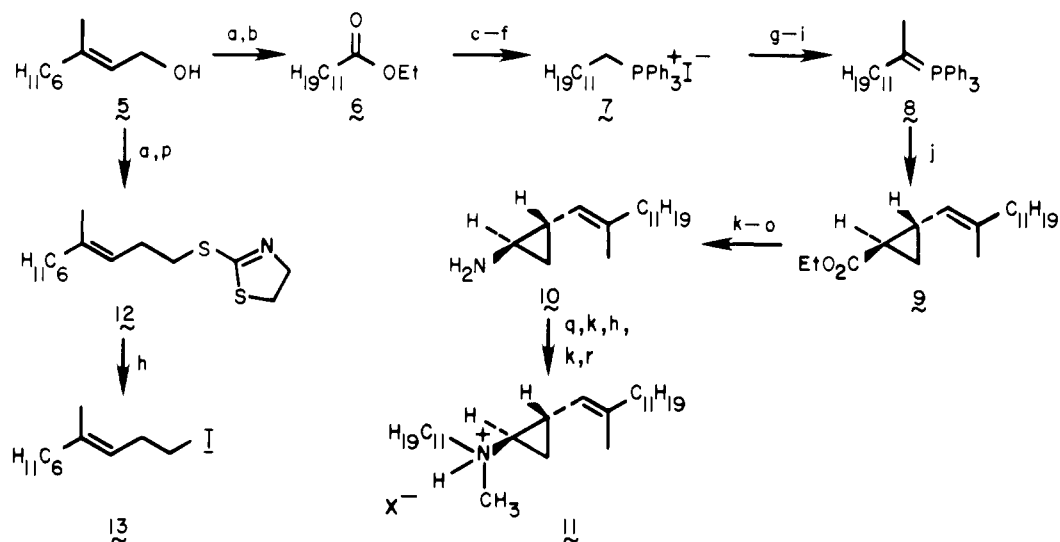


Scheme II



^a PBr_3 . ^b $(\text{EtOOCCH}_2)_2\text{CuLi}$, -78°C . ^c LiAlH_4 . ^d MsCl , pyridine. ^e NaI . ^f PPh_3 . ^g BuLi . ^h CH_3I . ⁱ BuLi . ^j ethyl *trans*-2-formyl-1-cyclopropanecarboxylate. ^k NaOH . ^l $\text{C}_2\text{O}_2\text{Cl}_2$. ^m NaN_3 . ⁿ MeOH , Δ . ^o Me_3SiH . ^p Lithium (2-methylthio)thiazolide. ^q 1-Iodo-4,8-dimethylnona-3,7-diene. ^r Buffer.

inhibition. The combination of ammonium analogue **11** and PP_i , however, resulted in a synergistic inhibition of the enzyme. At 0.25 mM PP_i , a concentration that alone produced a negligible effect, ammonium analogue **11** inhibited the rate of squalene synthesis by 33% at 3 μM and by 73% at 10 μM concentrations.

It is evident that this analogue, which mimics the topological and electrostatic properties of the reactive intermediate **3**, inhibits squalene synthetase.²² When **3** was first proposed as an intermediate in the reaction,⁹ compounds with the 1'-1-2 isoprene linkage¹² were unknown in nature. Recently, however, Epstein and Gaudioso²³ reported the discovery of rothrockene, a monoterpene readily derived from the C_{10} equivalent of **3**, in *Artemisia tridentata rothrockii*. This variety of sage and closely related species are known to produce compounds with irregular isoprenoid carbon skeletons,²⁴ including rothrockene and chrysanthemol, a C_{10} analogue of presqualene alcohol.²⁵ Related carbocationic rearrangements were proposed for the biosynthesis of these nonhead-to-tail monoterpenes.²⁴

Duplication of the topological and electrostatic features of **3** is, in itself, insufficient for inhibition of squalene synthetase.²⁶ The synergism found between **11** and PP_i or, to a lesser extent, P_i suggests that the enzyme binds the carbocation: PP_i ion pair much more tightly than either partner. The strong influence of PP_i on the binding of the ammonium analogue is particularly striking. The pyrophosphate moiety is known to be a major contributor to enzyme-substrate interactions for squalene synthetase^{3,4} and other enzymes in the terpene pathway.²⁷ In the case of farnesyl PP synthetase, Barnard and Popjak²⁸ found evidence for arginyl residues in the active site that presumably facilitate binding of the negatively charged portions of the substrates. If similar

features are present in squalene synthetase, it is not surprising that the enzyme fails to bind the ammonium analogue unless the positively charged region of the active site is shielded by the appropriate anion.

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Registry No. **5**, 106-24-1; **6**, 19894-83-8; **7**, 32205-44-0; **8**, 83732-41-6; (*E*)-**9**, 83732-42-7; **10**, 83732-43-8; **11**, 83732-44-9; **12**, 83732-45-0; **13**, 22339-13-5; ethyl *trans*-2-formyl-1-cyclopropanecarboxylate, 13949-93-4; lithium (2-methylthio)thiazolide, 57662-52-9; squalene synthetase, 9077-14-9; pyrophosphate, 14000-31-8.

A Long Si-H Bond or a Short Si-H Nonbond? Neutron Diffraction Study of ($\eta^5\text{-CH}_3\text{C}_5\text{H}_4$)(CO)₂(H)MnSiF(C₆H₅)₂

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Metal complexes containing both a hydride and a silyl ligand play an important role in hydrosilylation and related reactions. These complexes are formed by oxidative addition of silanes to metal complexes and can be isolated if both the metal complex moiety and the substituents at silicon provide sufficient stabilization. In most cases the reaction is reversible because of facile dissociation of the silane from the complex. A number of hydrido silyl complexes have been investigated by X-ray structure analyses. In some, close contact between the hydride ligand and the silicon atom has been postulated from the evidence of bond lengths and angles involving the silicon and metal atoms,¹⁻³ or in a few cases,

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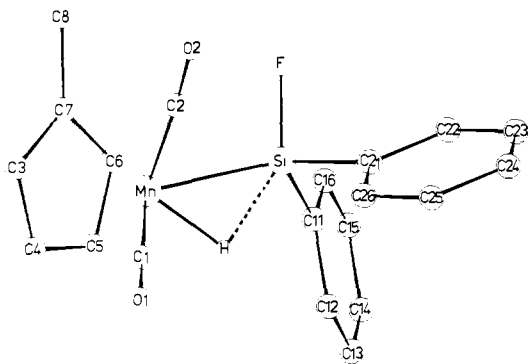


Figure 1. Perspective drawing of $(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)(\text{CO})_2(\text{H})\text{MnSiF}(\text{C}_6\text{H}_5)_2$. All hydrogen atoms except the bridging one have been omitted for clarity.

by location of the hydrogen atom from difference Fourier maps.^{4,5}

However, X-ray structure determinations of hydrogen positions have a low degree of accuracy, and for systematic reasons, the bond lengths involving hydrogen are shorter than their true values.⁶ In order to put further discussions and planned MO calculations on firm ground, we have carried out the first neutron diffraction structure determination of one of these complexes at 120 K.

Light yellow crystals of $(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)(\text{CO})_2(\text{H})\text{MnSiF}(\text{C}_6\text{H}_5)_2$ were grown by cooling a pentane solution. They belong to the monoclinic space group $P2_1/c$ with $a = 1622.6$ (8) pm, $b = 703.2$ (3) pm, $c = 2020.3$ (14) pm, $\beta = 128.55$ (3)°, $V = 1802 \times 10^6$ pm³ (120 K), $Z = 4$, and $d_{\text{calc}} = 1.45$ g/cm³. 3364 intensity data were collected from a crystal of 0.388 mm³ volume on the D8 four-circle diffractometer at the Institut Laue-Langevin in Grenoble, France ($\lambda = 126.500$ pm, $T = 120 \pm 1$ K, $\theta \leq 45^\circ$). Data reduction, which included an analytical absorption correction, yielded 2652 independent reflections. Atom positions, taken from a previously determined X-ray structure, were refined with anisotropic thermal parameters for all atoms. Final convergence in the refinement of 388 parameters was reached with $R = 0.046$ and $R_w = 0.031$ for 2382 structure factors with $F_o \geq 1.2\sigma(F_o)$. A drawing of the complex is shown in Figure 1, and important bond lengths and angles are given in Table I. The positional and thermal parameters are listed in Table II, which is deposited as supplementary material.

Three observations can be made that seem important for a discussion of bonding in $(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)(\text{CO})_2(\text{H})\text{MnSiF}(\text{C}_6\text{H}_5)_2$.

(1) The Mn–H distance of 156.9 (4) pm is very similar to the other Mn–H distance that has been derived from single-crystal neutron diffraction data (160.1 (16) pm in $\text{HMn}(\text{CO})_5$). Nevertheless, a Si–H distance of 180.2 (5) pm is found, which is distinctly shorter than the sum of the van der Waals radii of silicon and hydrogen (about 300 pm). Covalent Si–H bond lengths are in the range of 148 ± 2 pm as found by microwave spectroscopy and electron diffraction for a number of silanes with tetrahedral silicon. In $(\text{CO})_5\text{ReSiH}_3$, a distance of 151 (4) pm has been found.⁹ Thus, the Si–H distance found in $(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)(\text{CO})_2(\text{H})\text{MnSiF}(\text{C}_6\text{H}_5)_2$ is only 30–35 pm longer than expected for a covalent Si–H bond.

(2) If a Si–H interaction is ignored, the silicon geometry is strongly distorted. The deviation of the substituents at silicon from a tetrahedral arrangement suggests incipient pentacoordination

Table I. Important Bond Lengths (pm) and Angles (deg) with Their Standard Deviations^a

Mn–Si	235.2 (4)	Si–F	163.4 (3)
Mn–H	156.9 (4)	Si–H	180.2 (5)
Mn–C(1)	179.6 (3)	Si–C(11)	187.8 (3)
Mn–C(2)	178.2 (3)	Si–C(21)	186.5 (3)
Mn–Cp	175.8		
H–Si–F	148.8 (2)	H–Mn–C(1)	76.4 (2)
H–Si–Mn	41.8 (1)	H–Mn–C(2)	108.3 (2)
H–Si–C(11)	91.9 (2)	H–Mn–Si	50.0 (2)
H–Si–C(21)	98.0 (2)	Si–Mn–C(1)	115.2 (1)
F–Si–Mn	107.4 (2)	Si–Mn–C(2)	78.1 (1)
F–Si–C(11)	102.0 (1)	Si–Mn–Cp	115.6
F–Si–C(21)	103.4 (2)	Cp–Mn–H	121.9
C(11)–Si–C(21)	109.0 (1)	Cp–Mn–C(1)	123.4
Mn–Si–C(11)	115.8 (1)	Cp–Mn–C(2)	123.9
Mn–Si–C(21)	117.3 (1)	C(1)–Mn–C(2)	89.7 (1)
Mn–H–Si	88.2 (2)		

^a Cp represents the center of gravity of the cyclopentadienyl ring.

by the close approach of the hydrogen atom. The coordination polyhedron at silicon can best be described as a distorted trigonal bipyramid with the hydrogen and fluorine atoms in the apical positions ($\text{H–Si–F} = 148.8$ (2)°), the mean angle within the equatorial plane being 114° and the mean F equatorial angle being 104° (see Table I). In metal complexes containing SiX_3 ligands the metal–Si–X angle generally is *increased* (for X = F, e.g., the mean Co–Si–F angle in $(\text{CO})_4\text{CoSiF}_3$ is 114.6 (4)°¹⁰ and the mean Fe–Si–F angle in $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})(\text{H})\text{Fe}(\text{SiF}_2\text{CH}_3)_2$ is 113.4 (1)°⁵). However, in $(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)(\text{CO})_2(\text{H})\text{MnSiF}(\text{C}_6\text{H}_5)_2$ the fluorine substituent is slightly bent *toward* the metal ($\text{Mn–Si–F} = 107.4$ (2)°). Though an unequivocal interpretation of this observation cannot be given at the present time, we believe that the silicon geometry is not distorted only by the different steric influences of the fluorine and phenyl substituents but, at least to some extent, also by the Si–H interaction.

(3) The vector perpendicular to both Mn–CO bonds points approximately to the middle of the Si–H vector, and the idealized Si sp³ hybrid orbital points to the middle of the Mn–H bond (but closer to Mn than to H).

Smith and Bennett^{4,5} have attributed the close Si–H contact in $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2(\text{H})\text{MnSiPh}_3$ to repulsion of the hydride ligand by other ligands. However, kinetics of the silane dissociation,¹¹ NMR studies,¹² and the chemical behavior^{12,13} of manganese complexes of this type distinctly indicate a bonding interaction between silicon and hydrogen. Various valence-bond representations have been proposed,^{11,12,14} the common feature of which is the assumption of an incipient three-center/two-electron bond in the Mn–H–Si triangle.¹⁵ Our observations strongly support this kind of bonding. As judged by the bond angles, the Si–H bond as a whole, not the individual hydrogen and silicon atoms, completes the coordination sphere of manganese. And the Mn–H bond as a whole may be regarded as a substituent to silicon. With a *strong* Mn–H–Si interaction both the Mn–H and the Mn–Si distances should lengthen. Since these distances are close to the values that are to be expected for noninteracting, terminally bonded silyl and hydride ligands,¹⁶ the degree of three-center

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(16) Structures of complexes that contain both a $\eta^5\text{-C}_5\text{H}_5$ ligand and a Mn–H or a Mn–Si bond are not known. The effect of the $\eta^5\text{-C}_5\text{H}_5$ ligand on these bond distances can only roughly be estimated. Any discussion about deviations from "normal" bond lengths therefore is quite indistinct.

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bonding should be low (i.e., hydrogen interacts more strongly with the metal than with silicon).

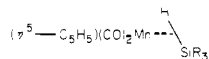
While the precise nature of this Si-H interaction is not established, it is obvious from our findings that migration of the hydrogen atom from a semibridging position between manganese and silicon to a terminal silicon position, in conjunction with a breakdown of the Mn-Si bond, can take place without major movements of atoms. The structure therefore can serve as an illustration of the proposed mechanism for the silane dissociation.¹⁶ Since silanes dissociate more slowly as the electronegativity of substituents on the silicon is increased,¹¹ we expect the Si-H distance in $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2(\text{H})\text{MnSiR}_3$ to increase with more electronegative substituents R and vice versa.

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Registry No. $(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)(\text{CO})_2(\text{H})\text{MnSiF}(\text{C}_6\text{H}_5)_2$, 78420-95-8.

Supplementary Material Available: Listings of the positional and thermal parameters (Table II) and of the observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

(17) Graham and Hart-Davis¹¹ have proposed a concerted single-stage mechanism for the silane dissociation and have pictured the activated complex in the form



Corriu et al.¹² have given evidence for a slow intramolecular equilibrium between the hydrido silyl complex and the deinserted complex $(\text{R}_3\text{SiH-CpMn}(\text{CO})_2)$. In the latter both moieties are associated, however.

Resolved ¹³C NMR Spectra of Carbonium Ions at Cryogenic Temperatures. The Norbornyl Cation at 5 K

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We report a solid-state ¹³C NMR study of the norbornyl cation in the 200–5 K region. Owing to a fortuitous combination of large chemical shift differences and fairly narrow chemical shift anisotropy patterns, these spectra allow clear identification of the resonance pattern of positively charged carbon atoms without the benefit of magic angle spinning (MAS). Given the applicability of classical rate theory, the 5 K spectrum of the norbornyl cation forces the conclusion that if this spectrum is attributed to rapid equilibration between structures with localized charges, the activation energy for interconversion cannot be more than 0.2 kcal mol⁻¹.

An intimate mixture of ¹³C-labeled norbornyl chloride and SbF₅ (~1:10) was prepared by vapor-phase codeposition.¹ A sample of this solid was transferred at <150 K to an 8 mm glass tube

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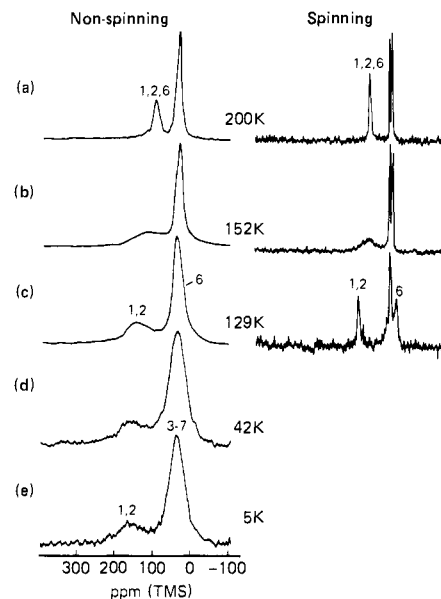


Figure 1. ¹³C proton- and fluorine-decoupled CP spectra (taken at 15 MHz) of the 2-norbornyl cation with and without magic angle spinning. The MAS spectra are taken from ref 1. All spectra were obtained by using 35-kHz matching radiofrequency fields for ¹H and ¹³C, 1–5-ms contact time, and 1- or 2-s delay between scans.

with the use of previously described techniques.² The tube was vacuum sealed, annealed at dry-ice temperature for several days to achieve ion formation, and then examined spectroscopically.

These low-temperature studies were performed with the same probe used for MAS experiments above 77 K.^{2,3} Cooling below 77 K was achieved by transfer of liquid helium from a storage tank into a stainless steel Dewar where it was vaporized. The cold gas was transported to the sample inside the NMR coil by means of a transfer Dewar.⁴ Temperature control was achieved by a heater and thermocouple assembly located inside the stainless steel Dewar. The sample temperature was measured with a Au/Fe-chromel thermocouple placed downstream from the sample. This was calibrated against a thermocouple placed in a stable carbonium ion salt sample located in the NMR coil during radiofrequency irradiation, to take electrical losses into account. The lowest temperature (5 K) is accurate to ± 1 K.

Spectra of the norbornyl cation between 5 and 200 K are shown in Figure 1.⁵ For comparison, corresponding MAS spectra recorded previously are also shown.¹ The higher temperature nonspinning spectra reported here have reasonably symmetric absorption patterns. It is important to note that these spectra are not obtained from an assembly of molecules that are tumbling isotropically as in a liquid or tricked into an apparent isotropic state by magic angle spinning. Rather, these are proton- and fluorine-decoupled spectra that show rather narrow, relatively symmetric chemical shift anisotropy patterns, which may be reduced in part owing to a molecular motion in the lattice.

A notable change in the spectrum of the norbornyl cation occurs at about 150 K, where the downfield band broadens and the center of gravity shifts downfield. At lower temperature this band narrows somewhat, and the center of gravity stabilizes at about 125 ppm. This change reflects the known slowing in rate of the 6,1,2-hydride shift of the norbornyl cation, a process seen more clearly in the MAS spectra in Figure 1.

At temperatures below 129 K the spectrum remains unchanged all the way down to 5 K. The temperature-invariant downfield

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