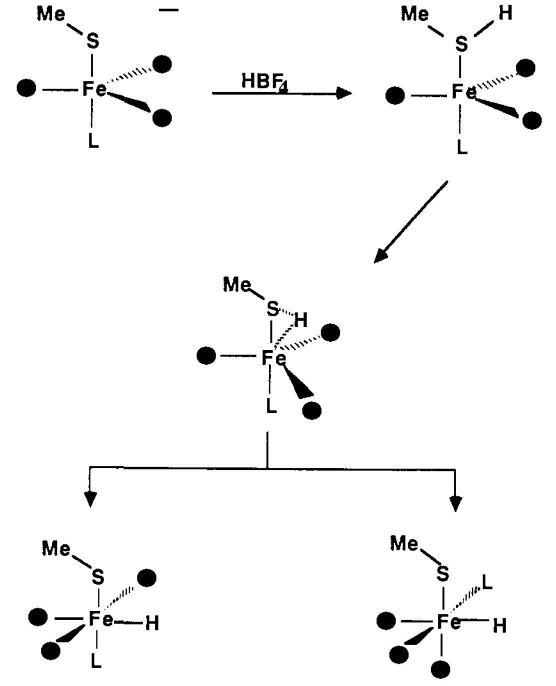
Table I. Spectral Parameters of *trans*-$REFe(CO)_3L^-$ and Protonated Derivatives

		anion				protonated derivatives		
entry		R	E	L	ν(CO)[a]		ν(CO)[e]	^1H NMR (ppm) (acetone-d_6)[j]
1	**1**$^-$	Me	S	CO	2007 (w), 1899 (vs)[b]	1H	2053 (m), 1966 (m), 1944 (s)[f]	2.35
2	**2**$^-$	Ph	S	$P(OEt)_3$	1957 (vw), 1865 (vs)[c]	2H	2076 (m) (2019 (sh), 2013 (s))[g]	−7.22 (d, J_{H-P} = 67 Hz), −7.48 (d, J_{H-P} = 57 Hz)
3	**3**$^-$	Me	Se	$P(OEt)_3$	1950 (vw), 1851 (vs)[c]	3H	2067 (m) (2006 (sh), 2001 (s))[f]	−8.20 (d, J_{H-P} = 56.5 Hz)
4	**4**$^-$	Me	S	$P(OEt)_3$	1952 (vw), 1851 (vs)[c]	4H	1997 (w) (1895 (s), 1890 (s))[f]	−7.65 (d, J_{H-P} = 58.5 Hz)
5	**5**$^-$	Me	S	PEt_3	1934 (vw), 1838 (vs), 1821 (s)[d]	5H	1870 (vs) (2050, 2000, 1980)[h]	−7.88 (d, J_{H-P} = 40.7 Hz)
						5H	2050 (m) (2000 (s), 1980 (vs))[i]	−7.70 (d, J_{H-P} = 42 Hz),[k] −7.97 (d, J_{H-P} = 40 Hz)[k]

[a] THF solution spectra of PPN^+ salts except entry **5**$^-$, which is $[Et_4N][MeSFe(CO)_3PEt_3]$. [b] Spectrum measured at 22 °C. [c] Ca. 0 °C. [d] Ca. −20 °C. [e] THF soluton spectra. [f] Temperature −30 °C, see ref 9a. [g] Temperature −50 °C, see ref 9b. [h] Temperature −57 °C; the species at 1870 cm^{-1} is ca. twice the intensity of the remaining bands. At 0 °C, the relative ratio is reversed. [i] Ca. 0 °C. [j] Varian XL, 400 MHz, spectra measured at −78 °C, except where noted. [k] Spectra measured at −20 °C.

Scheme I



Entries 4 and 5 of Table I are illustrative of attempts to more delicately balance electrophilic site competition. At −78 °C, the ^1H NMR spectrum of **5H** had only one resonance in the high-field region, −7.88 ppm, with J_{H-P} = 40.7 Hz. Although persistent at −78 °C, this resonance decayed on warming, with formation of two new doublets centered at −7.70 ppm (J_{H-P} = 42 Hz) and −7.97 ppm (J_{H-P} = 40 Hz). By −20 °C, the −7.88-ppm doublet was barely visible. On cooling to −78 °C again, the original spectrum did not reappear. The reasonable assumption that the species giving rise to the initial doublet was the kinetic product of a hydride that isomerized into more stable forms at higher temperatures was not corroborated by IR spectral studies. At the lowest temperature that can be achieved in our labs for IR spectral analysis, −57 °C, the predominate product resulting from protonation of $MeSFe(CO)_3(PEt_3)^-$ clearly matched that of an Fe(0) rather than Fe(II) product![18] On warming, the band at 1870 cm^{-1} disappeared, with concomitant formation of a spectrum similar to that observed for **2H** and **3H**, i.e., that of a hydrido thiolate derivative. The hydrido thiolate did not reconvert to the **5H** complex upon subsequent lowering of the temperature.

The scenario presented in Scheme I accounts for the spectral observations of the protonation of **5**$^-$ and invokes the first example of an S–H bond "arrested"[7,8] in its path toward oxidative addition. The high-field resonance for the η^2 (RS–H) proton is entirely consistent with what has been observed for three-center M, H, Si bonding in complexes such as $(\eta^6\text{-}C_6Me_6)(CO)_2\overline{Cr(H)Si}Ph_2H$ (Cr(Si–H) = −11.5 ppm)[19] and the agostic C–H interaction in $(CO)_3(\eta^3\text{-}C_6H_9)Mn$ (Mn(C–H) = −12.8 ppm).[20] That the analogous protonated derivatives of methyl selenate and phenyl thiolate are observed only in the iron(II) hydride form under the conditions of our studies may be explained by the smaller MeSe–H and PhS–H bond energies as compared to MeS–H (75 kcal/mol for MeSe–H and PhS–H vs 90 kcal/mol for MeS–H),[21] requiring a larger activation energy for conversion from the collision complex/kinetic product for the MeSH case. That for L = CO the thiol complex is the only observable low-temperature species represented in Scheme I attests to the extreme sensitivity of Fe to its ligands. It also raises the question of whether oxidative addition is imperative to account for the ultimate products of H_2 elimination and $(\mu\text{-}MeS)_2Fe_2(CO)_6$ formation. Attempts are being made to address this question.

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(18) A band at 2337 cm^{-1} (−57 °C) assigned to the metal-bound ν(MeS–H) disappears upon formation of the Fe(II) hydride (−20 °C). The ν(MeS–H) is 2550 cm^{-1} for the free thiol. The ν(Fe–H) stretch for the latter species could not be definitively assigned due to masking by the ν(CO) bands.

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Predominant Inversion of Configuration in an Intramolecular Carbene Addition to an Alkene

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The reaction of the dibromide **1** with methyllithium was shown by Skattebøl to give the tricyclic hydrocarbon **2**.[1] The ^{13}C NMR spectrum showed that it has C2 symmetry[2] and indicated the bridgehead hydrogens to be trans. The detailed structure of **2** has recently become available via an X-ray crystallographic study.[3]

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(1) Skattebøl, L. *J. Org. Chem.* **1966**, *31*, 2789.

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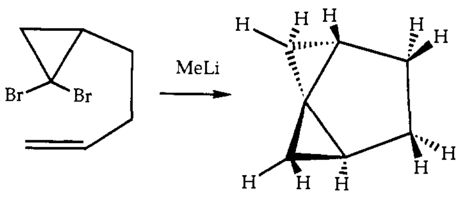
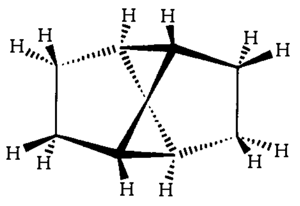
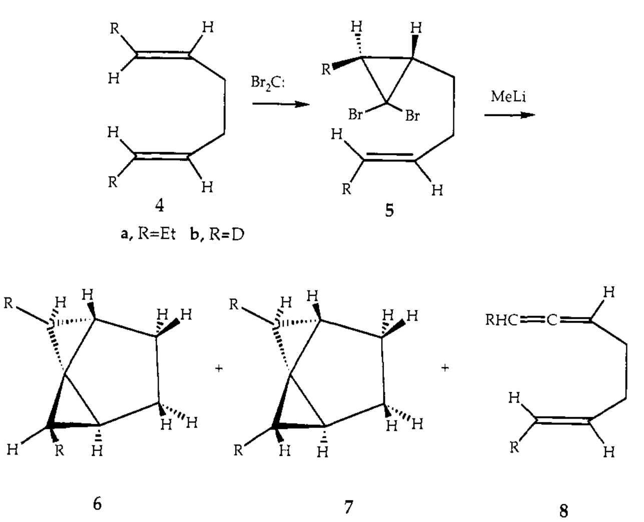


1 2



3

As a model study for a planned synthesis of the tetracyclic hydrocarbon **3**, a related series of reactions starting with *trans*,*trans*-decadiene-3,7 (**4a**) was carried out.



4 5

a, R=Et b, R=D

6 7 8

The reaction of **5a** with methyllithium (−78 °C, ether, 30 min, followed by 30 min at room temperature) proceeded well, giving 40% of the tricyclic hydrocarbon. Two isomers were formed in a 12:1 ratio. The ^{13}C NMR spectrum ($CDCl_3$, 62.9 MHz) of the major isomer had resonances at δ 43.4 (s), 41.8 (d), 40.2 (t), 34.2 (d), 33.0 (t), 25.7 (t), 25.4 (d), 24.8 (d), 21.0 (t), and 13.4 (q, 2 CH_3's),[4] indicating no symmetry. If one assumes a normal stereospecific addition of dibromocarbene to the diene in the first step, the product formed via a normal addition to the double bond in **5a** would have been **7a**, which again has a C2 rotational axis. The lack of symmetry indicates that the hydrogens of the second cyclopropane ring must be cis as in **6a**, corresponding to predominant inversion of configuration in the carbene closure reaction.

In his analysis of the carbene–alkene reaction, Hoffmann concluded that the addition proceeded via an unsymmetrical activated complex.[5] This has been confirmed via high-level ab initio calculations, which suggested that the reaction began via an electron transfer from the alkene to the carbene, followed by a reverse transfer while the second bond was being formed.[6] This description suggests that a two-step process proceeding via a trimethylene diradical may be energetically close to the normal concerted (not synchronous) process. Such a two-step process would be in accord with our observations. The compound formed via a retention of configuration in the carbene addition to the double bond (**7a**) would have the two R groups as close as possible, and a rotation before ring closure would reduce the steric interaction.

In order to learn more about the details of this process, we repeated the reaction sequence with R = D. Here, the steric interaction would be essentially eliminated, and one might expect a 1:1 ratio of the two isomers. 1,5-Hexadiene-*trans*,*trans*-1,6-d_2 (**4b**) was prepared by the treatment of 1,5-hexadiyne with disiamylborane[7] followed by addition of acetic acid-*d* and had a band in the ^{2}H NMR spectrum ($CHCl_3$, 71.8 MHz) at δ 5.00. The addition of dibromocarbene to **4b** was stereospecific, as shown by the observation of a single resonance at δ 1.73 in the ^{2}H NMR spectrum of **5b**, along with the δ 5.00 band for the remaining vinyl group. The hydrogens of the cyclopropane ring had an NMR coupling constant of 7 Hz, which is consistent with a trans arrangement.[8] The reaction of **5b** with methyllithium gave a product having two signals in the ^{2}H NMR spectrum at δ 1.79 and 1.42 in a 3:2 ratio. The ^{1}H NMR spectrum of **2** had signals at δ 1.74 and 1.37 for the cyclopropyl methylene protons cis and trans to the tertiary hydrogen, respectively. A stereospecific reaction giving **7b** would have led to a ^{2}H NMR band at only δ 1.79, and a reaction giving a 1:1 ratio of **6b** to **7b** would have given a 3:1 ratio of the two observed bands. The observed 3:2 ratio shows that the reaction occurred with predominant (80%) *inversion* of configuration, giving **6b** as the major product!

1,5-Hexadiene-*cis*,*cis*-*1*,*6*-d_2 also was prepared from 1,5-hexadiyne-*1*,*6*-d_2 by reduction with disiamylborane and treatment with acetic acid. The ^{2}H NMR spectrum had a band at δ 5.11, and the dibromide formed by addition of dibromocarbene had bands at δ 1.20 and 5.11. The reaction of the dibromide with methyllithium gave the tricyclic hydrocarbon with ^{2}H signals at δ 1.79 and 1.42 in a 2:3 ratio, again in accord with predominant inversion of configuration.

The partial retention of configuration could be a normal characteristic of the reaction, or it could be due to a reversible initial attack of the carbene on the double bond, leading to some loss of stereochemistry. The carbene undergoes a competitive cleavage to an allene (**8b**), and if partial loss of stereochemistry at the double bond occurred during the reaction, it also should be seen in the vinyl group. The allene was isolated, and the ^{2}H NMR spectrum showed no loss of stereochemistry at the double bond.

The reaction may proceed in either of two ways. First, in analogy with the preferred mode of reaction of the 5-hexenyl radical (i.e., five-membered ring formation),[9] the initial attack of the carbene center may be at the inner carbon of the double bond. If this led to a near-planar trimethylene diyl, it could close in a conrotatory fashion[5] and would lead to the observed stereochemistry. Alternately, the initial attack may be at the terminal carbon. The observations would then require inversion at the radical site before closure. In either case, the experimental results require that electronic control be operative in giving apparent inversion at the terminal carbon.

The intramolecular carbene addition competes with the ring opening of the cyclopropylidene to an allene. The fact that about half of the product is formed via the addition reaction shows that it is not markedly slowed by the necessity to proceed via this unusual process. Thus, the reaction proceeding via the trimethylene diyl must have an activation energy only somewhat higher than that for the normal addition. A more detailed understanding of this reaction cannot readily be obtained via experimental studies alone. Therefore, ab initio calculations dealing with the course of the reaction are in progress.

Acknowledgment. This investigation was supported by a grant from the National Science Foundation.

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(4) For comparison, the ^{13}C NMR spectrum of **2** had bands at δ 20.75 (d), 25.48 (t), 32.80 (s), and 40.12 (t), whereas spiropentane had bands at δ 6.11 (t) and 8.53 (s).

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