

Table I. Selected Distances (Å) and Angles (Deg) in $[\text{Li}(\text{dme})_3][(\text{C}_5\text{H}_5)_2\text{Sm}(\text{Si}(\text{CH}_3)_3)_2]$ with Standard Deviations in Parentheses

Bond Distances			
Sm-Si	2.880 (2)	Sm-C7	2.582 (7)
Sm-C4	2.637 (8)	Sm-C8	2.604 (8)
Sm-C5	2.636 (7)	Sm-Cp ^a	2.316 (7)
Sm-C6	2.602 (7)		
Bond Angles			
Si-Sm-Si' ^b	90.07 (7)	Si-Sm-Cp'	107.8 (2)
Si-Sm-Cp	105.9 (2)	Cp-Sm-Cp'	131.6 (2)

^a Cp denotes the centroid of the cyclopentadienyl ring.

^b Primed atoms represent transformed coordinates of the type $1.5 - x, y, 1.5 - z$.

perature, even when kept in an argon atmosphere. Both derivatives were identified by elemental analyses¹⁴ and NMR spectroscopy.¹⁵ Hydrolysis yields $(\text{CH}_3)_3\text{SiH}$ identified by its absorption in the IR spectrum¹⁶ at 2123 cm^{-1} .

The molecular structure shows $[\text{Li}(\text{dme})_3][(\text{C}_5\text{H}_5)_2\text{Sm}(\text{Si}(\text{CH}_3)_3)_2]$ as discrete cation and anion pairs. Both the cation and the anion possess crystallographically imposed C_2 symmetry;¹⁷ half of both is unique.

The anion $[(\text{C}_5\text{H}_5)_2\text{Sm}(\text{Si}(\text{CH}_3)_3)_2]^-$, shown in Figure 1, is composed of two cyclopentadienyl and two trimethylsilyl ligands arranged in a distorted tetrahedral fashion around the samarium atom, providing a formal coordination number of eight for Sm. The length of the five Sm-C(η^5) bonds varies between 2.582 (7) and 2.637 (8) Å with an average of 2.61 (3) Å (Table I). This value appears surprisingly short when compared with the $d(\text{Sm}-\text{C}(\eta^5))$ for octacoordinated compounds reported earlier¹⁹ (2.75 (5),¹⁸ 2.76 (3),²⁰ 2.72 (3) Å⁷).

It has been shown¹² that the distance M-C(η^5) for bis- and tris(cyclopentadienyl)lanthanide and -actinide complexes varies in direct proportion to the metal ion size, which is a clear indication of predominantly ionic bonding in these compounds. The effective ionic radius for the C_5H_5 ligand was calculated by subtracting the metal ion radius²¹ from $d(\text{M}-\text{C}(\eta^5))$ and determined to be 1.64 (4) Å for 23 organolanthanide and -actinide derivatives included in the calculations.

For the three accurately described bis(cyclopentadienyl)samarium derivatives^{7,18,20} effective ionic radii

between 1.68 and 1.64 Å are obtained for the C_5H_5 ligand ($r_{\text{Sm}} = 1.08 \text{ Å}$ for octacoordinated compounds²¹). In contrast to this, the Sm-C(η^5) distance for the anion $[(\text{C}_5\text{H}_5)_2\text{Sm}(\text{Si}(\text{CH}_3)_3)_2]^-$ would lead to an effective ionic radius of only 1.53 Å for the cyclopentadienyl group. We take this as an indication for a considerably degree of "covalency" in the Sm-C bonds of this anion which was not yet observed this clearly. This trend persists, when the Sm-Si bonds are considered. For the predominantly ionic bonding in $(\text{C}_5\text{H}_5)_2\text{Zr}(\text{Cl})(\text{Si}(\text{C}_6\text{H}_5)_3)$,²² the Zr-Si separation is 2.813 (2) Å. The ionic radius of Sm is 0.239 Å greater;²¹ however, the Sm-Si bond is only 0.067 Å longer ($d(\text{Sm}-\text{Si}) = 2.880 (2) \text{ Å}$) than the Zr-Si bond. Again a covalent shortening of the bonds to samarium may be taking place.

Since all bonds to samarium are shorter than expected for a typical ionic complex, we propose that there is a transfer of electronic charge from the ligands to the metal atom. This behavior can introduce partially covalent bonding into the bonds to samarium and thus cause the observed shortening of the bonds. To examine this possibility, we are presently investigating the f-f transitions of the complex. The bonding parameters associated with the $[\text{Li}(\text{dme})_3]^+$ cation are normal.

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Registry No. Dme, 110-71-4; $\text{Na}(\text{C}_5\text{H}_5)$, 4984-82-1; SmCl_3 , 10361-82-7; $(\text{C}_5\text{H}_5)_2\text{SmCl}$, 56200-25-0; $\text{LiSi}(\text{CH}_3)_3$, 18000-27-6; $[\text{Li}(\text{dme})_3][(\text{C}_5\text{H}_5)_2\text{Sm}(\text{Si}(\text{CH}_3)_3)_2]$, 95156-25-5; $[\text{Li}(\text{dme})_3][(\text{C}_5\text{H}_5)_2\text{Lu}(\text{Si}(\text{CH}_3)_3)_2]$, 95156-27-7; $(\text{C}_5\text{H}_5)_2\text{LuCl}$, 76207-13-1.

Supplementary Material Available: Tables of data collection details, final fractional coordinates, thermal parameters, bond distances and angles, calculated hydrogen positions, least-squares planes, and structure factor amplitudes (19 pages). Ordering information is given on any current masthead page.

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(14) Anal. Calcd for $\text{C}_{28}\text{H}_{58}\text{LiO}_6\text{Si}_2\text{Sm}$: C, 47.75; H, 8.31; Sm, 21.35. Found: C, 46.55; H, 7.25; Sm, 22.12; decomp pt, 136 °C. Anal. Calcd for $\text{C}_{28}\text{H}_{58}\text{LiLuO}_6\text{Si}_2$: C, 46.14; H, 8.03; Lu, 24.00. Found: C, 45.51; H, 7.73; Lu, 24.04; decomp pt, 86 °C. Satisfactory microanalytical data were difficult to obtain since the crystalline products lose coordinatively bonded dme when dried in vacuo.

(15) ¹H NMR (C_6D_6): Sm derivative, δ 0.18 (s, $(\text{CH}_3)_3\text{Si}$, half width 14.5 Hz), 3.15 (s, CH_2O), 3.26 (s, CH_2O), 12.09 (s, C_5H_5 , half width 37.8 Hz); Lu derivative, δ 0.515 (s, $(\text{CH}_3)_3\text{Si}$), 3.07 (s, CH_2O), 3.15 (s, CH_2O), 6.13 (s, C_5H_5).

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(17) Crystal data: space group $P2_1/n$, monoclinic (nonstandard setting of $P2_1/c$, No. 13), $a = 14.460 (4) \text{ Å}$, $b = 9.018 (3) \text{ Å}$, $c = 14.558 (7) \text{ Å}$, $\beta = 103.96 (3)^\circ$, $\rho_{\text{calcd}} = 1.269 \text{ g cm}^{-3}$, $Z = 2$ cation-anion units. Raw data corrected for Lorentz and polarization effects, but because of the low absorption coefficient ($\mu = 15.89 \text{ cm}^{-1}$) not for absorption. Full-matrix least-squares refinement based on 2621 observed reflections ($I \geq 3\sigma(I)$) led to a final $R = \sum(|F_o| - |F_c|) / \sum|F_o| = 0.062$. All non-hydrogen atoms were refined with anisotropic thermal parameters. Sm and Li lie on a special position on the twofold axis (Wyckoff notations e and f). The twofold axis bisects one of the three dme ligands of the cation.

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ESR Study of Paramagnetic Intermediates in the Low-Temperature Photochemistry of Olefins and $\text{Fe}(\text{CO})_5$

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Summary: The low-temperature UV irradiation of dilute pentane solutions of $\text{Fe}(\text{CO})_5$ and tetramethylethylene produces intense ESR spectra of (1,1,2-trimethylallyl)Fe(CO)₃• radicals (I). Similar irradiation of 2,3-dimethyl-1-butene yields the isomeric (2-isopropylallyl)Fe(CO)₃• radical II at -130 °C but only I at -80 °C. The mechanism for the formation and isomerization of these and homologous radicals is discussed.

The thermal and photochemical isomerization of olefins in the presence of simple iron carbonyls has been exten-

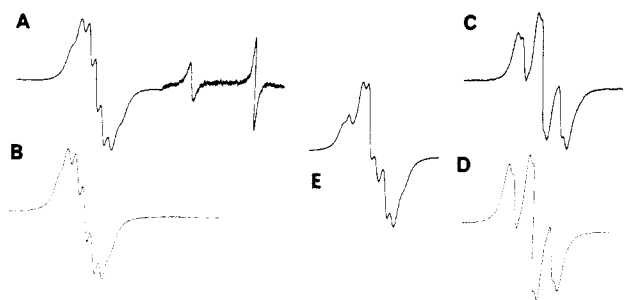
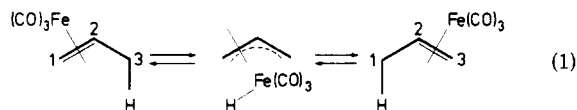


Figure 1. (A) ESR spectrum at $-130\text{ }^{\circ}\text{C}$ obtained by UV photolysis also at $-130\text{ }^{\circ}\text{C}$ of a dilute pentane solution of $\text{Fe}(\text{CO})_5$ and tetramethylethylene. The spectrum at lower field (left side) belongs to I and that at higher field (recorded at higher gain) belongs to $\text{HFe}_2(\text{CO})_8$. (B) Computer-calculated spectrum for I. (C) ESR spectrum at $-130\text{ }^{\circ}\text{C}$ of II obtained by analogous photolysis using 2,3-dimethyl-1-butene. (D) Computer-calculated spectrum for II. (E) ESR spectrum at $-130\text{ }^{\circ}\text{C}$ of a mixture of I and II obtained from 2,3-dimethyl-1-butene (see text).

sively studied as a model process in homogeneous catalysis.¹ A key step in this isomerization is believed to be a 1,3 hydrogen shift which is brought about by a highly reversible interconversion between short-lived 16-electron (alkene) $\text{Fe}(\text{CO})_3$ intermediates and the corresponding 18-electron allyl hydrides (eq 1). The latter have not yet



been detected in solution, and the only direct evidence for their existence rests on a recent matrix-isolation IR study.² We wish to report now that the low-temperature UV irradiation of pentane solutions of certain simple olefins and $\text{Fe}(\text{CO})_5$ produces $(\pi\text{-allyl})\text{Fe}(\text{CO})_3$ radical species³ evidently by hydrogen atom transfer from allyl hydride precursors. We find that these radicals can exist in isomeric forms of different relative stabilities which convert at higher temperatures to the most stable form through the mediation of the elusive allyl hydrides.

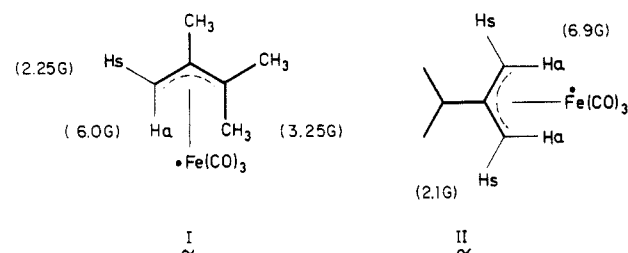
¹ On leave of absence from the Central Research & Development Department, E.I. du Pont de Nemours and Company, Wilmington, DE 19898.

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(3) The parent complex of this series $(\pi\text{-C}_3\text{H}_5)\text{Fe}(\text{CO})_3$ and several of its phosphorus-substituted analogues have been studied before: Murdock, H. D.; Lucken, E. A. C. *Helv. Chim. Acta* **1964**, *47*, 1517. Muettterties, E. L.; Sosinsky, B. A.; Zamaraev, K. I. *J. Am. Chem. Soc.* **1975**, *97*, 5299. Putnik, C. F.; Welter, J. J.; Stucky, G. D.; D'Aniello, M. J., Jr.; Sosinsky, B. A.; Kirner, J. F.; Muettterties, E. L. *Ibid.* **1978**, *100*, 4107. Several $(\pi\text{-cycloalkenyl})\text{Fe}[\text{P}(\text{OMe})_3]_3$ analogues are also known: Ittel, S. D.; Krusic, P. J.; Meakin, P. *J. Am. Chem. Soc.* **1978**, *100*, 3264.

The ESR spectrum of Figure 1A was obtained when a dilute pentane solution of tetramethylethylene ($\sim 0.05\text{ M}$) and $\text{Fe}(\text{CO})_5$ ($\sim 0.02\text{ M}$) was irradiated in a sealed quartz tube for about 10 s at $-130\text{ }^{\circ}\text{C}$ with UV light rich in 254-nm radiation.⁴ The two lines at higher fields ($g = 2.0120$; $a^{\text{H}} = 22.2\text{ G}$) decay rapidly at $-100\text{ }^{\circ}\text{C}$ and have been previously assigned to the very unstable paramagnetic hydride $\text{HFe}_2(\text{CO})_8$.⁵ The intense spectrum at lower fields ($g = 2.0402$),⁶ on the other hand, survives repeated warmings to room temperature. Optimum line widths are obtained at $-125\text{ }^{\circ}\text{C}$. The spectrum can be simulated satisfactorily (Figure 1B) in terms of two doublets (6.0 G; 2.25 G) and a quartet (3.25 G; $\Delta H = 3.0\text{ G}$) and belongs to the $(\pi\text{-allyl})\text{Fe}(\text{CO})_3$ radical I shown below with the assignments



of the hyperfine splittings based on the spectra of simpler analogues.⁷ An appreciable hyperfine interaction for the protons of the methyl group in the anti position of I probably means that these protons can approach closely the metal center during the rotation of the anti methyl group.

If the isomeric 2,3-dimethyl-1-butene (III) is irradiated under exactly the same conditions for about 10 s at $-130\text{ }^{\circ}\text{C}$, the spectrum of Figure 1C ($g = 2.0422$) is detected together with that of the transient $\text{HFe}_2(\text{CO})_8$ radical. The former can be computer simulated in terms of two triplets (Figure 1D; 6.9 G; 2.1 G; $\Delta H = 2.5\text{ G}$) and therefore belongs to the isomeric radical II. It is remarkable that no appreciable amount of I is evident under these conditions although it could have been formed by activation of the tertiary allylic hydrogen in III.

If now the temperature of the sample in the ESR cavity is raised *in the dark* to $-80\text{ }^{\circ}\text{C}$ for several minutes and is then lowered again to $-125\text{ }^{\circ}\text{C}$ to achieve optimum resolution, the spectrum of Figure 1E is obtained which is that of a mixture of I and II. Repeated cycling of this kind brings out more I at the expense of II. After a few cycles, no further changes occur by this procedure. When the photolysis of III and $\text{Fe}(\text{CO})_5$ was carried out directly at $-80\text{ }^{\circ}\text{C}$, however, I was the only paramagnetic species observed. We have established that II cannot by itself rearrange to I. This was done by shortening the irradiation at $-130\text{ }^{\circ}\text{C}$ to 1–3 s. Under these conditions, the spectrum of II was unchanged, save for intensity, even after brief

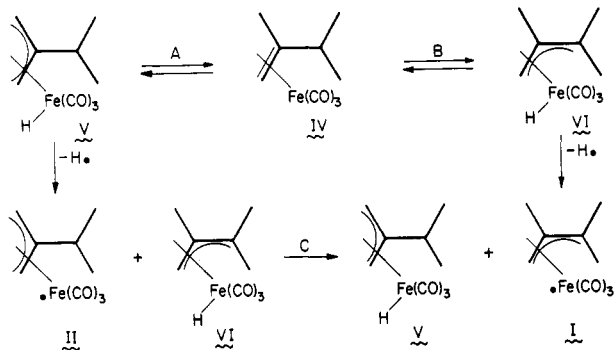
(4) A typical procedure: an ESR quartz tube is filled under nitrogen or argon with 0.4 mL of olefin-free pentane, 1 μL of $\text{Fe}(\text{CO})_5$, and 2 μL of an olefin. The low-temperature irradiation is carried out in a standard quartz Dewar for variable-temperature ESR surrounded by the coils of a low-pressure mercury discharge tube in the shape of a tight spiral. The cooling is provided by a flow of nitrogen cooled by passage through a heat exchanger in liquid nitrogen, and the temperature is measured by a thermocouple. After low-temperature irradiation the tube is quickly plunged into liquid nitrogen and is thus transferred to the ESR cavity kept at the desired low temperature without appreciable warming.

(5) Krusic, P. J. *J. Am. Chem. Soc.* **1981**, *103*, 2131.

(6) The powder spectrum in 3-methylpentane at $-170\text{ }^{\circ}\text{C}$ corresponds to a nearly symmetric g tensor with $g_{\perp} = 2.058$ and $g_{\parallel} = 2.0043$.

(7) Krusic, P. J.; Briere, R.; Rey, P., to be submitted for publication. The 6-G proton splitting must be assigned to the anti allylic proton since it disappears in the spectra of the cycloalkenyl analogues. The protons of CH_3 groups in the 2-position and in the terminal syn position are invisible as they are in the 2-methylallyl and 1-methylallyl analogues.

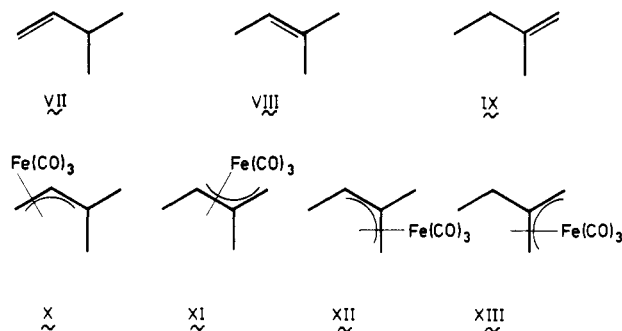
heating to the boiling point of pentane. Evidently sufficient UV irradiation produces a species, invisible by ESR, which is dormant at $-130\text{ }^\circ\text{C}$ but becomes active at higher temperatures in the dark and promotes the conversion of II to I.



We consider that UV irradiation of III and $\text{Fe}(\text{CO})_5$ produces initially the well-known (alkene) $\text{Fe}(\text{CO})_4$ complex and then the short-lived 16-electron intermediate IV by a second photoejection of CO. IV can rearrange to either allyl hydride V or VI, but the exclusive formation of II at $-130\text{ }^\circ\text{C}$ indicates that at this temperature the rearrangement to V is much faster than the rearrangement to VI. The reaction at $-130\text{ }^\circ\text{C}$ is therefore kinetically controlled. It is evidently easier for the coordinatively unsaturated iron center in IV to accept a hydrogen from the freely rotating 2-methyl group than the hydrogen from carbon 3. The low-temperature geometry of IV probably determines this preference. Radical II is formed next by hydrogen atom transfer from V. It is not yet clear exactly how this occurs. We favor a direct homolysis of the Fe-H bond⁸ with concomitant capture of the hydrogen atom by an iron carbonyl fragment or a hydrogen atom abstraction by an iron carbonyl fragment in an excited electron state. Light of short wave length is certainly required for this step to occur efficiently since the use of Pyrex tubes in otherwise identical experiments dramatically reduces the yield of radical species. Be as it may, the removed hydrogen atom is seen in the short-lived radical hydride $\text{HFe}_2(\text{CO})_8$. When the temperature is raised in the dark, II disappears and I appears in its place only after sufficient irradiation, that is, only if there has been sufficient buildup of allyl hydride V. When the sample is warmed, an increased reversibility of equilibria A and B leads to VI which, being the precursor of the thermodynamically more stable radical I, transfers the hydrido hydrogen atoms to II, thus giving rise to I and V (path C). The latter equilibrates again with VI, and path C is repeated until there is no more allyl

hydride or radical II—whichever comes first. In the photolysis at $-80\text{ }^\circ\text{C}$, VI is kinetically accessible, and the more stable radical I is the only observed species.⁹

The greater thermodynamic stability of I relative to its isomer II (without terminal methyl substituents) appears to be related to the syn methyl substituent in I. This conclusion emerges from the results obtained for the isomeric methylbutenes VII-IX. Photolysis at $-80\text{ }^\circ\text{C}$,



exactly as above of each of these olefins, produced the same intense triplet-of-doublets spectrum ($g = 2.0420$; $a(2\text{H}) = 6.4\text{ G}$; $a(1\text{H}) = 2.1\text{ G}$) appropriate for an allylic species with two anti protons and one syn proton which must therefore be attributed to XI. No noticeable amount of the other three possible isomers X, XII, and XIII is formed at this temperature. We conclude that anti methyl substituents as in X and XII have a destabilizing effect and that allylic structures with syn methyl substituents (XI) are more stable than those without terminal substituents (XIII).

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(9) Following the suggestion of a reviewer, we attempted to establish if a separate hydride source would catalyze the $\text{II} \rightarrow \text{I}$ interconversion. We found that addition of tributyltin hydride at low temperatures rapidly quenches the intense spectra of either I or II after brief warmup of the ESR tube to room temperature. Although this result does not answer the reviewer's question, it is consistent with a ready hydrogen atom transfer as postulated in path C. The reviewer also pointed out that the proposed mechanism for the interconversion of allylic iron carbonyl radicals should cause a crossover of deuterium from a deuterated alkene to a nondeuterated one. Such crossover was not observed in a previous mechanistic study of a thermal olefin isomerization catalyzed by $\text{Fe}_3(\text{CO})_{12}$ which was shown to involve an intramolecular 1,3 hydrogen shift (cf. Casey, C. P. et al., ref 1). We are now pursuing this point further and we hope to report the results in the full paper. We note, however, that our ESR concentration measurements indicate that only 1-3% of the starting $\text{Fe}(\text{CO})_5$ is converted to allyliron carbonyl radicals under the typical conditions used.

(8) Cf. Sweany, R. L. *Inorg. Chem.* 1980, 19, 3512; 1982, 21, 752.