law (5) if $k_2$ were rate-limiting and $k_3$ very large. In contrast, and as suggested by existing

$$\nu_{\text{cyclohexane}} = k_2[\tfrac{1}{2}K_1\text{Lanthanide}]^{1/2}[\text{olefin}] = k_{\text{obsd}}[\text{Lanthanide}]^{1/2}[\text{olefin}] \qquad (5)$$

data on $Cp'_2Lu(\mu\text{-}H)Lu(H)Cp'_2$, a high degree of dissociation under the experimental conditions would lead to rate law (6).

$$\nu_{\text{cyclohexane}} = k_2[\text{Lanthanide}][\text{olefin}] \qquad (6)$$

Alternatively, the Lu dimer may react directly with the olefin, abrogating the prerequisite of prior dissociation. For 1-hexene hydrogenation where $k_2$ and $K_2$ are very large and hydrogenolysis is rate-limiting, such molecularity differences as a function of M would not have been discernible. When the $(Cp'_2LaH)_2$-catalyzed hydrogenation is carried out with $D_2$, the cyclohexane produced under non-mass-transport-limited conditions is $\geq$98% cyclohexane-*1,2*-$d_2$ by $^{13}$C NMR and GC/MS.[10d-f,i] If the reaction is stopped at either 15% or 80% conversion, the unreacted cyclohexene contains traces (ca. 1%) of cyclohexene-$d_1$. This isotopic distribution is suggestive of a minor $\beta$-hydride elimination pathway (vide infra). In the case of $(Cp'_2LuH)_2/D_2$ under non-mass-transport-limited hydrogenation at 95% conversion, the cyclohexane produced contains large quantities of non-$d_2$ products: $d_4$ (ca. 7%), $d_3$ (ca. 24%), $d_2$ (ca. 38%), and $d_1$ (ca. 25%). At 95% conversion, the unreacted cyclohexene contains principally cyclohexene-$d_2$ (ca. 50%) and cyclohexene-$d_1$ (ca. 50%). These results are best rationalized by a combination of $\beta$-hydride elimination–readdition sequences (eq 2 and 7) and possibly allylic hydrogen atom abstraction (cf., reaction B, Scheme I, and the ca. 1:1 $d_1/d_3$ ratio observed). Since the hydride is expected to exchange rapidly with dissolved $D_2$,[24] incorporation of the label in the cyclohexene is expected. That $\beta$-H elimination is more favorable in this secondary alkyl system is readily argued on steric and thermodynamic grounds[19] as well as on the basis of empirical observations concerning other $Cp'_2MR$ systems where R is bulky.[21c,22] Under mass-transport-limited conditions (slower stirring), $(Cp'_2LaH)_2/D_2$ gave cyclohexane which was approximately 11% $d_3$, 78% $d_2$, and 12% $d_1$ at 100% conversion. Under conditions of very slow stirring at 10% conversion, the cyclohexene in a $(Cp'_2LuH)_2/D_2$ reaction mixture was already 8% $d_1$. The cyclohexane produced was approximately 21% $d_2$, 47% $d_1$, and 31% $d_0$, the latter suggesting incorporation of the Cp′, allylic (Scheme I, process B), or (less likely) cyclohexane solvent hydrogen atoms[21c] in the product at this stage in the reaction.



(7)

The rate laws for the $(Me_2SiCp''_2MH)_2$-catalyzed cyclohexene reactions parallel the results for the lighter members of the $(Cp'_2MH)_2$ series—the reactions are first-order in olefin, one-half-order in [Lanthanide], and zero-order in $P_{H_2}$ (eq 5). Rate constant data are set out in Table I. That Lu is not anomalous in this series is in accord with structural similarities across the Nd → Lu series deduced by infrared spectroscopy.[3] It is also interesting to note that, excluding M = Lu, the catalytic activities for the $(Me_2SiCp''_2MH)_2$ complexes are greater than those of the corresponding $(Cp'_2MH)_2$ complexes. A similar trend was noted in $(Me_2SiCp''_2ThH_2)_2$- vs. $(Cp'_2ThH_2)_2$-catalyzed olefin hydrogenation;[25] however, the differences are even more pronounced for the thorium complexes. In viewing the data in Table I, it can be seen that general trends in activity for cyclohexene hydrogenation parallel ionic radius, i.e., La > Nd > Sm > Lu (excepting anomalous $(Cp'_2LuH)_2$). This is opposite the trend for 1-hexene hydrogenation (vide infra). When cyclohexene hydrogenation by $(Me_2SiCp''_2SmH)_2/D_2$ was carried out with adequate stirring, the cyclohexane produced was $\geq$ 98% cyclohexane-*1,2*-$d_2$.[10d-f,i]

Experiments were also conducted in the presence of added THF. Under the conditions in which the overall rate of $(Me_2SiCp''_2NdH)_2$-catalyzed 1-hexene hydrogenation is reduced by a factor of ca. 16 (but still zero-order in olefin), the rate of cyclohexene hydrogenation was immeasurably slow. This result argues that for less reactive olefins, rate-limiting addition to the hydride (eq 2) can be drastically impeded (cf., **D**).

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[23] Laidler, K. H. "Chemical Kinetics", 2nd. ed.; McGraw-Hill: New York, 1963; pp 15–17.

[24] (a) Mauermann, H.; Marks, T. J., unpublished observations. (b) Fagan, P. J.; Manriquez, J. M.; Maatta, E. A.; Seyam, A. M.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 6650–6667.

[25] (a) Fendrick, C. M.; Mintz, E. A.; Schertz, L. D.; Marks, T. J.; Day, V. W. *Organometallics* **1984**, *3*, 819–821. (b) Fendrick, C. M.; Day, V. W.; Marks, T. J., submitted for publication.

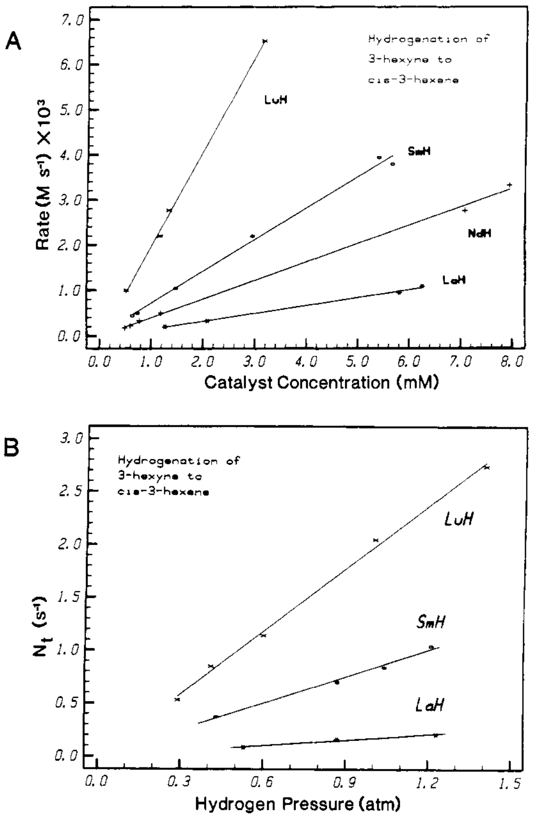
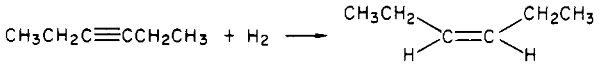


**Figure 5.** Hydrogenation of 3-hexyne to *cis*-3-hexene catalyzed by $(Cp'_2MH)_2$ complexes. (A) Hydrogenation rate as a function of catalyst concentration ($P_{H_2}$ = 0.87 atm). (B) Turnover frequency as a function of hydrogen pressure.

**Hydrogenation of 3-Hexyne.** The hydrogenation of 3-hexyne was of interest since lanthanide atom-derived catalysts are very weakly active in reducing this substrate to *cis*-3-hexene (maximum $N_t \approx 1.2$ h$^{-1}$ at 25 °C, 1 atm of $H_2$) and are even less active in reducing the *cis*-3-hexene to *n*-hexane.[13b] Experiments with the present hydrides would help to differentiate between the two classes of catalysts. In addition, Evans et al.[26] have reported that several $Cp'_2Sm$-derived catalysts reduce 3-hexyne to *n*-hexane with a maximum $N_t$ = 220 h$^{-1}$ (ca. 60 h$^{-1}$ for $(Cp'_2SmH)_2$). In view of our results with other substrates and lanthanides, it was of interest to determine whether either the 3-hexyne or Sm was intrinsically anomalous. It will be seen that neither is the case.

Hydrogenation of 3-hexyne to *n*-hexane by $(Cp'_2MH)_2$ complexes, M = La, Nd, Sm, and Lu, or by $(Me_2SiCp''_2NdH)_2$ occurs in two kinetically and mechanistically discrete stages, which can be readily understood on the basis of the foregoing 1-hexene, cyclohexene results as well as supplementary experiments with *cis*-3-hexene. As monitored manometrically and by GC/MS, the hydrogenation proceeds slowly (relatively) until essentially all of the 3-hexyne is converted to *cis*-3-hexene (eq 8) at which point the rate of gas uptake accelerates by a factor of ca. 10. The



$$CH_3CH_2C{\equiv}CCH_2CH_3 + H_2 \longrightarrow (CH_3CH_2)(H)C{=}C(H)(CH_2CH_3) \quad (8)$$

relative rates for the first stage are Lu > Sm > Nd > La > $(Me_2SiCp''_2NdH)_2$, with $N_t$(Sm) = 2940 ± 200 h$^{-1}$. Representative plots are shown in Figure 5, and data are set out in Table I. This relative ordering of rates is reminiscent of the 1-hexene system, as is the rate law (eq 9), determined over the concentration ranges illustrated in Figure 5 (cf. eq 1–3). Thus, the alkyne

$$\nu_{3\text{-hexyne}} = k_3[\text{Lanthanide}][H_2] \quad (9)$$

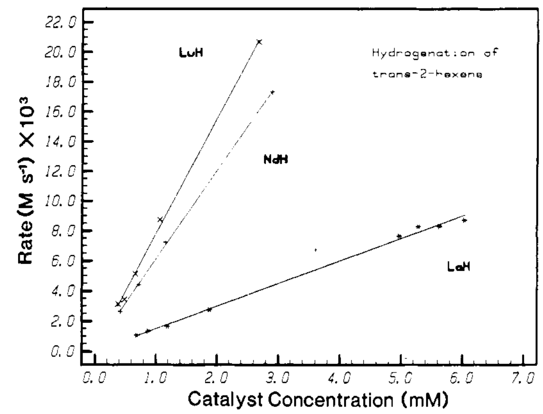
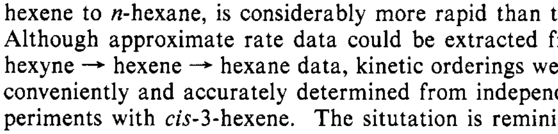


**Figure 6.** Hydrogenation of *trans*-2-hexene by $(Cp'_2MH)_2$ complexes. Hydrogenation rate as a function of catalyst concentration ($P_{H_2}$ = 0.87 atm).

addition (eq 9) to the substrate is both rapid and thermodynamically favorable ($k_2$ and $K_2$ of eq 10 are very large) and hydro-



$$M{-}H + CH_3CH_2C{\equiv}CCH_2CH_3 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} (M)(CH_3CH_2)C{=}C(H)(CH_2CH_3) \quad K_2 \quad (10)$$

**E**

genolysis of what is reasonably formulated as alkenyl **E** is rate-limiting. The relative magnitudes of $k_2$ and $K_2$ can be rationalized both in terms of the steric accessibility and high unsaturation of the C≡C bond (compared to an analogous olefin—vide infra) and the relatively large anticipated bond disruption enthalpy of a lanthanide vinyl.[19,27] That only the *cis*-3-hexene isomer is produced in the hydrogenation argues that free 3-hexenyl radicals do not play an important role.[28]

The second stage of 3-hexyne reduction, conversion of *cis*-3-hexene to *n*-hexane, is considerably more rapid than the first. Although approximate rate data could be extracted from the hexyne → hexene → hexane data, kinetic orderings were more conveniently and accurately determined from independent experiments with *cis*-3-hexene. The situation is reminiscent of cyclohexene (as were the experimental conditions) in that metal hydride addition to the substrate is rate-limiting, with the kinetics being half-order in metal for the lighter lanthanides (eq 11) and first-order for Lu (eq 12). Kinetic data are given in Table I. The

$$\nu_{cis\text{-3-hexene}} = k_2[\tfrac{1}{2}K_1\text{Lanthanide}]^{1/2}\underset{M\,=\,\text{Nd, Sm}}{[\text{olefin}]} \quad (11)$$

$$\nu_{cis\text{-3-hexene}} = k_2[\text{Lanthanide}]\underset{M\,=\,\text{Lu}}{[\text{olefin}]} \quad (12)$$

reason why the hydrogenation rate appears to accelerate as 3-hexyne consumption nears completion is straightforwardly explained by the kinetic results. Although hydrogenolysis of **E** is relatively slow (eq 10), $k_2$ and $K_2$ are so large that *cis*-3-hexene cannot successfully compete for M–H (it becomes more competitive as the olefin concentration increases) until the alkyne is nearly exhausted.

It is interesting to note from Table I that the rate of *cis*-3-hexene hydrogenation is not as sensitive to the identity of M as is the rate of cyclohexene hydrogenation. This argues that the rate differences for cyclohexene are largely steric/reactivity ($k_2$) rather than dimer dissociation ($K_1$) in origin. Our $(Cp'_2SmH)_2$ turnover

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(26) (a) Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1983**, *105*, 1401–1403. (b) Evans, W. J. China-Japan-U.S. Symposium on Organometallic Chemistry and Catalysis, Santa Cruz, CA, Aug 5–9, 1984.

(27) (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 43–90. (b) Connor, J. A. *Top. Curr. Chem.* **1977**, *71*, 71–110. (c) Kochi, J. K. "Organometallic Mechanisms and Catalysis"; Academic Press: New York, 1978; Chapter 11.

(28) Vinylic radicals display inversion rates which are competitive with diffusion out of solvent cages: Kochi, J. K. In "Free Radicals"; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. I, Chapter 11.

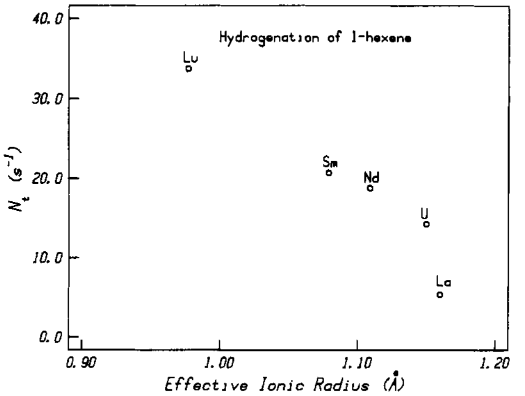


**Figure 7.** Turnover frequencies (1.0 atm of $H_2$ pressure) for 1-hexene hydrogenation catalyzed by $(Cp'_2MH)_2$ complexes plotted as a function of effective ionic radius (eight-coordinate) of M(III). The M = U datum is from ref 29b.

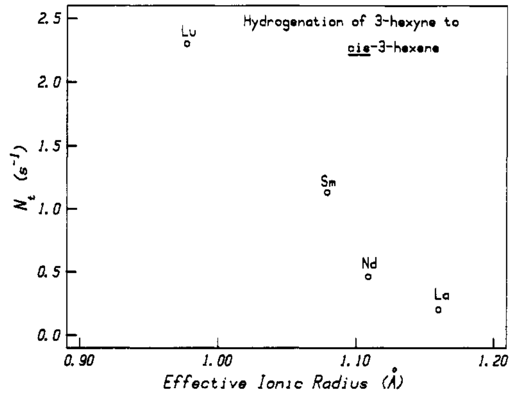


**Figure 8.** Turnover frequencies (1.0 atm of $H_2$ pressure) for 3-hexyne → *cis*-3-hexene hydrogenation catalyzed by $(Cp'_2MH)_2$ complexes plotted as a function of effective ionic radius (eight-coordinate) of M(III).

frequencies are far in excess of those reported by Evans et al.[26] We suggest that poisoning (e.g., by $O_2$ or $H_2O$) or inadequate attention to mass-transport effects are the cause of this discrepancy.

**Hydrogenation of Other Hexenes.** Exploratory hydrogenation investigations were also carried out with *trans*-2-hexene, *trans*-3-hexene, and *cis*-2-hexene with $(Cp'_2MH)_2$ catalysts. A representative kinetic plot is shown in Figure 6. The rate laws for the former two substrates parallel the behavior of 1-hexene (eq 1–3, Table I), with the rate-limiting process being M–C bond hydrogenolysis. For *trans*-2-hexene, the activity trend Lu > Sm > Nd > La parallels that observed for 1-hexene. Hydrogenation rates for *trans*-3-hexene were the greatest of any substrate studied, and the extreme rapidity as well as only an approximate adherence to eq 4 introduced inaccuracy in the kinetic analysis. As can be seen in Table I, for constant M (La, Nd, and Sm) and rate law kinetic orders, the relative reactivities *trans*-3-hexene > 1-hexene > *trans*-2-hexene are obeyed. Since hydrogenolysis is rate-limiting, the high reactivity of a lanthanide 3-hexyl compound could presumably be rationalized via steric and electronic destabilization of the lanthanide–C bonding. However, the relationship between 1-hexene and *trans*-2-hexene reactivities is less easy to understand. In any case, these results provide no kinetic evidence that rapid isomerization of all three hexenes to a common lanthanide 1-hexyl compound precedes hydrogenation. The same is concluded from isotopic labels (vide infra). The kinetic behavior of *cis*-2-hexene parallels that of *cis*-3-hexene and cyclohexene in that the $(Cp'_2NdH)_2$-catalyzed reaction is half-order in [Nd] and first-order in olefin, while the $(Cp'_2LuH)_2$-catalyzed reaction is first-order in metal and olefin. For both metals, the relative hydrogenation rates are *cis*-2-hexene > *cis*-3-hexene ≫ cyclohexene, which in view of the observed rate laws must be a measure of relative olefin reactivity with respect to a given hydride (eq 5).

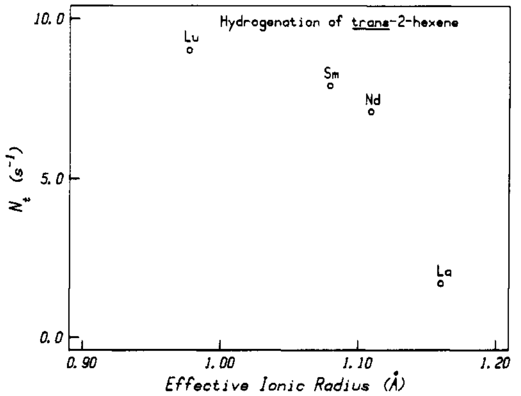
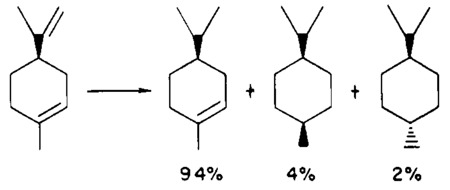


**Figure 9.** Turnover frequencies (1.0 atm of $H_2$ pressure) for *trans*-2-hexene hydrogenation catalyzed by $(Cp'_2MH)_2$ complexes plotted as a function of effective ionic radius (eight-coordinate) of M(III).

For both *trans*-2-hexene and *cis*-2-hexene, $(Cp'_2NdH)_2$-catalyzed reduction under $D_2$ yields *n*-hexane which is ≥95% *n*-hexane-*2,3*-$d_2$ by GC/MS and $^{13}C$ NMR.[10d-g] This result indicates that under the reaction conditions, migration of the initially formed Nd–C $\sigma$ bond (e.g., by $\beta$-hydride elimination and readdition) is not competitive with hydrogenolysis.

**Hydrogenation of Other Olefins.** Several exploratory experiments were conducted with other olefins. It was found that tetramethylethylene could not be hydrogenated by any of the present catalysts at a measurable rate (25 °C, 1 atm of $H_2$ pressure). Using $(Me_2SiCp''_2NdH)_2$ as a catalyst, it was found that *trans*-stilbene was rapidly hydrogenated to 1,2-diphenylethane. In a single experiment, neat (*R*)-(+)-1limonene was hydrogenated largely at the terminal C=C bond in 1.5 h (eq 13). Presumably

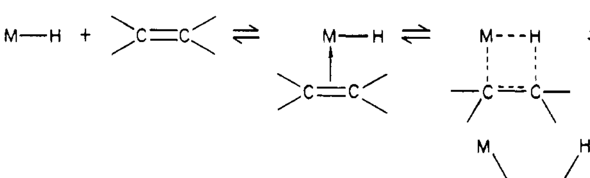


(13)

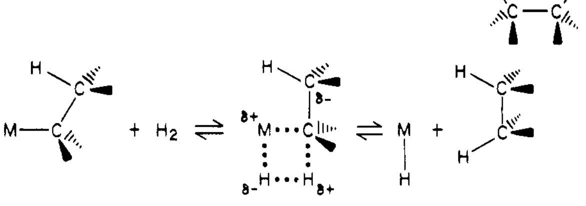
the regio- and stereoselectivity of this type of reaction could be modified by varying the reaction time or conditions (e.g., $H_2$ pressure, addition of THF). These aspects of the catalysis are presently under investigation.

## Discussion

This work establishes that organolanthanides of the type $(Cp'_2MH)_2$ and $(Me_2SiCp''_2MH)_2$ are some of the most active homogeneous olefin hydrogenation catalysts yet discovered. There is no evidence that oxidative addition/reductive elimination sequences[4] are involved in the catalysis but rather a close coupling of olefin/hydride insertion (eq 14) followed by "four-center" hydrogenolysis[7] (eq 15, drawn arbitrarily in an eclipsed conformation). We presume eq 14 to be a "*cis*-addition",[4] although



(14)

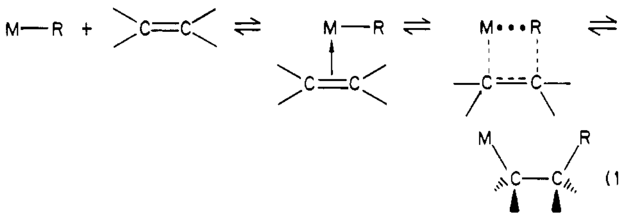


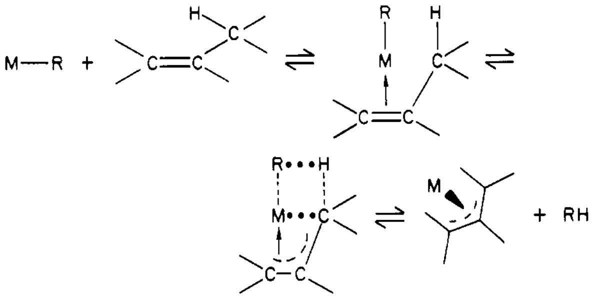
(15)

this has so far only been established for an alkyne. One interesting nuance introduced by f-element bond disruption enthalpy trends[19] (*D*(M–H)–*D*(M–primary alkyl) ≪ 30 kcal/mol) is that for $\alpha$-

olefins, eq 14 is probably exothermic on the order of ca. 15 kcal/mol or more. For an α-olefin such as 1-hexene, it can be calculated that the rate constant for this insertion must be in excess of ca. 3000 $M^{-1}$ $s^{-1}$. Assuming that essentially all the lanthanide is present as an alkyl, metal–carbon bond hydrogenolysis is the rate-limiting step in the hydrogenation. For constant supporting ligation, the rate constant and $N_t$ at fixed $H_2$ pressure for this process decrease almost linearly with increasing lanthanide effective ionic radius,[29] suggesting that higher charge/radius ratios accelerate the "heterolytic" activation[30] of $H_2$ (eq 15) and that the accompanying steric changes are not as important. These qualitative relationships are illustrated for 1-hexene, 3-hexyne, and *trans*-2-hexene in Figures 7, 8, and 9, respectively. It is also interesting to note in the 1-hexene data (Figure 7) that the nearly linear relationship between $N_t$ and effective ionic radius includes the actinide catalyst $(Cp'_2UH)_2$.[29b] Rate constants for the M–(*n*-hexyl) hydrogenolysis process as high as 7700 $M^{-1}$ $s^{-1}$ have been measured. The marked electron deficiency of the $Cp'_2M$ and $Me_2SiCp''_2$ centers, which is reasonably a requisite for heterolytic $H_2$ activation, is also evident in our structural results.[2,3] For bulkier olefins, eq 14 is neither as rapid nor (apparently) as exothermic, and the insertion reaction now becomes rate-limiting. In these cases, the qualitative sensitivity of the hydrogenation rate to lanthanide ionic radius is reversed, and the larger and more "open" $(Me_2SiCp''_2M^3)$ metal centers are also more reactive. The structural/dissociation characteristics of the hydride dimers must necessarily influence these trends, and the effect is most apparent in the case of $(Cp'_2LuH)_2$, which has a different structure from the other $(Cp'_2MH)_2$ compounds as well as a different rate law.

The results in this and the two accompanying[2,3] papers in this issue also underscore the necessity of maintaining catalytic conditions in a regime where mass-transport effects are not important. For these organolanthanide catalysts, hydrogen "starvation" enhances the role of competing side reactions such as olefin insertion (eq 16)[2,31] and allylic hydrogen atom transfer (eq 17),[2,22] as well as more common[4] hydrogen scrambling due to β-hydride elimination processes. The competing insertion reaction (eq 16) is another lanthanide nuance which is generally rare (and/or slow) for middle and late transition elements.[32] Interestingly, for M = $Cp'_2La$, R = primary alkyl, and olefin = ethylene, it can be calculated using tabulated ethylene solubilities[33] and approximate rate data in the preceding paper[2] that the rate constant for insertion exceeds 12 600 $M^{-1}$ $s^{-1}$ at 25 °C! This insertion process also exhibits a strong steric sensitivity, and the rate falls significantly for substituted olefins. Insertion also appears to exhibit a metal sensitivity, in the general direction observed for the aforementioned rates of M–H + olefin insertion (eq 14). Likewise, the reactivity response on substituting $Me_2SiCp''_2M$ centers for $Cp''_2M$ centers is similar.


(16)


(17)

Another interesting feature of the present catalysts is the extent to which the metal coordination sphere is immobilized and screened by the bis(pentahaptocyclopentadienyl) ligation. Such a structural arrangement must restrict the catalytic chemistry to the "equatorial girdle" and necessarily imposes considerable discrimination upon the substrates which can enter into catalytic chemistry and the stereochemistry of the transformations that can occur. Future efforts will focus upon exploring the range of substrates which are compatible with organo-f-element catalysts as well as on tuning the substrate discrimination and reaction stereochemistry.

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**Registry No.** THF, 109-99-9; $(Cp'_2LaH)_2$, 98720-39-9; $(Cp'_2NdH)_2$, 93303-98-1; $(Cp'_2SmH)_2$, 84751-30-4; $(Cp'_2LuH)_2$, 98838-53-0; $(Me_2SiCp''_2NdH)_2$, 98690-08-5; $(Me_2SiCp''_2SmH)_2$, 98690-10-9; $(Me_2SiCp''_2LuH)_2$, 98690-11-0; $CH_3(CH_2)_3CH{=}CH_2$, 592-41-6; $CH_3(CH_2)_4CH_3$, 110-54-3; $CH_3(CH_2)_3CHDCH_2D$, 92475-64-4; $CH_3CH_2C{\equiv}CCH_2CH_3$, 928-49-4; *cis*-$CH_3CH_2CH{=}CHCH_2CH_3$, 7642-09-3; *trans*-$CH_3CH_2CH{=}CHCH_2CH_3$, 13269-52-8; *cis*-$CH_3(CH_2)_2CH{=}CHCH_3$, 7688-21-3; *trans*-$CH_3(CH_2)_2CH{=}CHCH_3$, 4050-45-7; $Ph(CH_2)_2Ph$, 103-29-7; cyclohexene, 110-83-8; cyclohexane, 110-82-7; cyclohexane-*1,2*-$d_2$, 98821-91-1; tetramethylethene, 563-79-1; *trans*-stilbene, 103-30-0; (*R*)-(+)-limonene, 5989-27-5; (*R*)-1-methyl-4-(1-methylethyl)cyclohexene, 1195-31-9; *cis*-1-methyl-4-(1-methylethyl)cyclohexane, 6069-98-3; *trans*-1-methyl-4-(1-methylethyl)cyclohexane, 1678-82-6; hexane-$d_3$, 98821-92-2; hexane-$d_2$, 98821-93-3; hexane-*d*, 98821-94-4; cyclohexane-$d_4$, 91447-84-6; cyclohexane-$d_3$, 90030-64-1; cyclohexane-$d_2$, 90992-61-3; cyclohexane-*d*, 98821-95-5; cyclohexene-$d_2$, 98821-96-6; cyclohexene-*d*, 80866-19-9.

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