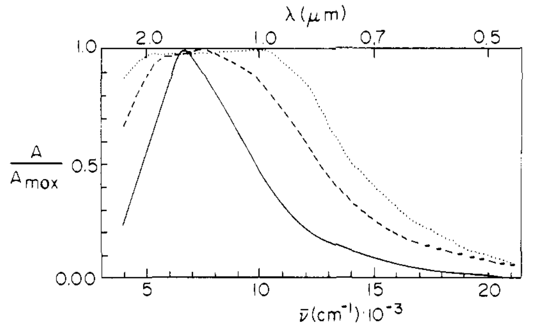

Figure 1. Optical spectra of solvent-free films from methylamine of freshly prepared Cs(18C6) (dotted line) "annealed" Cs(18C6) (dashed line), and $Cs(18C6)_2$ (solid line).

Table I. Some ^{133}Cs Chemical Shifts

compound	δ^a	ref
0.7 M CsI/H_2O	−23	12
$Cs^+I^-(s)$	+284	*b*
$Cs^+SCN^-(s)$	+109	*b*
$Cs^+Cl^-(s)$	+232	*b*
$Cs^+18C6{\cdot}SCN^-(s)$	+73	*b*
$Cs^+18C6{\cdot}I^-(s)$	+179, +171, +164	*b*
Cs^+18C6/Me_2SO	+24	5
Cs^+18C6/pyridine	+10	5
$Cs^+(18C6)_2{\cdot}SCN^-(s)$	−59	*b*
$Cs^+(18C6)_2{\cdot}I^-(s)$	−59	*b*
$Cs^+(18C6)_2$·tetraphenylborate (s)	−43	*b*
$Cs^+(18C6)_2/Me_2SO$	−49	5
$Cs^+(18C6)_2$/pyridine	−48	5
$Cs^+18C6{\cdot}Na^-(s)$	−61	13
$Cs^+(18C6)_2{\cdot}Cs^-(s)$	−61 and −228	*b*
$Cs^+(18C6)_2{\cdot}e^-(s)$	+81	*b*
Cs^-/THF	−292	14

[a] Referred to $Cs^+(aq)$ at infinite dilution. [b] This work.

rie–Weiss slope that is ~75% of that expected for a stoichiometric electride and a Weiss constant of −1.4 K indicating only weakly interacting electrons. EPR studies showed an intense single narrow line with $g = 2.0023$ and a peak-to-peak line width of 0.48 ± 0.5 G independent of temperature from 3 to 260 K. The line showed asymmetry characteristic of high microwave conductivity as described by Dyson[11] with a ratio of low- and high-field intensities A/B that increased with increasing temperatures and corresponded to an apparent "band gap" of ~0.1 eV at these frequencies (9 GHz). Direct current powder conductivities yielded a band gap of 0.9 ± 0.1 eV and a limiting specific conductance at infinite temperature of $\sim 10^2\ \Omega^{-1}\ cm^{-1}$, suggesting that the electride is an intrinsic semiconductor.

In contrast to the measurements with Cs(18C6), *all* of the results with $Cs(18C6)_2$ were as expected for an electride. Thus, we could have two electrides, $Cs^+(18C6){\cdot}e^-$ and $Cs^+(18C6)_2{\cdot}e^-$, or the former could be the ceside $Cs^+(18C6)_2{\cdot}Cs^-$. Definitive proof that one is a ceside and the other is an electride was obtained by ^{133}Cs NMR studies with magic-angle sample spinning (MASS). The chemical shift data are given in Table I along with the chemical shifts of a number of model compounds. The compound Cs(18C6) shows *two* peaks, one at −61 ppm, close to that of other compounds that contain the sandwich complex $Cs^+(18C6)_2$. The second peak is at −228 ppm, clearly so diamagnetically shifted from Cs^+ that it must be due to the anion Cs^-. We conclude that Cs(18C6) is the first stable *ceside* $Cs^+(18C6)_2{\cdot}Cs^-$. The change in the spectrum of a film of the ceside with time toward that characteristic of an electride suggests that the reaction

$$Cs^+(18C6)_2{\cdot}Cs^-(s) \rightarrow Cs^+(18C6)_2{\cdot}e^-(s) + Cs(s) \quad (1)$$

is thermodynamically favored.

The ^{133}Cs MASS-NMR spectrum of $Cs(18C6)_2$ shows only a single peak at +81 ppm, clearly originating from Cs^+. The paramagnetic shift of ~140 ppm from that typical of Cs^+ in the sandwich complex is probably caused by the high concentration of unpaired electrons in this salt. Thus we conclude that $Cs(18C6)_2$ is the *electride* $Cs^+(18C6)_2{\cdot}e^-$.

Acknowledgment. This work was supported by the National Science Foundation under Grant DMR-79-21979. We are grateful to S. Dawes for assistance with sample preparation.

Registry No. $Cs^+(18C_6)_2{\cdot}e^-$, 87039-73-4; $Cs^+(18C_6)_2{\cdot}Cs^-$, 87039-74-5; $Cs^+(18C_6){\cdot}e^-$, 82065-73-4.

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Methane Exchange Reactions of Lanthanide and Early-Transition-Metal Methyl Complexes

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Reactions of alkane C–H bonds are of both commercial and academic interest. We reported[1] recently that lutetium methyl and hydride complexes $Lu(\eta^5\text{-}C_5Me_5)_2R$ ($R = CH_3$, H) react readily with various sp^2 and sp^3 C–H bonds. We now find that the lanthanide complexes also react with the completely unactivated sp^3 bonds of methane, as detected by the exchange reaction (eq 1) with $^{13}CH_4$. This is the first well-characterized example

$$M(\eta^5\text{-}C_5Me_5)_2CH_3 + {}^{13}CH_4 \rightleftarrows M(\eta^5\text{-}C_5Me_5)_2{}^{13}CH_3 + CH_4 \quad (1)$$

1a, M = Lu
1b, M = Y

of the reaction of methane with a homogeneous organometallic complex. A general understanding of the mechanisms involved in this process[2] and of analogies with the transition-metal C–H activation systems[3-14] could facilitate rational approaches to

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functionalization of saturated hydrocarbons.

The methane exchange reactions (eq 1) were discovered during kinetic investigations of the reaction of **1a** with benzene (eq 2).[1,15]

$$\mathrm{Lu}(\eta^5\text{-}\mathrm{C_5Me_5})_2\mathrm{CH_3} + \mathrm{C_6H_6} \rightarrow \underset{\mathbf{2}}{\mathrm{Lu}(\eta^5\text{-}\mathrm{C_5Me_5})_2\mathrm{C_6H_5}} + \mathrm{CH_4} \qquad (2)$$

Detailed kinetics suggested a predominately bimolecular mechanism but with a component zero order in benzene, leading to the rate equation $-d[\mathbf{1a}]/dt = (k_1 + k_2[\text{benzene}])\,[\mathbf{1a}]$. At 70 °C k_1 is about 0.2×10^{-4} s^{-1} and k_2 is about 5.6×10^{-4} M^{-1} s^{-1}. With benzene-d_6 as reagent the real kinetic isotope effect k_H/k_D of the bimolecular term is 5.5, while the k_1 term shows no isotope effect and generates only CH_4.[16] The first mechanism in Figure 1 (eq 3 forward) could account for the apparent unimolecular pathway, where rapid reaction of benzene with the intermediate complex **3** then generates the phenyl product **2**. It was reasoned that in the absence of a reactant such as benzene, k_1 should also be the apparent decomposition rate constant for **1a**. From previous studies it was clear, however, that the rate of thermal decomposition of **1a** in a sealed NMR tube is in fact much, much slower, about 10^{-9} s^{-1}. These observations were reconciled by postulating that the methane elimination reaction must be reversible.

Exchange of $^{13}CH_4$ with either **1a** or the analogous yttrium complex **1b** indeed does occur. Kinetic studies using **1a** show, however, that a bimolecular process is again the major reaction pathway. Heating **1a** or **1b** in cyclohexane-d_{12} at 70 °C with several equivalents of $^{13}CH_4$ in sealed NMR tubes results in the incorporation of the ^{13}C label into the MCH_3 sites of the organometallic complexes (eq 1).[17] A concomitant decrease in $^{13}CH_4$ intensity and increase in that of $^{12}CH_4$ is seen by both ^1H and ^{13}C NMR.[18] Also, CD_4 and **1a** give $\mathrm{Lu}(\eta^5\text{-}\mathrm{C_5Me_5})_2\mathrm{CD_3}$ by ^2H NMR. Figure 2 shows typical ^1H NMR spectra as a function of time for complex **1a**. The half-life of the reaction shown in Figure 2 is about 3.7 h at 70 °C, with $k_{obsd} = 0.52\ (\pm 0.1) \times 10^{-4}$ s^{-1}. With solution concentrations of $^{13}CH_4$ between 0.02 and 1.7 M, a linear relationship between k_{obsd}[19] and $[^{13}CH_4]$ is evident. As shown in Figure 3 a small, nonzero intercept is observed, leading to the rate equation $-d[\mathbf{1a}]/dt = (k_1 + k_2[^{13}CH_4])\,[\mathbf{1a}]$. Preliminary values[20] of $k_1 = 0.23\ (\pm 0.05) \times 10^{-4}$ s^{-1} and $k_2 = 4.7\ (\pm 0.1) \times 10^{-4}$ M^{-1} s^{-1} are obtained. The major, bimolecular mechanism accounting for the k_2 term in the rate equation could proceed through the symmetrical transition state shown (eq 4, Figure 1). Monomer **1a** (rather than dimer **4**) appears to be the active species since the observed rate constant decreases with increasing total lutetium concentration (decreasing proportion of monomer) at constant methane pressure.[21] Further evidence is required to confirm existence of the slow k_1 term which could

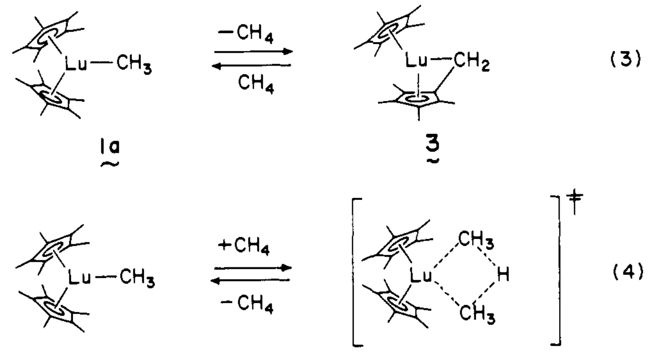

Figure 1. Probable mechanisms for the methane exchange reaction.

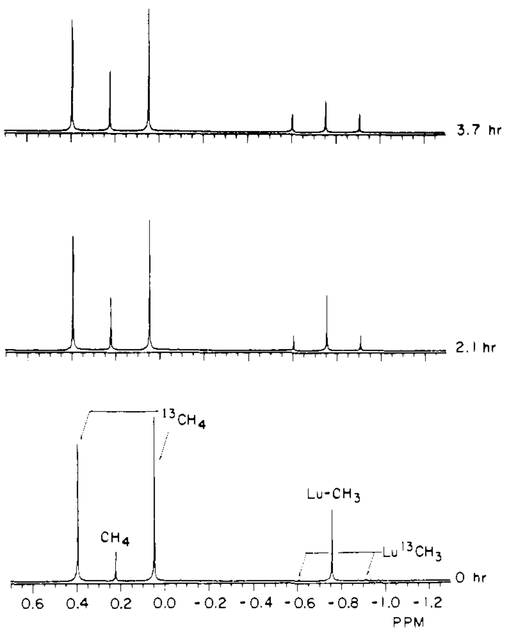

Figure 2. 360-MHz ^1H NMR spectra of **1a** (~0.06 M in cyclohexane-d_{12}) and $^{13}CH_4$ (0.15 M) in a sealed tube as a function of time at 70 °C.[18] (The C_5Me_5 resonance at 1.96 *ppm* is not shown.)

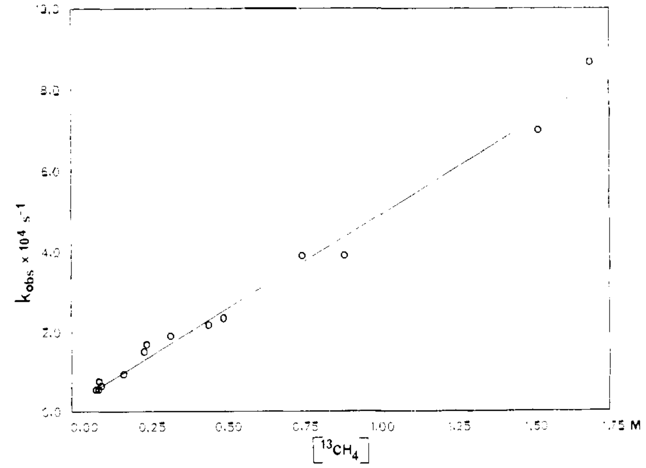

Figure 3. Values of k_{obsd} (obtained from plots of -ln [**1a**] vs. time) as a function of $^{13}CH_4$ solution concentration (in cyclohexane-d_{12} solution at 70 °C). Reactions were pseudo first order in $^{13}CH_4$ even at 0.02 M due to gas-phase buffering. Data are uncorrected for pressure effects.

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(15) As discussed further in the text, **1a** reversibly dimerizes to 4 in solution. To simplify discussion "**1a**" in the text refers to the rapidly equilibrating mixture of **1a** and 4 unless the monomer **1a** is specifically designated as such.

(16) The "observed" isotope effect therefore is a function of reagent concentrations and also varies anomalously with temperature.

(17) Kinetic samples in sealed 5-mm NMR tubes contained **1a** (0.00003 mmol), C_6D_{12} (0.5 m*L*), and $^{13}CH_4$ (0.0006–0.0054 mmol). At 70 °C, an estimated 20% CH_4 was in solution; accurate (±5%) concentrations were obtained with cyclooctane as internal standard. $^{13}CH_4$ (Merck or Stohler) was typically 90% $^{13}CH_4$, 10% $^{12}CH_4$.

(18) Diffusional mixing between gas and solution phases is slow in 5-mm tubes. Spectra in Figure 2 reflect this, but kinetic runs with similar low $^{13}CH_4$ concentrations were shaken between data points to ensure equilibration with excess $^{13}CH_4$ in the gas phase.

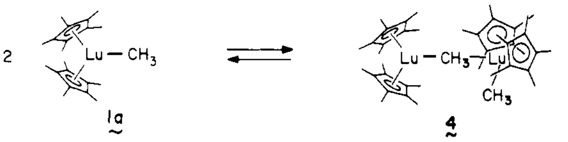
(19) The observed rate constants are taken as the slope of plots of -ln $[\mathbf{1a}\text{-}^{12}\mathrm{C} + 2\,\mathbf{4}\text{-}^{12,12}\mathrm{C}_2 + 4\text{-}^{12,13}\mathrm{C}_2]$, i.e., the single averaged Lu-$^{12}CH_3$ resonance vs. time. Because eq 5 is a rapid preequilibrium ($k_{forward}$, $k_{reverse} >> 10$ s^{-1}) and because the ratio of total monomer $[\mathbf{1a}\text{-}^{12}\mathrm{C} + \mathbf{1a}\text{-}^{13}\mathrm{C}]$ to dimer $[4\text{-}^{12,12}\mathrm{C}_2 + \mathbf{4}\text{-}^{12,13}\mathrm{C}_2 + \mathbf{4}\text{-}^{13,13}\mathrm{C}_2]$ does not change at a given total concentration, $[\mathbf{1a}\text{-}^{12}\mathrm{C}] = \text{constant } x\ [\mathbf{1a}\text{-}^{12}\mathrm{C} + 2\ 4\text{-}^{12,12}\mathrm{C,C} + 4\text{-}^{12,13}\mathrm{C,C}]$. Plots of −ln $[\mathrm{Lu}\text{-}^{12}\mathrm{CH_3}]$ vs. time should be linear over 2–4 half-lives (depending on the ratio of ^{12}C to ^{13}C in the system) in these experiments with excess $^{13}CH_4$. Typically only data from the first 20–30% of reaction was used.

(20) Rate constants in the text are not corrected for the preequlibrium (eq 5). Extrapolation of equilibrium data obtained between −20 and +40 °C gives K_{eq} for eq 5 = 14.3 M^{-1} at 70 °C in cyclohexane.[25] Total lutetium concentration in the methane exchange reactions described was 0.06 M and the concentration of monomer thus would be 0.0315 M. Since the monomer concentration $[\mathbf{1a}\text{-}^{13}\mathrm{C} + \mathbf{1a}\text{-}^{12}\mathrm{C}]$ must remain constant throughout the exchange reaction, a correction factor (multiplication by 1.9) could be applied to k_1 and k_2 to obtain the preequilibrium-independent values.

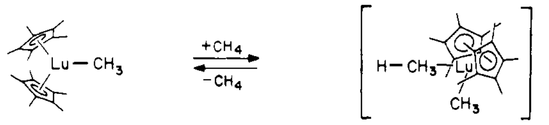
(21) Total lutetium concentrations ranged from 0.12 to 0.019 M, with $[^{13}CH_4]$ constant at 0.4 M.

involve intermediate **3**[22,23] or metalated dimers derived from **4** by loss of CH_4.

Both the lutetium and yttrium methyl complexes $M(\eta^5\text{-}C_5Me_5)_2CH_3$ (**1a**, M = Lu; **1b**, M = Y) exist as asymmetric dimers in the solid state. Dimeric structure **4** (shown in eq 5)



1a **4** (5)



(6)

is confirmed by the solid-state ^{13}C NMR spectra (for M = Lu, Y)[24] and X-ray crystallography (for M = Lu).[25] In hydrocarbon solution the dimers dissociate rapidly and reversibly (eq 5, fast on the NMR time scale above −40 °C), providing measurable concentrations of the coordinatively unsaturated monomers. Monomer **1a** was shown to be the reactive species in olefin insertion chemistry[26,27] and C–H activation reactions.[1] Features pertinent to reactivity are the following: (1) Steric bulk of the $M(\eta^5\text{-}C_5Me_5)_2$ unit prevents formation of a more stable, symmetrical dimer with both methyl groups bridging as in $Ln[(\eta^5\text{-}C_5H_5)_2CH_3]_2$.[28] (2) The monomers are strong Lewis acids and electron density requirements can be satisfied either by coordination of Lewis bases[27] or via three-center interactions with σ-CH bonds.[29] The structural analogy between bridging coordination of a methyl group as in the dimer and weak initial coordination of a hydrocarbon such as methane (eq 6) should be emphasized. (3) For d_0 metals such as lutetium and yttrium, oxidative addition and reductive elimination sequences would generate intermediates in unreasonable oxidation states (e.g., +5 or +1) and are considered unlikely.

Other hydrocarbons, such as ethane and propane, also react with **1a** and **1b** but the products decompose via β-hydrogen elimination. The kinetic advantage of methane over the solvent cyclohexane-d_{12} in these experiments is probably both steric and isotopic in origin.

In conclusion, alkane activation in these systems probably depends on the electrophilicity of the metal center. The C–H bond(s) of the substrate alkane initially acts as an electron donor, a source of electron density. This type of interaction is structurally and spectroscopically characterized in intramolecular transition-metal complexes.[30] Having demonstrated the alkane exchange reaction for both lanthanide and group 3 metals, we expect reactivity with other electron-deficient, coordinately unsaturated organometallic species and are currently investigating reaction mechanisms for the isostructural series $M(\eta^5\text{-}C_5Me_5)_2CH_3$.

Acknowledgment. The excellent technical assistance of W. Dietrich and B. Dunn is gratefully acknowledged. Discussions with G. W. Parshall, F. N. Tebbe, and D. C. Roe are most appreciated as are the efforts of R. Farlee in obtaining solid-state ^{13}C NMR spectra.

Registry No. 1a, 85962-87-4; **1b**, 87136-56-9; $Lu(\eta^5\text{-}C_5Me_5)_2{}^{13}CH_3$, 87136-57-0; $Y(\eta^5\text{-}C_5Me_5)_2{}^{13}CH_3$, 87136-58-1; $^{13}CH_4$, 6532-48-5; CH_4, 74-82-8.

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(24) NMR shows only dimers in solid state at 23 °C and in solution below −60 °C. Spectrum of **1a**: solid-state ^{13}C NMR 11.1, 11.7, 12.4 (ring CH_3, 1:2:1), 20, 24 ($LuCH_3$ very broad, 1:1) 114.4, 114.9, 119.6, 120.6 (ring C, 1:1:1:1), ppm; ^{13}C NMR (−80 °C, toluene) 119.4, 118.9, 114.2 (ring C, 1:1:2), 25.6, 20.6 ($LuCH_3$, 1:1), 12.0, 10.8, 10.7 (ring CH_3, 2:1:1). ^{13}C NMR of **1b** (−80 °C, toluene) 119.6, 119.0, 114.7 (ring C, 1:1:2), 22.0, 21.8 (YCH_3, 1:1, J_{YC} 42.7, 51.1 Hz, respectively), 12.0, 10.7 (ring CH_3, 1:1) ppm. ^1H NMR of **1a**: (−90 °C, toluene-d_8) δ −1.47, −0.30 ($LuCH_3$, 1:1), 1.76, 1.81, 2.22 (ring CH_3, 1:1:2); (20 °C, cyclohexane-d_{12}) δ 1.98 (s, ring CH_3), −1.00 (s, $LuCH_3$). ^1H NMR of **1b**: (−95 °C, toluene-d_8) δ −1.65, −0.41 (YCH_3, 1:1), 1.69, 1.74, 2.18 (ring CH_3, 1:1:2); (20 °C, cyclohexane-d_{12}) δ 1.97 (s, ring CH_3), −1.22 (br s, YCH_3).

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Experimental and Theoretical Evaluation of the Mechanism of HCN Formation in the Reaction between Carbon and Ammonia

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In a recent investigation of the reaction of atomic carbon with ammonia, we have reported that methyleneimine (**1**) and HCN are initial products.[1,2] Although it is reasonable to postulate that **1** arises via the series of reactions in eq 1, the mechanism of HCN

$$\mathrm{C} + \mathrm{NH_3} \rightarrow \underset{\mathbf{2}}{\overset{-}{\mathrm{C}}\text{–}\overset{+}{\mathrm{N}}\mathrm{H_3}^{+}} \rightarrow \underset{\mathbf{3}}{\mathrm{H{—}C{—}NH_2}} \rightarrow \underset{\mathbf{1}}{\mathrm{H_2C{=}NH}} \tag{1}$$

formation is not clear. The fact that carbon is an extremely high-energy species leads to the possibility that **1**, **2**, or **3** could be generated with sufficient excess energy to eliminate hydrogen. We now report a combined theoretical and experimental evaluation of the mechanism of HCN formation in which we reach the interesting conclusion that HCN is generated via elimination of H_2 from initial complex **2** followed by rearrangement of HNC to HCN.

In order to estimate the most plausible route to HCN in this system, we have calculated the relative energies of **1**, **2**, and **3** and the activation enthalpies for loss of hydrogen from each of these species. The geometries of all intermediates and transition states were initially optimized at the Hartee–Fock level with a 3-21G basis.[4] Energies were then calculated by the MP3/6-31G** method.[4] The energies of **1**–**3** were also calculated with a multiconfiguration approach (MCSCF).[5] The geometry of **2** was reoptimized with imposed C_{3v} symmetry by using a MCSCF wave function with a 3-21G basis[6] and the energy of this geometry calculated by the MCSCF/CI/6-31G** method.[7] Since the above geometry of **2** differs little when calculated by single

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