

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

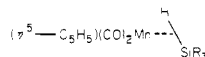
While the precise nature of this Si-H interaction is not established, it is obvious from our findings that migration of the hydrogen atom from a semibridging position between manganese and silicon to a terminal silicon position, in conjunction with a breakdown of the Mn-Si bond, can take place without major movements of atoms. The structure therefore can serve as an illustration of the proposed mechanism for the silane dissociation.<sup>16</sup> Since silanes dissociate more slowly as the electronegativity of substituents on the silicon is increased,<sup>11</sup> 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.**  $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2(\text{H})\text{MnSiF}(\text{C}_6\text{H}_5)_2$ , 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-Davis<sup>11</sup> have proposed a concerted single-stage mechanism for the silane dissociation and have pictured the activated complex in the form



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

## Resolved <sup>13</sup>C NMR Spectra of Carbonium Ions at Cryogenic Temperatures. The Norbornyl Cation at 5 K

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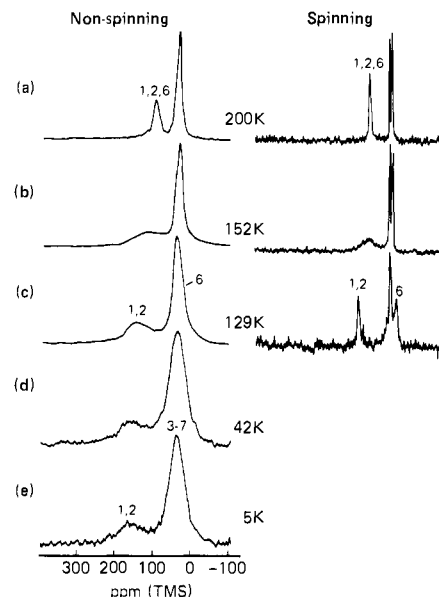
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We report a solid-state <sup>13</sup>C NMR study of the norbornyl cation in the 200–5 K region. Owing to a fortuitous combination of large chemical shift differences and fairly narrow chemical shift anisotropy patterns, these spectra allow clear identification 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<sup>-1</sup>.

An intimate mixture of <sup>13</sup>C-labeled norbornyl chloride and SbF<sub>5</sub> (~1:10) was prepared by vapor-phase codeposition.<sup>1</sup> A sample of this solid was transferred at <150 K to an 8 mm glass tube

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(1) Yannoni, C. S.; Macho, V.; Myhre, P. C. *J. Am. Chem. Soc.* **1982**, *104*, 907.



**Figure 1.** <sup>13</sup>C 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 <sup>1</sup>H and <sup>13</sup>C, 1–5-ms contact time, and 1- or 2-s delay between scans.

with the use of previously described techniques.<sup>2</sup> 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.<sup>2,3</sup> 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.<sup>4</sup> 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  $\pm 1$  K.

Spectra of the norbornyl cation between 5 and 200 K are shown in Figure 1.<sup>5</sup> For comparison, corresponding MAS spectra recorded previously are also shown.<sup>1</sup> 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.

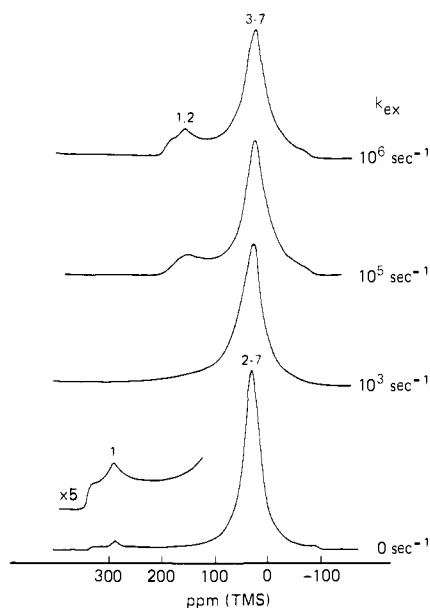
At temperatures below 129 K the spectrum remains unchanged all the way down to 5 K. The temperature-invariant downfield

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(3) Fyfe, C. A.; Mossbrugger, H.; Yannoni, C. S. *J. Magn. Reson.* **1979**, *36*, 61.

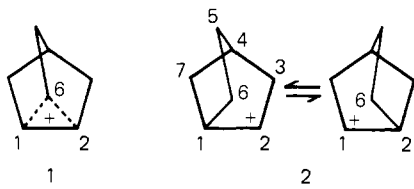
(4) Macho, V.; Kendrick, R. D.; Yannoni, C. S. *J. Magn. Reson.*, to be published.

(5) Standard cross polarization (CP) techniques (Schaefer, J.; Stejskal, E. O. *Top. Carbon-13 NMR Spectrosc.* **1979**, *3*, 281) were used with the addition of strong <sup>19</sup>F decoupling. Spectral parameters are given in Figure 1.



**Figure 2.** Simulation of two-site chemical exchange between carbons 1 and 2 of a classical 2-norbornyl cation structure (**2**). The calculation is for a nonspinning solid sample and includes the effects of a chemical shift anisotropy for carbon in a site of less-than-tetrahedral symmetry (i.e., the charged carbon). The spectrum observed at 5 K (Figure 1e) most closely resembles exchange-narrowed spectra ( $k_{ex} \geq 10^5 \text{ s}^{-1}$ ).

band is the nonspinning equivalent of the low field resonance observed in liquid-state and MAS solid-state spectra. This resonance can be interpreted in terms of the positively charged carbons of the  $\sigma$ -bridged (nonclassical) structure (**1**) or as the time average of rapidly equilibrating localized (classical) ions (**2**).



If one adopts the latter view, the spectrum at 5 K requires the activation energy for interconversion of localized (or partially localized) ions to be no greater than 0.2 kcal mol<sup>-1</sup>.

This conclusion may be reached in the following way. The chemical shift anisotropy (CSA) patterns for C1 and C2 in **2** were calculated in the slow and fast exchange limits with the following assumptions. It was assumed that the CSA pattern for the positively charged carbon in **2** would be similar to that of the charged carbon in the isopropyl cation and that the uncharged carbon of the equilibrating pair in **2** as well as the other five carbons have isotropic environments. The CSA parameters for the charged carbon (480 ppm) were obtained from the static spectrum of the charged carbon of the isopropyl cation at 5 K, and were used to simulate the spectrum of **2** at various exchange rates (Figure 2).<sup>6</sup> Comparison of these calculated spectra with the observed 5 K spectrum of the norbornyl cation indicates that the observed spectrum could be explained by equilibration of localized ions (**2**) with an exchange frequency of 10<sup>5</sup> s<sup>-1</sup> or greater. If classical rate theory applies, this indicates that the activation energy for interconversion is less than 0.2 kcal mol<sup>-1</sup>.<sup>7</sup>

(6) The isopropyl cation was prepared from <sup>13</sup>C-enriched 2-chloropropane by the codeposition procedure described in ref 2. The relative insensitivity of  $E_a$  to the value of  $k_{ex}$  should be noted. A change of 10<sup>2</sup> in either  $k_{ex}$  or the preexponential factor will alter  $E_a$  by less than 50 cal mol<sup>-1</sup>.

(7) Fong has criticized classical rate process theory and has suggested that it might be possible to account for very rapid equilibration rates of degenerate, classical norbornyl cations by a tunneling mechanism even if the intrinsic barrier is several kcal mol<sup>-1</sup>. See: Fong, F. K. *J. Am. Chem. Soc.* **1974**, *96*, 7638.

The results reported here could be taken as the most direct evidence yet obtained for the  $\sigma$ -bridged ion in super acid media.<sup>8</sup> The possible alteration of the potential surface of the norbornyl cation in the presence of solvent has been noted.<sup>9</sup> It will be interesting to see if solid-state NMR techniques may be useful in the investigation of the effects of solvent on the norbornyl cation potential surface.

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**Registry No.** 2-Norbornyl cation, 24321-81-1.

(8) Recent calculations of relative SCF energies of the norbornyl cation with a 4-21 G basis set augmented by d polarization functions on all carbons indicated that the nonclassical form is 0.2 kcal mol<sup>-1</sup> more stable than the "classical" form. See Goddard, J. D.; Osamura, Y.; Schaefer, H. F. *J. Am. Chem. Soc.* **1982**, *104*, 325.

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### Experimental Evidence for the Existence of Catalytic Sites with Different Steric Structures in Supported Ziegler-Natta Catalysts

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Catalytic systems prepared from TiCl<sub>4</sub> supported on MgCl<sub>2</sub> and aluminum trialkyls polymerize  $\alpha$  olefins to form polymers having widely different stereoregularities.<sup>1</sup>

It has been assumed<sup>1,2</sup> that, as is the case for traditional Ziegler-Natta catalysts,<sup>3</sup> there are sterically different catalytic centers in the supported catalysts which would produce isotactic polymers or mostly stereoirregular polymers. However, experimental evidence for this assumption is very scarce.

We present some results concerning the polymerization of racemic 4-methyl-1-hexene (4-MH) with the above catalytic systems in the presence of (*l*)-menthyl-*p*-methoxybenzoate ((-)-MA) that show that atactic and isotactic polymers are indeed produced by sterically different catalytic centers.

In a typical experiment (*R,S*)-4-MH (0.14 mol) was polymerized at room temperature in heptane (100 cm<sup>3</sup>) in the presence of Al(*i*-C<sub>4</sub>H<sub>9</sub>)<sub>3</sub> (0.012 mol) and a catalyst (0.377 g), containing 3.9% Ti, prepared by grinding anhydrous MgCl<sub>2</sub> with the complex (-)-MA-TiCl<sub>4</sub>.<sup>4</sup>

Different amounts of (-)-MA were added to the mixture, the molar ratio [(-)-MA]/([Al] + [Ti]) (*r*) varying between 0.131 and 0.796 (Table I). Furthermore, in a series of experiments the above ratio was kept constant (*r* = 0.293) and the conversion of monomer to polymer was varied between 8% and 90% (Table II). The polymers obtained were fractionated by boiling solvents extraction<sup>5</sup> and characterized as reported in Tables II and III.

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(3) Boor, J. *Ind. Eng. Chem., Prod. Res. Dev.* **1970**, *9*, 437-466.

(4) Pure (-)-MA showed  $[\alpha]^{25}_{546} = -97.9^\circ$  (c 5.14, methanol).

(5) Natta, G.; Pino, P.; Mazzanti, G. *Gazz. Chim. Ital.* **1957**, *87*, 528-548.