

Organolanthanides in Catalysis

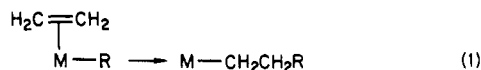
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The 13 metals following lanthanum in the periodic table, generally referred to as the lanthanide or rare earth metals, have attracted little attention until recently. Some, such as lutetium, were unfamiliar to the average chemist. However, in recent years, many organic derivatives of these metals have been synthesized.^{1,2} These organolanthanides have a rich chemistry sometimes distinct from that of the neighboring transition metals. We and others have found that the alkylanthanides are quite active as olefin polymerization catalysts. Various organolanthanides are also very reactive with C-H bonds of arenes, olefins, and alkanes. Indeed an organolanthanide compound yielded the first well-characterized organometallic reaction of methane.

Our research in this area began with attempts to examine some folklore about Ziegler-Natta catalysts for olefin polymerization. It was widely believed by workers in this area that such catalysts contain paramagnetic species at the active site for olefin insertion. The hypothesis was that an unpaired electron on the metal ion at the active site somehow aided the insertion of the C=C bond into the C-M bond at the end of the growing polymer chain (eq 1). It was unclear whether

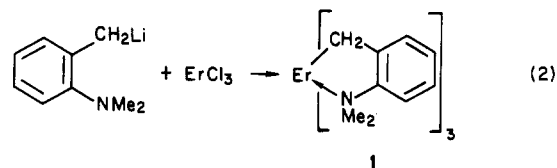


the unpaired electron would destabilize the M-R bond or if it would change the character of the π bond between the olefin and the metal.

Leo Manzer, who joined our organometallic group in 1973, set out to establish some facts about these hypothetical effects by first synthesizing some paramagnetic organotransition-metal compounds. Simple alkyl derivatives of ions such as titanium(III) (one unpaired electron) were difficult to prepare. Many attempts to obtain stable $\text{RTi}(\text{C}_5\text{H}_5)_2$ compounds gave mixtures of materials. Manzer reasoned that undesired side reactions occurred at vacant coordination sites on the metal ion and decided to use chelating alkyls for stability. Paramagnetic benzylic derivatives of titanium, vanadium, chromium, and other transition metals were also prepared, as were paramagnetic derivatives of the lanthanide metals such as the erbium(III) complex 1 shown in eq 2.³ Here the unpaired electrons are in f orbitals rather than in d orbitals as in the transition metals.

Patricia L. Watson was born in Australia and received her baccalaureate degree in organic chemistry from the Australian National University. She earned a Ph.D. in inorganic chemistry from Cornell University under the late Professor Earl Muettterties. She is currently leader of a group working on organometallic and bioinorganic chemistry in the Central Research and Development Department of Du Pont.

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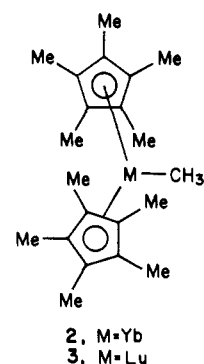
Manzer then worked with Charles Tullock, a senior polymer scientist in our department who was studying the polymerization of ethylene onto the surface of minerals to make mineral-polyethylene composites. They found that compounds such as 1 were inert by themselves, but reaction of 1 with alumina gave a highly reactive surface onto which ethylene polymerized rapidly.⁴

At this time (1975), the collaboration moved toward development of practical processes for the alumina-polyethylene composites. The organolanthanide chemistry, though interesting, was set aside for future study.

Organolanthanide Synthesis

Our interest in lanthanide chemistry resumed in 1979 when Patricia Watson joined the organometallic group. The area of lanthanide organometallic chemistry seemed relatively undeveloped at the time. However, extensive work in China showed that lanthanide catalysts effect the stereospecific polymerization of dienes⁵ and Ballard's group at ICI in England found modest ethylene polymerization activity for compounds such as $[(\text{C}_5\text{H}_5)_2\text{ErCH}_3]_2$, a methyl-bridged dimer.⁶

Our new program focused on chemistry of compounds such as 2 and 3. The bulky pentamethylcyclo-



pentadienyl (Cp^*) ligands confine most of the chemistry

(1) (a) Gysling, H.; Tsutsui, M. *Adv. Organomet. Chem.* 1970, 9, 361. (b) Cotton, S. A. *J. Organomet. Chem. Libr.* 1977, 3, 217. (c) Marks, T. J. *Prog. Inorg. Chem.* 1978, 24, 51. (d) Schumann, H. "Organometallic Chemistry of the f Elements"; Marks, T. J., Fischer, R. D., Eds.; D. Reidel Publishing Co.: Dordrecht, Holland, 1979; pp 81-112.

(2) Schumann, H.; Genthe, W.; Bruncks, N.; Pickardt, J. *Organometallics* 1982, 1, 1194.

(3) Manzer, L. E. *J. Am. Chem. Soc.* 1978, 100, 8068.

(4) Manzer, L. E. U.S. Patent 4 057 565, 1977.

(5) Wang, F.-S.; Sha, R.-Y.; Jin, Y.-T.; Wang, Y.-Li.; Zheng, Y.-L. *Sci. Sin. (Engl. Ed.)* 1980, 23, 172.

(6) Ballard, D. G. H.; Curtis, A.; Holton, J.; McMeeking, J.; Pearce, R. *J. Chem. Soc., Chem. Commun.* 1973, 994.

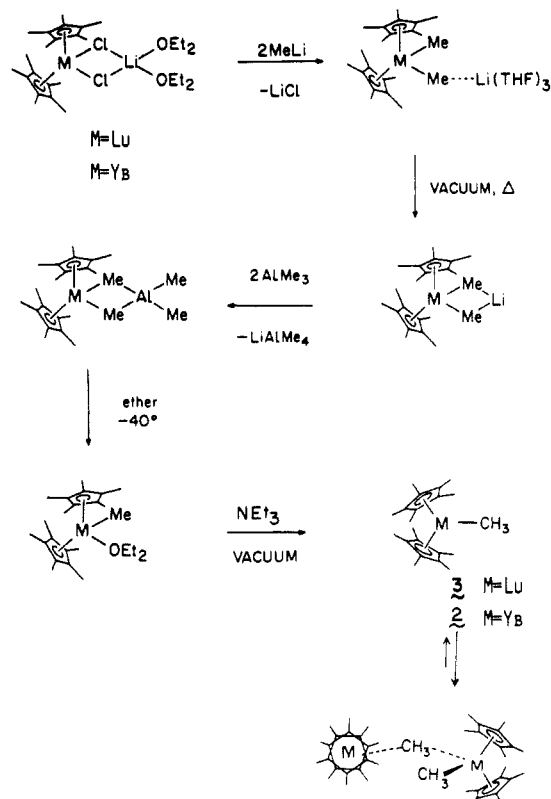
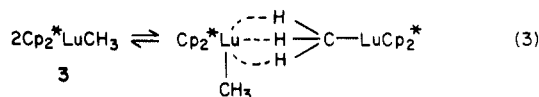


Figure 1. Synthesis of solvent-free $\text{Cp}^*_2\text{MCH}_3$.

of **2** and **3** to reactions at the single $\text{M}-\text{CH}_3$ bond and at the empty nonbonding orbitals present in the narrow belt between the two canted Cp^* rings.

Ytterbium and lutetium, the heaviest lanthanide elements, were chosen because their small ionic radii would accentuate steric crowding by the Cp^* rings. Their position in the periodic table is close to early transition metals such as hafnium and tantalum. We have found many chemical analogies to trivalent titanium and to the main group metal aluminum. Lutetium has the useful property that the f orbitals are filled and $\text{Lu}(\text{III})$ derivatives such as **3** are diamagnetic and suitable for study by NMR. The +3 oxidation state of ytterbium, on the other hand, is paramagnetic (^{13}f) with ligand-to-metal charge-transfer electronic transitions that are very sensitive to the environment about the metal. Yb^{2+} (^{14}f) is also, of course, diamagnetic.

Synthesis of solvent-free, coordinatively unsaturated **2** and **3** was tedious because the metal ions seemed determined to retain some kind of donor ligand in the vacant orbital adjacent to the methyl group. The extended series of displacement reactions of Figure 1 was necessary to obtain the "simple" compounds **2** and **3**.⁷ Simple is a misnomer because the electron deficiency of the metals is such that even the hydrogen atoms of the methyl ligands are acceptable as donors. Compound **3** exists in a monomer-dimer equilibrium (eq 3). Both



in solution and in the crystalline state (Figure 2), the unsymmetrical dimer has a structure in which a methyl

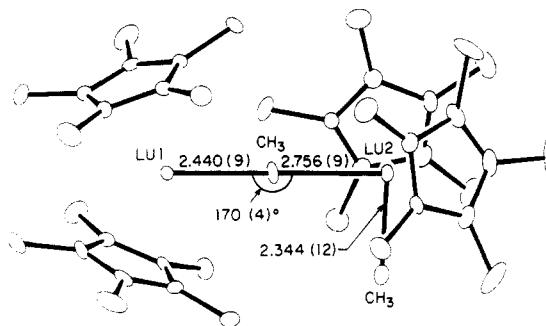


Figure 2. Crystal structure of the methyl lutetium dimer. The methyl group of one monomer donates electron density to the second monomer.

group from one metal coordinates to vacant metal orbitals of a second molecule.⁸ At room temperature in cyclohexane, about 15% of the compound is in the form of the simple monomer **3**, and equilibration is rapid on the NMR time scale. For dissociation of one dimer to two monomers, $\Delta H_0 = 12.6$ kcal/mol and $\Delta S_0 = 32.8$ eu in cyclohexane.

The effort to synthesize coordination-deficient **2** and **3** was repaid by a wealth of interesting new chemistry. These compounds provide one of the best soluble models for Ziegler-Natta catalysis.^{7,9} Compound **3** mimics the initiation, propagation, and termination steps of the industrially used heterogeneous catalysts. Beyond this, **2** and **3** show remarkable activity in reactions with C-H bonds of hydrocarbons and display a new reaction not yet observed with alkyl transition metal compounds, namely, β -methyl extrusion. Most of the chemistry has been explored by NMR studies of **3**, but the reactions of **2** appear to be qualitatively similar.

Olefin Polymerization Catalysis

The methyl lutetium compound **3** met the first test as a model for Ziegler-Natta catalysis by polymerizing ethylene at an astonishing rate. Even in the presence of an equimolar quantity of ether, it produced high-density polyethylene at a rate of at least 115 g/mmol of Lu (min^{-1} (kg cm^2 of C_2H_4) $^{-1}$) at 50–80 °C in cyclohexane. Polymerization slows as expected when the reactions are carried out at low temperature but is evident even at –90 °C. Parenthetically, the paramagnetic methyl ytterbium compound **2** shows no significant rate enhancement compared to the diamagnetic lutetium analogue.

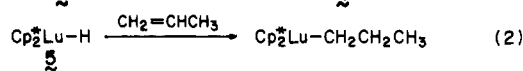
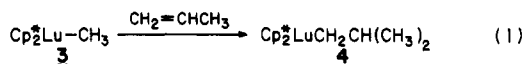
Propylene reacts with **3** at room temperature to produce a mixture of oligomers. Initially one can observe a regiospecific stoichiometric insertion of propylene into the $\text{Lu}-\text{CH}_3$ bond to give exclusively the isobutyl derivative **4** (Figure 3, reaction 1). Subsequent insertion of propylene into the $\text{Lu}-\text{C}$ bond of the isobutyl derivative **4** occurs, but it is a 1000-fold slower than reaction of **3**, because of the bulk of the isobutyl ligand. This insertion step is stereospecific and gives only one diastereomer of the $\text{LuCH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}(\text{CH}_3)_2$ compound as the initial product. The stereospecificity probably arises from a concerted *cis* insertion of propylene. The ethylene insertion was definitely shown to be *cis* by polymerization of *cis*- and *trans*-

(7) Watson, P. L., presented at the 183rd National Meeting of the American Chemical Society, Las Vegas, NV, March 1982. Watson, P. L.; Herskovitz, T. *ACS Symp. Ser.* **1983**, *212*, 459.

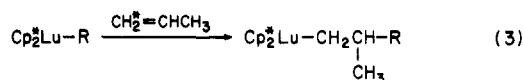
(8) Watson, P. L.; Calabrese, J. C., to be published.

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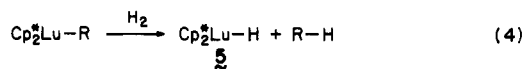
Initiation



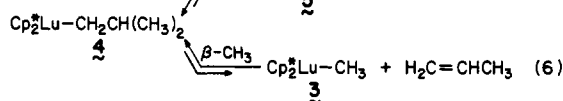
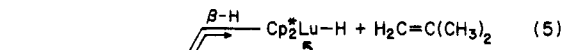
Propagation



Termination and Chain Transfer



Termination and Chain Transfer by Olefin Extrusion



Termination by C-H Activation

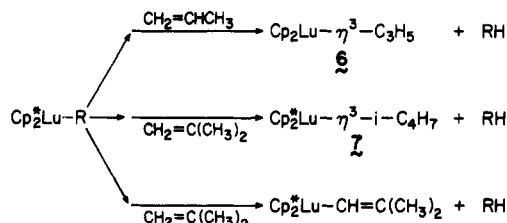


Figure 3. Key steps in olefin polymerization catalysis illustrated by the lanthanide model (R = CH₃, n-C₃H₇, i-C₄H₉).

ethylene-1,2-d₂, which gave polyethylenes with predominantly threo and erythro repeat units,¹⁰ respectively.

The difference in rates between the first and second insertions permits the determination of the kinetics of each propylene insertion, which are models for the propagation steps in olefin polymerization (Figure 3, reactions 1, 3). The insertions are kinetically first order in both Lu complex and olefin. Overall, these results are consistent with the classical Cossee mechanism¹¹ for polymerization in which the olefin simply inserts into the M-R bond of the growing polymer chain. No evidence for a discrete olefin complex with the metal is detectable.

With commercial catalysts, the molecular weight of polyethylene and polypropylene is controlled by two methods. Addition of hydrogen to the gaseous olefin fed to the polymerization reactor controls the degree of polymerization by hydrogenolysis of the M-C σ bond at the growing end of the polymer chain. This reaction is certainly simulated by the lutetium model (Figure 3, reaction 4). Both methyl- and isobutyl lutetium compounds react with hydrogen at room temperature and atmospheric pressure to form alkane and the lutetium hydride 5. The hydride is evidenced by a signal in the NMR spectrum at 9.27 ppm in C₆D₁₂.

(10) Tasumi, M.; Shimanouchi, T.; Ikeda, S. *J. Polym. Sci., Polym. Chem. Ed.* **1966**, *4*, 1023.

(11) Cossee, P. *J. Catal.* **1964**, *3*, 80. Arlman, E. J. *Ibid.* **1966**, *5*, 178.

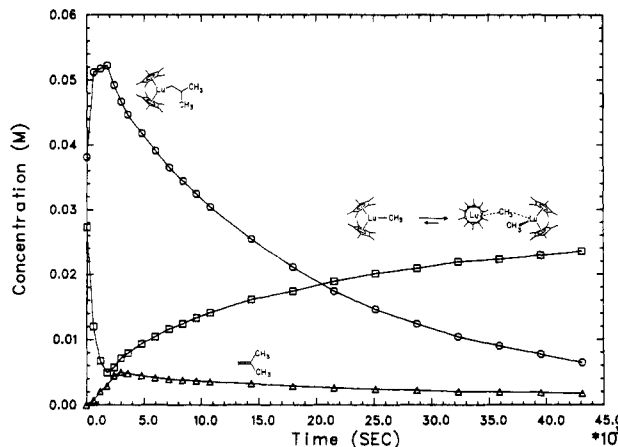


Figure 4. Concentrations of isobutylene and the methyl- and isobutyl lutetium compounds as a function of time.

In context of the polymerization catalysis model, the lutetium hydride illustrates reinitiation of polymerization. Compound 5 reacts with propylene to form an *n*-propyl derivative (Figure 3, reaction 2) and with isobutylene to reform the isobutyl derivative 4. Even at -80 °C, the *n*-propyl derivative rapidly inserts propylene to give LuCp₂*CH₂CH(CH₃)CH₂CH₂CH₃.

The olefin insertion into the Lu-H bond that can initiate polymerization is simply the reverse of the β-hydrogen elimination reaction ubiquitous with alkyl derivatives of the transition metals. β-Hydrogen elimination is the second major method for molecular weight control in ethylene polymerization (Figure 3, reaction 5). A common industrial practice is to polymerize ethylene at a temperature at which a β-hydrogen of the growing polymer will transfer to the transition-metal catalyst at a suitable rate. This reaction produces a metal hydride which reinitiates polymerization and a polymer chain of the desired length. However, the extruded polymer chain has an olefinic end group rather than the saturated end group produced by hydrogenolysis.

The β-hydrogen elimination reaction is usually thermodynamically unfavorable but clearly discernible for many alkylmetal compounds. In measuring the equilibrium constant for reaction 5 by following the decomposition of 4 in solution at room temperature, it became evident that a second reaction also reduced the concentration of 4. More interestingly, it became clear that the second thermal process is β-methyl elimination from the isobutyl ligand of 4 (Figure 3, reaction 6).¹²

One experiment illustrating these two termination steps as well as propagation is recorded in Figure 4. Propylene and 3 (~1:1) in C₆D₁₂ at 22 °C reacted almost completely in 10 min to form the isobutyl derivative 4 (Figure 3, reaction 1). This compound underwent very slow (but rapidly reversible) β-hydrogen elimination to form isobutylene and the lutetium hydride 5 (not shown). Simultaneously, the methyl compound reformed as the β-methyl extrusion proceeded and allylic C-H activation reactions consumed coproduct propylene. The methyl extrusion dominates since $K_{\text{extrusion}} = \text{ca. } 10^{-3}$ while $K_{\text{H elimination}} = \text{ca. } 10^{-5}$. Both reactions are thermodynamically unfavorable but proceed detectably because other reactions consume the olefinic coproducts.

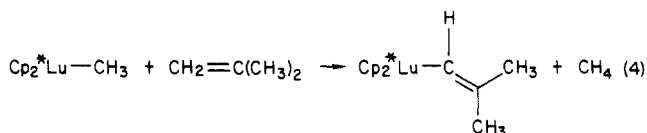
(12) Watson, P. L.; Roe, D. C. *J. Am. Chem. Soc.* **1982**, *104*, 6471.

The β -alkyl extrusion reaction (Figure 3, reaction 6), in which an alkyl group attached to the β -carbon of a ligand transfers to the metal ion, has not yet been observed for transition-metal organometallic compounds. Precedent exists in the decomposition of tri-n-pentylaluminum at elevated temperatures to give trimethylaluminum and isobutylene.¹³ This novel reaction may be quite significant as a third, generally unrecognized process¹⁴ for termination of a polymer chain growing from a metal site in a Ziegler-Natta catalyst.

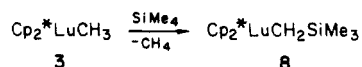
Overall, unsolvated **3** is an excellent model for the active site of a Ziegler-Natta catalyst. It emulates the major initiation, propagation, and termination steps. Also, it reacts with added bases which block an essential site for olefin reaction. Like the commercial catalysts, the active species **3** is a powerful Lewis acid that interacts with various alkylmetal compounds via multi-center bonds. This latter feature is important in the interactions with hydrocarbons.

Reactions with C-H Bonds

The polymerization studies provided hints that the methyltitanium compound **3** reacts with the C-H bonds of hydrocarbons. One major clue was the disappearance of the olefinic products of the β -hydrogen and β -methyl elimination reactions.¹² Allyl (**6**) and methallyl (**7**) (see Figure 3) complexes were identified by proton and carbon NMR spectra during thermal decomposition of the isobutyl complex **4**. These products appeared to arise from reaction of **3** (or, particularly for **7**, an intermediate derived therefrom) with propylene and isobutylene, respectively. These reactions involve C-H activation at the allylic sites of the olefins, but vinylic activation can also occur, for example, in the reactions of either **3** or **4** with excess isobutylene. In the clean bimolecular reaction of **3** with this olefin, only the 1-isobutenyl complex is formed (eq 4).



Another curious C-H bond reaction was detected while studying insertion reactions of trimethylsilyl-substituted olefins. The complex product mixtures were puzzling until it was realized that the trimethylsilyl group was not "inert". Gently warming **3** with tetramethylsilane in fact gave the simple derivative **8** cleanly.¹⁵



The synthesis of **8** was not noteworthy in itself because (trimethylsilyl)methyl analogues were prepared earlier by conventional methods,² but the reaction which gave rise to **8** was certainly remarkable. Most previous C-H bond activation studies¹⁶⁻¹⁸ had involved

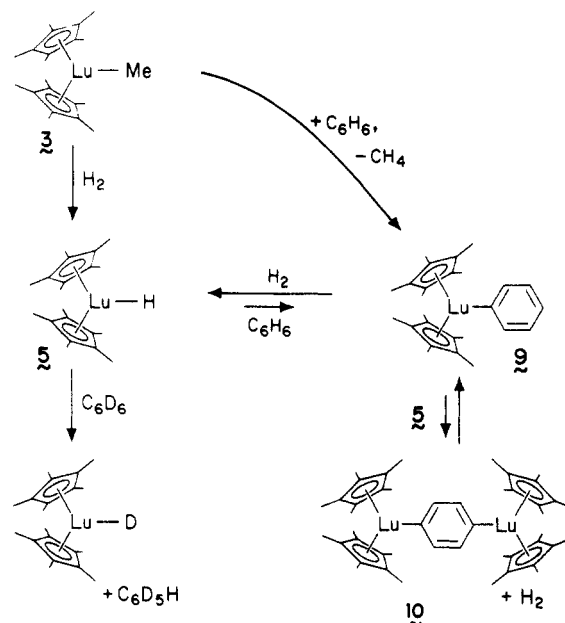


Figure 5. Reactions of benzene with the hydrido- and methyltitanium compounds.

arenes, olefins, or other functional compounds in which some precoordination to the metal could occur. Among the few exceptions were Shilov's work on alkane reactions¹⁷ and a previous reaction of tetramethylsilane with photoactivated tungsten complex.¹⁹ Janowicz and Bergman²⁰ had recently reported that irradiation of $\text{Ir}(\text{C}_5\text{Me}_5)(\text{H})_2(\text{PR}_3)$ gives a reactive species that undergoes formal oxidative addition of C-H bonds as inert as those of neopentane. Jones also synthesized a similarly active rhodium complex.²¹

Benzene Reactions. Yet another C-H bond activation came from an experiment in which a benzene- d_6 solution of the hydride complex **5** was observed at room temperature. The proton NMR signal of the hydride disappeared and the $\text{C}_6\text{D}_5\text{H}$ signal increased in intensity. This apparent exchange between Lu-H and C_6D_6 turned out to be one in a family of reactions with the carbon-hydrogen bonds of benzene (Figure 5).¹⁵

The hydride **5** can play a central role in the reactions with benzene. In addition to H/D exchange, there is a reversible reaction with benzene to form the phenyltitanium complex **9**. When H_2 is removed from solution, **9** forms cleanly. However, in NMR tubes sealed under H_2 , thermodynamics strongly favor hydrogenolysis of **9** to form the hydride.

While the initial reaction of benzene with the hydride **5** is rapid, a slower secondary reaction also occurs to form the para-dimetalated compound **10**. The equilibrium for metalation of **9** is again unfavorable, but the reaction proceeds if H_2 is purged or scavenged. The para specificity almost certainly reflects steric constraints imposed by the pentamethylcyclopentadienyl ligands. The structure of **10** is greatly distorted, probably resulting from an interaction between the electrophilic metal and an ortho C-H bond.

The methyltitanium complex **3** also reacts with benzene. As indicated in Figure 5, this overall reaction can be catalyzed by even small amounts of hydrogen,

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(14) Longi, P.; Mazzauti, G.; Roggero, A.; Lachi, A. M. *Makromol. Chem.* **1963**, 61, 63.

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(17) Shilov, A. E.; Shteinman, A. A. *Coord. Chem. Rev.* **1977**, 24, 97. Shilov, A. E. *Soviet Sci. Rev., Sect. B* **1982**, 4, 71.

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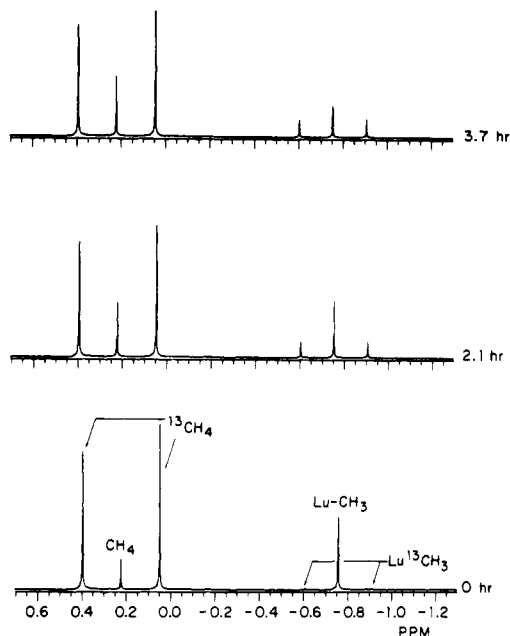


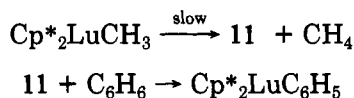
Figure 6. Proton NMR spectrum of a mixture of $\text{Cp}^*_2\text{LuCH}_3$ and methane- ^{13}C as a function of time.

via formation of the hydride **5**, which in turn reacts with benzene to give **9**.¹⁵

The direct reaction of benzene with **3** is much slower, and proved to be a summation of at least two reactions.²² The rate equation from kinetic studies (eq 5)

$$-(d[\mathbf{3}]/dt) = (k_1 + k_2[\text{C}_6\text{H}_6])[\mathbf{3}] \quad (5)$$

showed both a unimolecular and a bimolecular component. At 70 °C, the bimolecular pathway, which is dependent on the concentration of benzene, dominates by more than an order of magnitude. The alternative, benzene-independent pathway suggests slow formation of an intermediate, **11**, which reacts rapidly with benzene. A possibility for intermediate **11** could be the



ring-metalated complex resulting from extrusion of methane. Such complexes are known for Ti^{23} and W .²⁴ However, simply heating **3** did not result in formation of this structure and methane at the anticipated rate. Complex **3** appeared quite stable at 70 °C. However, the mechanism would be valid if the methane extrusion reaction were reversible. This possibility would demand the direct reaction of methane with an organometallic compound. Other members of our group had sought reactions of methane, but none of the attempts with transition-metal systems had been successful.

Methane Activation. A simple test of the hypothetical methane reaction was available. A solution of the methyl complex **3** in cyclohexane- d_{12} was sealed in an NMR tube along with an atmosphere of methane- ^{13}C (about 10% methane- ^{12}C). The proton NMR spectrum was recorded (Figure 6, time 0) and the sample was heated to 70 °C. Initially the $\text{Lu}-\text{CH}_3$ signal showed

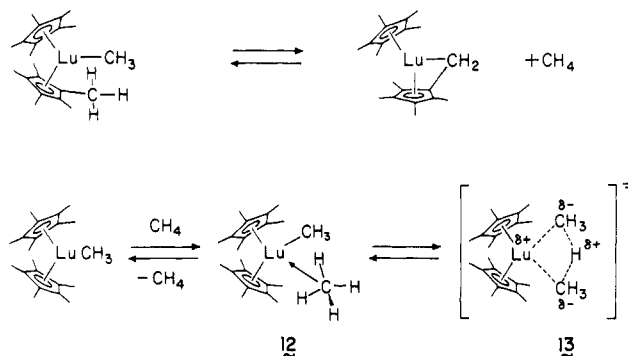
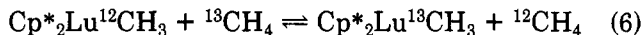


Figure 7. Proposed mechanisms for the unimolecular and bimolecular exchange of methane with the methyl lutetium compound.

only the tiny ^{13}C satellites assignable to the 1.1% natural abundance of ^{13}C . Over the course of 3.7 h, the combined area of the satellites grew to equal that of the central peak. Simultaneously, the methane- ^{12}C peak increased in intensity. Clearly, the $^{13}\text{CH}_4$ was exchanging with the methyl group of **3**.²² The reaction was then studied as a function of methane concentration, and it was found that in fact the major pathway was bimolecular. Methane perhaps coordinates very weakly to the electrophilic Lu center (**12**), followed by electrocyclic rearrangement with proton transfer which results in methyl group exchange (eq 6).



Our thoughts turned to the implications of this reaction. If methane, the most recalcitrant of the alkanes, would react with **3**, why not higher paraffins? We knew from the methane experiment that cyclohexane, which was used as the solvent, did not compete detectably with methane. Presumably, the C_6H_{12} molecule is too large to enter the narrow belt between the two C_5Me_5 ligands in **3**. But what about linear alkanes? Ethane and propane did react, although more slowly than $^{13}\text{C}-\text{H}_4$, but the alkyl lutetium products decomposed by β -hydrogen transfer. A polarized transition state (Figure 7, **13**) would explain the slower reactivity of higher alkanes.

The complexity of the methane exchange reaction can be explained by assuming that both reaction paths of Figure 7 are significant. The methane-dependent route might involve very weak coordination of methane to **3** in a complex **12** in which C-H bonds supply electron density to a vacant orbital of **3** in a structure like that of the methyl lutetium dimer (although, of course, less stable). This precoordination sets the stage for hydrogen transfer from methane to the methyl group of **3**.

Further studies of the reaction of methane- ^{13}C with the metal-variant complexes $\text{Cp}^*_2\text{M}-\text{CH}_3$ ($\text{M} = \text{Sc}$,²⁵ Lu, and Y) are in progress. Results so far indicate that the rate increases with electrophilicity of the metal center; thus, $\text{Cp}^*_2\text{Y}-\text{Me}$ —the most electrophilic—is about an order of magnitude more reactive than the lutetium complex (Figure 8).

Conclusions

This study of organolanthanide chemistry nicely illustrated the rewards potentially available from the

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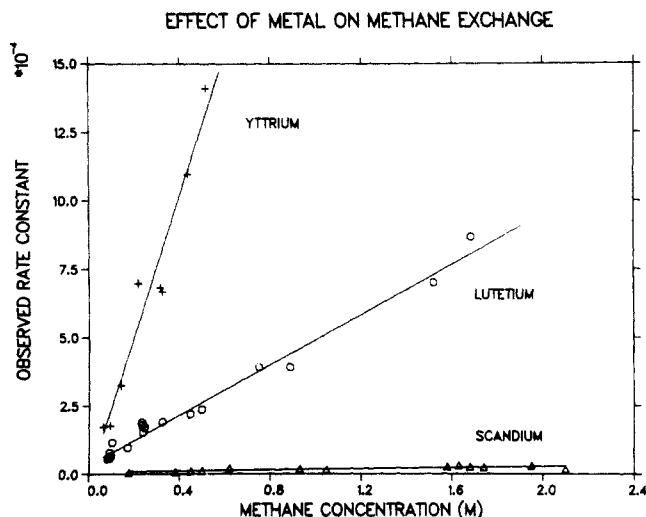


Figure 8. Variation of the metal center in CH_3 ($M = \text{Y, Lu, Sc}$) complexes causes significant variation in the rate of the methane exchange reaction. The apparent bimolecular rate constants for exchange are $0.01 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ (Sc), $0.460 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ (Lu), and $2.6 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ (Y).

exploration of new, highly reactive compounds. The olefin polymerization catalysis was extremely informative. Even though the types of complexes we explored are unlikely to have commercial application, they pro-

vide excellent models for study of coordination polymerization. The possible significance of paramagnetism in olefin insertion has not been established.

Beyond illustration of known processes, the lutetium model also called attention to generally unappreciated reaction pathways for termination of polymer chain growth. The termination and chain-transfer mechanism, β -alkyl extrusion, unknown for transition-metal alkyl compounds, will probably prove ubiquitous as we learn how to detect it. Indeed, it may become a model for catalytic C-C bond activation in hydrocarbons. The importance of both allylic and vinylic C-H bond activation in termination or chain transfer may be particularly important in the polymerization of α -olefins where chain propagation is much slower than for ethylene and alternative reactions of the olefins can compete.

The discovery of C-H bond reactions involving olefins, arenes, and even alkanes was important in the chemistry of the organolanthanides. In retrospect, it is reasonable that depriving a lanthanide complex of conventional donor ligands would create a fiercely electrophilic species and that such an electrophile might seize upon the C-H bond of a hydrocarbon as a source of electrons. The unexpected reaction of methane dramatically illustrated this point.

Metal-Pentadienyl Chemistry

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The cyclopentadienyl (C_5H_5) and allyl (C_3H_5) groups¹ are two of the most important ligands in inorganic and organometallic chemistry. Interestingly, these two ligands are important for two different reasons. The former, a closed, five-membered ligand, is noted for its great abilities as a stabilizing ligand, which can be well exemplified by the now classic metallocene compounds. As a result many detailed physical studies have been carried out on these systems and a great deal of information regarding structure and bonding is known. However, in chemical reactions the cyclopentadienyl ligand generally plays the role of an uninvolved spectator, although organic ring-substitution processes must not be overlooked.² In contrast, the open, three-membered allyl ligand can hardly be regarded as a stabilizing ligand. In particular, few homoleptic first-row transition-metal allyl compounds, $\text{M}(\text{allyl})_n$, are thermally stable.³ Hence, comparatively little detailed physical data has been gathered for these systems. However, the chemical and catalytic properties of these compounds can be characterized as nothing less than remarkable,⁴

even the very unstable compound tris(allyl)cobalt (decomp pt -40°C) showing versatile reaction chemistry.^{4a}

In comparison, the transition-metal chemistry of the open, five-membered pentadienyl ligand has been all but ignored until recently.⁵ It did not seem to be recognized that pentadienyl ligands, in and of themselves, should have much to contribute to transition-metal chemistry. However, some detailed comparisons (vide infra) involving the general features of a pentadienyl group and those of cyclopentadienyl and allyl groups suggested that the pentadienyl group should be capable of imparting thermal stability as well as chem-

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