106-250 amu range, while toluene yields only a small amount of 128^+ and 129^+ above mass 105.

Acknowledgment. We thank J. J. Gajewski for the samples of **1** and **2** for helpful discussions and the National Science Foundation for financial support.

Registry No. 1, 20679-59-8; **2**, 3217-87-6; toluene, 108-88-3.

Ziegler-Natta Polymerization: The Lanthanide Model[1]

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The formal insertion of an olefin into a metal-carbon (M-C) or metal-hydrogen (M-H) bond is of fundamental significance in a large number of catalytic reactions. While complexes arising from insertion of olefins into the M-H bond have been observed directly[2-4] primary insertion products from the analogous reaction with M-C bonds (reaction 1) have proved experimentally elusive.[5-8] The existence of the latter type of insertion product has often been inferred from the isolation of secondary products which derive from the initial insertion product via such processes as β-hydrogen elimination[9,10] (reaction 2) or further olefin insertion[11] (reaction 3).

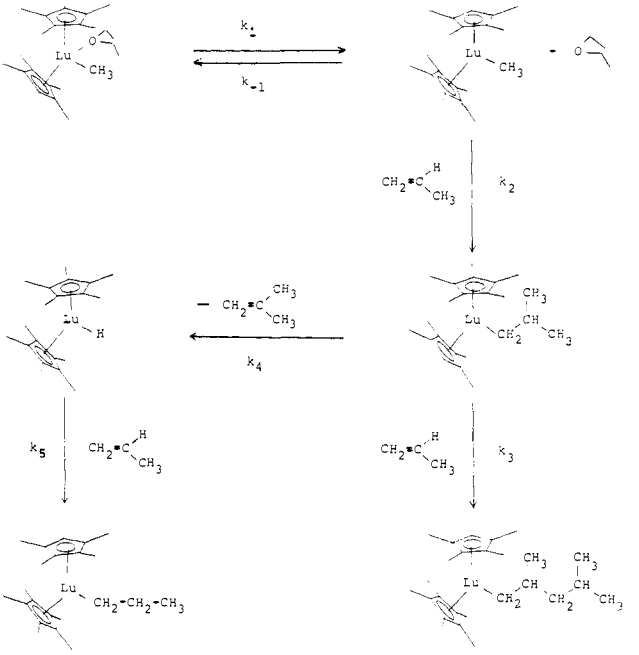
$$L_nM-CR_3 + CH_2=CH_2 \rightarrow L_nM-CH_2-CH_2-CR_3 \quad (1)$$

$$L_nM-CH_2-CH_2-CR_3 \rightarrow L_nM-H + CH_2=CH-CR_3 \quad (2)$$

$$L_nM-CH_2-CH_2-CR_3 + CH_2=CH_2 \rightarrow L_n-CH_2-CH_2-CH_2-CH_2-CR_3 \quad (3)$$

The direct insertion shown in reaction 3 has been postulated[12] to be a major reaction pathway for olefin polymerization using Ziegler-Natta catalysts[13,14] (group 6 transition metal with aluminum alkyl). One important difference between this insertion mechanism[15] and the alternative McKinney[16] or Green[17] mechanisms for olefin polymerization is that the latter two schemes require oxidative additions in order to generate the active metallacyclic or carbenoid intermediates. While these routes may be reasonable for transition metals having at least two d electrons, they are not so reasonable for the lanthanide elements where reversible two-electron couples are generally precluded by the lack of accessible oxidation states.

Scheme I



During our investigations of the reactivity of lanthanide-carbon bonds, we observe insertion of a variety of olefins and acetylenes into the ytterbium- and lutetium-methyl bonds of $M(\eta^5\text{-}C_5Me_5)_2CH_3$·ether (M = Yb, Lu). In these reactions the primary insertion products are observable by spectroscopic and chemical techniques. This preliminary communication describes the synthesis of $M(\eta^5\text{-}C_5Me_5)_2CH_3$·ether (**1**, M = Lu) and the reaction of **1** with propene to give the isobutyl complex $M(\eta^5\text{-}C_5Me_5)_2\text{-}CH_2\text{-}CH(CH_3)_2$ (**2**, M = Lu). The chemistry of $Lu(\eta^5\text{-}C_5Me_5)_2CH_3$·ether and $Yb(\eta^5\text{-}C_5Me_5)_2CH_3$·ether is qualitatively similar with respect to the olefin insertion reaction.

The dimethyl complexes $[M(\eta^5\text{-}C_5Me_5)_2(CH_3)_2]Li(THF)_3$ (M = Yb, Lu) are prepared as described[18] earlier for M = Yb. Conversion of these complexes to the neutral monomethyl species is achieved in several steps. The THF-free materials, $[M(\eta^5\text{-}C_5Me_5)_2(CH_3)_2]Li$ (obtained from the solvated precursors by heating under vacuum at 75 °C), react with $Al(CH_3)_3$ in pentane to give the soluble adducts $M(\eta^5\text{-}C_5Me_5)_2Al(CH_3)_4$.[19] Cleavage of these adducts by dissolution in diethyl ether yields $M(\eta^5\text{-}C_5Me_5)_2CH_3$·ether (M = Yb, Lu)[20,21] which can be crystallized

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(20) These complexes have been completely characterized. Anal. Calcd for $C_{25}H_{43}OYb$: C, 55.37; H, 8.14; O, 3.00; Yb, 32.49. Found: C, 56.05; H, 8.13; O, 2.90; Yb, 32.40. Calcd for $C_{25}H_{43}OLu$: C, 56.16; H, 8.11; O, 2.99; Lu, 32.73. Found: C, 55.97; H, 8.00; O, 2.90; Lu, 32.90. Also, quantitative measurements of the amounts of CH_4 and C_5Me_5H released upon hydrolysis of $M(C_5Me_5)_2CH_3$·ether (M = Yb, Lu) are satisfactory.

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from the solution at −40 °C. The ^{1}H NMR spectrum of the diamagnetic lutetium complex (**1**) shows C_5Me_5 (s, 2.18) and Lu–CH_3 (s, δ −0.49) as well as diethyl ether peaks (q, δ 3.48 and t, δ 1.11) in toluene-d_8.

Solutions of **1** (0.05 M in toluene or cyclohexane) react with propene ([propene]/[**1**] = 5–15) at temperatures between −30 and +20 °C giving the isobutyl complex **2**. The concentration of **2** maximizes at 30–50% of the lutetium present after about 5 min at 20 °C followed by the appearance of secondary products. The ^{1}H NMR spectrum of **2** in toluene-d_8 shows Lu–CH_2–CH-$(CH_3)_2$ (septuplet of triplets, δ 2.42, J_{HH} = 6.59 and 8.28 Hz), C_5Me_5 (s, δ 2.11), $CH(CH_3)_2$ (d, δ 1.17, J_{HH} = 6.59 Hz), and Lu–CH_2 (d, δ 0.53, J_{HH} = 8.2 Hz) peaks. These assignments are based not only on the correct relative intensities but also on a series of isotopic labeling experiments. For example, reaction of **1** with propene-d_6 or reaction of Lu(η^5-$C_5Me_5)_2CD_3$·ether with propene-*1,1,2-d*$_3$ gives as the initial product Lu(η^5-$C_5Me_5)_2$–CD_2–$CD(CH_3)$–CD_3. This complex has peaks only at δ 2.11 and 1.17 in the ^{1}H NMR spectrum. Hydrolysis of the complex generates CHD_2–$CD(CH_3)$–CD_3, as shown by GC–MS analysis. The reaction is quite regiospecific since no *n*-butane is detected.

Secondary products (arising from reactions of **2**) include lutetium 2,4-dimethylpentyl species and isobutene. The relative rates of formation of these products suggest that insertion of propene into the Lu–C σ bond of **2** has a lower activation barrier than that for β-hydrogen elimination from **2**. Confirmation of these species as true reaction products is again achieved by using an isotopic label. Propene-d_6 and **1** produce CD_2=$C(CD_3)$–CH_3 in the reaction mixture, and subsequent hydrolysis yields specifically CHD_2–$CD(CD_3)$–CD_2–$CD(CH_3)$–CD_3 as the only C_7 fragment. Concurrent with production of isobutene is the formation of lutetium propyl species, detected by the appearance of propane in hydrolyzed reaction mixtures. That these arise from reaction of propene with a lutetium hydride[22,23] (presumably the organometallic product of β elimination, Lu(η^5-$C_5Me_5)_2H$[24]) is also suggested by products from reaction of **1** and propene-d_6 in cyclohexane.[25] Protonolysis of this labeled system gives CD_3–CD_2–CD_2H, indicative of an intermediate Lu–$CD_2CD_2CD_3$ moiety arising from insertion of propene-d_6 into a Lu–D bond. Finally, higher oligomers of propene are also observed. Experiments are in progress to determine the tacticity of these oligomers in addition to their modes of decomposition.

Kinetic features of the reaction of **1** with propene leads us to propose the general mechanism shown in Scheme I. This mechanism would also be operative in the polymerization of ethylene for which **1** is a good catalyst.[26]

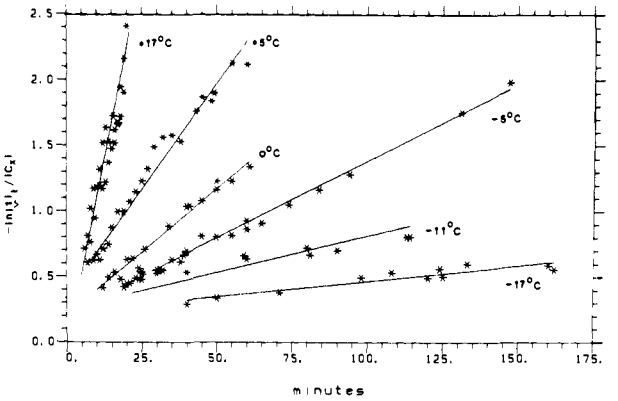

Figure 1. Kinetics of the reaction with excess propene as a function of temperature. Time-dependent values, −ln [**1**]/C_x, were obtained from ^{1}H NMR spectra by using the relative intensities of peaks due to the Lu–CH_3 resonance of **1** and the internal standard bis(trimethyl)silyl ether (C). [Variations of intercept values reflect slightly different concentrations, [C_x], of internal standard in different runs and have no kinetic significance].

Under conditions that are pseudo first order in propene ([propene]/[**1**] = 5–15), the rate of disappearance of **1** (as monitored by ^{1}H NMR spectroscopy) is cleanly first order in [**1**]. The effect of temperature on the rate is illustrated in Figure 1 (0.05 M solutions of **1** in toluene-d_8, [propene]/[**1**] = 12–15). Dependence of the reaction rate on propene concentration is examined by plotting the apparent rate constants (obtained from slopes of −ln [**1**]$_t$ vs. time) against [propene]/[**1**]$_0$ ratios in the range 5–15. The linearity of this plot shows the reaction to be also first order in propene concentration. Dependence of the rate on ether concentration is inverse, shown by a linear plot of (initial rate)$^{-1}$ vs. [ether] for reaction mixtures with [ether]/[**1**]$_0$ = 1–50. These data accommodate the mechanism shown in Scheme I, which predicts the rate eq 4, where the k_{-1}[ether] term controls the denominator. A rapid preequilibrium involving ether dissociation–reassociation is indeed in effect, since solutions of **1** (0.2 M in toluene) in the presence of 1 equiv of ether show rapid exchange of free and coordinated ether sites down to −60 °C. Preliminary computer modeling[28] of data obtained from 0.05 M solutions of **1** in toluene-d_8 gives relative values $k_1/k_{-1}/k_2$ = 0.1:10:0.015 (in s^{-1}). Measured rate constants (approximated by k_1k_2/k_{-1}[ether]) range from 4.0 ± 0.4 × 10^{-3} mol^{-1} s^{-1} at +17 °C to 5.7 ± 0.5 × 10^{-5} mol^{-1} s^{-1} at −17 °C.

$$-\frac{d[\mathbf{1}]}{dt} = \frac{k_1k_2[\mathbf{1}][\text{propene}]}{k_{-1}[\text{ether}] + k_2[\text{propene}]} \quad (4)$$

In conclusion, this system provides the clearest experimental model to date for coordination catalysis of olefin polymerization.[27] It is interesting to note that the M–CH_3 bonds of the alkyl bridged complexes M(η^5-$C_5Me_5)_2Al(CH_3)_4$ (M = Yb, Lu) also insert olefins but at rates significantly lower than for the monomeric M(η^5-$C_5Me_5)_2CH_3$·ether complexes.[29] The scope of these in-

(21) The X-ray determined crystal structures of both [Yb(η^5-$C_5Me_5)_2$-$(CH_3)_2$]Li(THF)$_2$(ether) and Yb(η^5-$C_5Me_5)_2CH_3$·ether will be described fully elsewhere.

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(24) Although the putative hydride Lu(η^5-$C_5Me_5)_2H$ has not been isolated, work toward this goal is in progress. The high chemical reactivity of the species is obvious by its reaction with toluene[25] and diethyl ether. Production of the hydride in situ via conventional hydrogenolysis (1 atm of H_2, 20 °C) of Lu(η^5-$C_5M_e)_2CH_3$·ether (in cyclohexane) is followed very cleanly by an elimination reaction which gives Lu(η^5-$C_5Me_5)_2OCH_2CH_3$ as the isolable organometallic product. Methane (1 equiv) and ethane (1 equiv) are the organic products. We note that elimination reactions are also possible for the methyl complex Lu(η^5-$C_5Me_5)_2CH_3$ with suitable coordinating ligands. For example, Lu(η^5-$C_5Me_5)_2CH_3$·pyridine transforms cleanly over 1 day at 20 °C to methane and Lu(η^5-$C_5Me_5)_2$-C=N(CH)$_4$. Both these elimination reactions are considerably slower than the olefin insertion reactions.

(25) The reaction proceeds similarly in toluene but with the additional complication (for isotopically labeled systems) of rapid hydrogen exchange between the lutetium hydride, Lu($C_5Me_5)_2H$, and toluene. This type of reactivity has been noted for actinide hydrides also.[30] Thus, reaction of Lu($C_5Me_5)_2CH_3$·ether with propene in toluene-d_8, followed by protonolysis, gives both CH_3–CH_2–CH_3 and CH_3–CHD–CH_3 in the C_3 fraction of organic products.

(26) The rate of ethylene polymerization in a batch reactor at 40 °C and 4.3 atm of ethylene is 66 g of polyethylene·(mmol **1**)$^{-1}$·h^{-1}·atm^{-1}. This may be compared with dimeric lanthanide alkyl complexes which exhibit slightly lower activity at higher temperatures (75–100 °C): Ballard, D. G. H.; Courtis, A.; Holton, J.; McMeeking, J.; Pearce, R. *J. Chem. Soc., Chem. Commun.* **1978**, 994–995. "Conference Europeenne des Plastiques et des Caoutchoucs, [Comptes Rendus], 5th"; Societe de Chimie Industrielle, Paris, 1978; pp 1 A4/1–A4/7.

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sertion reactions is under further study, as are alternative reaction pathways available to the lanthanide alkyl and hydride complexes exemplified by the intermediates shown in Scheme I.

Acknowledgment. The fine technical assistance of R. M. Swiatek is gratefully acknowledged. Discussions with Dr. F. N. Tebbe have been most helpful.

Registry No. 1, M = Lu, 80145-92-2; **1**, M = Yb, 80145-93-3; **2**, M = Lu, 80145-94-4; $Lu(\eta^5\text{-}C_5Me_5)_2CH_2CH(CH_3)CH_2CH(CH_3)_2$, 80160-33-4; $[Yb(\eta^5\text{-}C_5Me_5)_2(CH_3)_2]Li(THF)_3$, 80145-96-6; $[Lu(\eta^5\text{-}C_5Me_5)_2(CH_3)_2]Li(THF)_3$, 80145-98-8; $Yb(\eta^5\text{-}C_5Me_5)_2Al(CH_3)_4$, 80145-99-9; $Lu(\eta^5\text{-}C_5Me_5)_2Al(CH_3)_4$, 80146-00-5; propene, 115-07-1.

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Biosynthesis of Elaiomycin. 1. Incorporation of Labeled Forms of *n*-Octylamine

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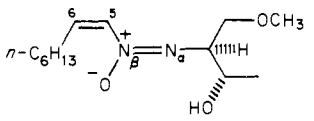
The antibiotic elaiomycin (**1**) is a naturally occurring azoxy compound isolated from the fermentation broth of *Streptomyces gelaticus*.[1] Elaiomycin exhibits novel biological activity since it only shows strong inhibition of certain virulent and avirulent mammalian strains of tubercle bacteria.[2] The antibiotic has also been found to induce tumors in rats.[3] As a naturally occurring azoxy compound, elaiomycin is a member of a small class of unusual natural products that includes (*p*-carboxyphenyl)azoxycyanide,[4] the cycad toxins macrozamin and cycasin,[5] and the antifungal agent LL-BH872α.[6] Up to the present time, no investigations of the biosynthesis of any of these naturally occurring azoxy compounds appear to have been carried out. We would now like to communicate the results of experiments that elucidate some aspects of the biosynthesis of elaiomycin.



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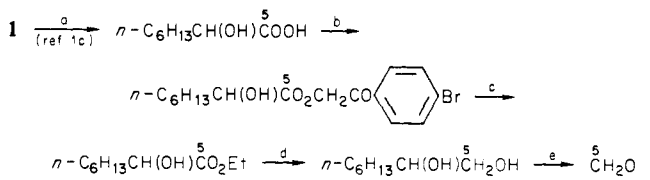
For the purpose of biosynthetic investigation, the elaiomycin molecule can be divided into two segments, a left-hand portion consisting of eight carbon atoms and a right-hand portion containing five carbon atoms. The left-hand portion has been the target of the experiments outlined here. The presence of an eight-carbon unit in the left-hand portion of elaiomycin led us to hypothesize that this part of the molecule would be derived from octanoic acid. Accordingly, sodium [1-^{14}C]octanoate was administered to cultures of *S. gelaticus* and radioactive elaiomycin was isolated (Table I, experiment 1). Intact incorporation of this precursor into elaiomycin was expected to label the antibiotic exclusively at C-5. However, degradation using the route outlined in Scheme I showed that the incorporation was largely nonspecific (Table I, experiment 1). *n*-Octylamine was therefore selected for evaluation as a precursor. [1-^{14}C]-*n*-Octylamine was synthesized by treatment of *n*-heptyl mesylate with potassium [^{14}C]cyanide followed by catalytic reduction of the resulting nitrile. Administration of the labeled *n*-octylamine to *S. gelaticus* yielded radioactive elaiomycin whose degradation proved that the incorporation was specific (Table I, experiment 2).

The specific incorporation of *n*-octylamine into elaiomycin having been established, an experiment was carried out to determine if the β-nitrogen atom of the antibiotic is derived from octylamine. [1-^{13}C,^{15}N]-*n*-Octylamine was synthesized from potassium [^{13}C,^{15}N]cyanide and *n*-heptyl mesylate, and the doubly labeled amine was administered to *S. gelaticus* cultures. The proton noise-decoupled ^{13}C NMR spectrum of the resulting elaiomycin exhibited a strong doublet ($^1J_{CN}$ = 16 Hz) at 135 ppm due to coupling between C-5 and N_β. The height of each of the

Table I. Incorporation of Radiolabeled Precursors into Elaiomycin

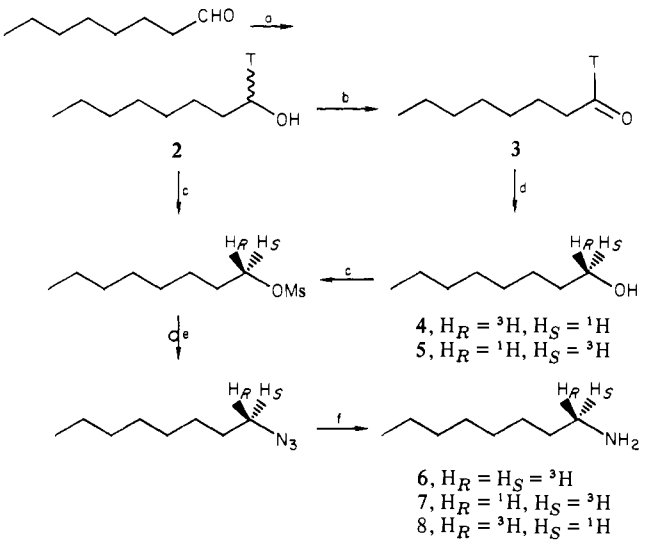
expt no.	precursor (^{3}H/^{14}C)	% incorpn (^{3}H/^{14}C)	labeling pattern (% ^{3}H retention)
1	sodium [1-^{14}C]octanoate	0.07	15% at C-5
2	[1-^{14}C]-*n*-octylamine	0.60	91% at C-5
3	[1(*R*,*S*)-^{3}H,1-^{14}C]-*n*-octylamine (6.16)	(3.06)	(49.7)
4	[1(*R*)-^{3}H,1-^{14}C]-*n*-octylamine (4.99)	(0.70)	(14.0)
5	[1(*S*)-^{3}H,1-^{14}C]-*n*-octylamine (4.09)	(4.07)	(99.5)
6	[2(*R*,*S*)-^{3}H,1-^{14}C]-*n*-octylamine (5.38)	(2.90)	(53.9)
7	[2(*R*)-^{3}H,1-^{14}C]-*n*-octylamine (3.88)	(0.34)	(8.8)
8	[2(*S*)-^{3}H,1-^{14}C]-*n*-octylamine (5.29)	(4.94)	(93.4)

Scheme I[a]



[a] (a) 6 N HCl. (b) *p*-BrPhCOCH$_2$Br, K_2CO_3, 18-crown-6. (c) NaOEt. (d) $LiAlH_4$. (e) $NaIO_4$, dimedone.

Scheme II[a]



[a] (a) [^{3}H]KBH_4. (b) PCC. (c) MsCl, Et_3N. (d) 9-BBN, (-)- or (+)-α-pinene. (e) LiN_3, DMF. (f) H_2, Pd/C.

†NSF Graduate Fellow.

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