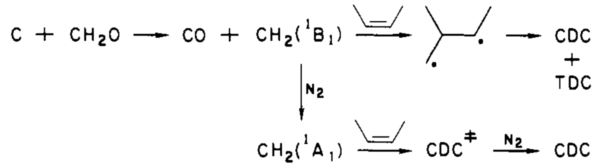
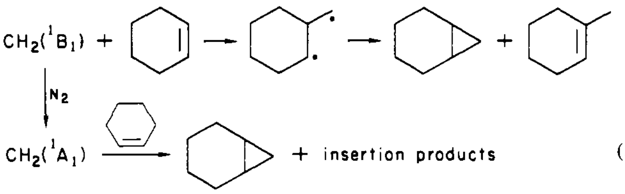
constant for $CDC^* \rightarrow TDC^*$ (k_g) as a function of the energy of CDC^*. If one assumes that the CH_2 carries away 30% of the exothermicity of eq 1,[16] the data of Simmons and Taylor[15] lead to the conclusion that the energy of CDC^* is $\simeq$ 129 kcal/mol and that $k_g \simeq 2 \times 10^9$ s^{-1}. However, the collisional frequency at 620 torr of (Z)-2-butene is on the order of 1.8×10^{10} s^{-1}, and a pressure effect on stereochemistry would be expected if highly energetic $CH_2(A_1)$ were the reactive species.

Thus these results are consistent with the formation of $CH_2(^1B_1)$ in the C atom deoxygenation of CH_2O. This $CH_2(^1B_1)$ is degraded to $CH_2(^1A_1)$ by N_2 but reacts with **1** in a nonstereospecific manner (eq 4) as predicted by Hoffmann.[2] The postulated degradation of $CH_2(^1B_1)$ to $CH_2(^1A_1)$ by N_2 is consistent with earlier observations by Herzberg[17] who reports that $CH_2(^1A_1)$ is only detectable in the flash photolysis of diazomethane when 200 torr of N_2 is added to degrade an initial excited species.



(4)

The reaction of deoxygenatively produced CH_2 with cyclohexene (eq 2) also indicates a CH_2 of different reactivity than that which has been previously observed. Table II compares the present results with those obtained by Rose, Haas, Powers, and Whitney[18] in the gas-phase photolysis of diazomethane with cyclohexene. It is particularly interesting that the product ratios, which have previously been demonstrated to be independent of pressure,[18] differ in the two reactions. In particular, there is far more 1-methylcyclohexene generated in the reactions of deoxygenatively produced CH_2 with cyclohexene than in the reactions of CH_2 formed from diazomethane. This fact is consistent with the production of $CH_2(^1B_1)$, which undergoes addition via a biradical (eq 5). Addition of N_2 serves to degrade the $CH_2(^1B_1)$ to $CH_2(^1A_1)$, which adds to cyclohexene to generate products in a ratio strikingly similar to that observed by Rose et al.[18]



(5)

Although these results do not require the intermediacy of $CH_2(^1B_1)$, they strongly indicate the presence of a nontriplet CH_2 or methylene transfer agent that is degraded to $CH_2(^1A_1)$ by N_2 and reacts with alkenes to generate cyclopropanes by a biradical mechanism. Although we cannot absolutely rule out the possibility that this high-energy species is some sort of a complex between C and $CH_2{=}O$, it seems unlikely that such a complex would live long enough to undergo second-order reaction with an alkene. Skell and Plonka[6a] find no evidence that a complex between C and carbonyl compounds is stable at 77 K. We are continuing to investigate the possiblity that deoxygenation of carbonyl compounds can provide a nonphotochemical route to excited singlet carbenes.

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Registry No. 1, 590-18-1; CH_2, 2465-56-7; C, 7440-44-0; CH_2O, 50-00-0; 5-diazotetrazole, 86457-85-4; cyclohexene, 110-83-8.

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Cesium 18-Crown-6 Compounds. A Crystalline Ceside and a Crystalline Electride

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We recently[1] reported the isolation of crystals of stoichiometry Cs(18C6) from solutions of cesium and 18-crown-6 (18C6) in a 2-aminopropane–diethyl ether mixture in the presence of dissolved lithium. Although the "sandwich" ceside, $Cs^+(18C6)_2{\cdot}Cs^-$, could not be ruled out, the properties suggested that this crystalline compound was an electride, $Cs^+(18C6){\cdot}e^-$. The strongest argument for the latter assignment was the optical transmission spectrum of a thin solvent-free film. As shown in Figure 1, this film initially had absorptions from both Cs^- and trapped electrons (e_t^-) but with time the absorption due to Cs^- decreased and that due to e_t^- increased. This suggested that the *electride* is the thermodynamically stable form. In addition, the compound $Cs^+(18C6){\cdot}Na^-$ had been isolated[2] so we reasoned that a ceside would have the stoichiometry $Cs_2(18C6)$, ($Cs^+(18C6){\cdot}Cs^-$), rather than Cs(18C6). The susceptibility, EPR spectra and electrical conductivity were compatible with either an electron-doped ceside or a largely spin-paired electride. Spin pairing in electrides had been observed previously[3,4] so the nearly diamagnetic susceptibility was not surprising. While the band gap of 0.8 ± 0.1 eV obtained from powder conductivities was too small for a pure ceside, it could result from electrons trapped at Cs^- vacancies. In fact, extrapolation of the conductivity to infinite temperatures gives a limiting specific conductance of only about 1 Ω^{-1} cm^{-1}, which suggests extrinsic semiconductivity.

In spite of the evidence in favor of the simple electride $Cs^+(18C6){\cdot}e^-$, the ceside $Cs^+(18C6)_2{\cdot}Cs^-$ could not be ruled out since "sandwich" complexes of Cs^+ with crown ethers exist in solution[5] and in solid salts.[6] We reasoned that if Cs(18C6) is the ceside $Cs^+(18C6)_2{\cdot}Cs^-$ then it might be possible to synthesize the corresponding electride $Cs^+(18C6)_2{\cdot}e^-$ by appropriate choices of solvents and solution composition. Black, shiny crystals were prepared by the same method used for Cs(18C6) but with a 1:2 mol ratio of cesium to 18C6. Both types of crystals were also precipitated from mixtures of dimethyl ether and trimethylamine in the absence of lithium.

Analysis of the new crystals by the methods described previously[1,2] showed that they have the stoichiometry $Cs(18C6)_2$, immediately suggesting that this compound is the electride $Cs^+(18C6)_2{\cdot}e^-$. The optical spectrum of a thin film obtained by dissolving the crystals in methylamine and evaporating the solvent from a liquid film as with other alkalides and electrides[7–9] is shown in Figure 1. Only a single narrow peak at 6700 cm^{-1}, independent of time, was observed, as expected for an electride.

Magnetic susceptibility measurements[10] on a sample of this compound showed that it is strongly paramagnetic with a Cu-

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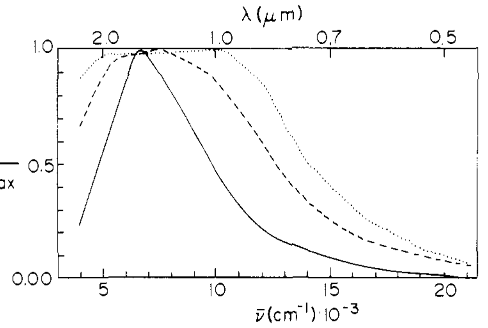

Figure 1. Optical spectra of solvent-free films from methylamine of freshly prepared Cs(18C6) (dotted line) "annealed" Cs(18C6) (dashed line), and $Cs(18C6)_2$ (solid line).

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*
$Cs^+(18C6)_2\cdot$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* $Cs^+(18C6)_2\cdot e^-$.

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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

$$\underset{\substack{\mathbf{1a},\ M = Lu\\ \mathbf{1b},\ M = Y}}{M(\eta^5\text{-}C_5Me_5)_2CH_3} + {}^{13}CH_4 \rightleftarrows M(\eta^5\text{-}C_5Me_5)_2{}^{13}CH_3 + CH_4 \quad (1)$$

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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