

Figure 1. Temperature dependence of the reciprocal paramagnetic susceptibility for carbene species generated in polycrystalline **1**. Inset: The plot at lower temperatures than 20 K is shown on an expanded scale.

in the range 260–380 mT, accompanied by weak quintet signals at 245.8 and 258 mT. In order to examine the average spin multiplicity and temperature dependence of the magnetization of bis(*p*-(octyloxy)phenyl)carbene (**2**), the magnetic susceptibility was measured by means of a Faraday-type magnetic balance system. Magnetization of the sample obtained by photolyzing crystals of **1** at 4 K was recorded at various temperatures under the field gradient of 5 T/m generated by auxiliary coils and the main coil of 0.5 T. A $1/(\chi - \chi_d)$ vs. T plot is approximated by a set of four straight lines with three break points at 84, 23, and 4 K (see Figure 1), indicating how the magnetic interaction develops among carbene species with magnetic and/or structural transitions on lowering temperatures.⁶ The line in region A is extrapolated to give a positive Weiss temperature of 35 K. The carbene molecules are considered to be in a ferromagnetic molecular field in this region. The slope of the line decreases at temperatures lower than 80 K, showing an increase of the apparent spin multiplicity.⁷ After it passes through region B with small antiferromagnetic molecular field ($\theta = -7$ K), the region C shows a ferromagnetic molecular field again ($\theta = 2$ K), resulting in an increase of spin multiplicity at temperatures lower than 4 K (region D). The average spin multiplicity was determined by the field dependence of magnetization (M) as a function of an external main field (H) at 2.1 and 4.5 K, and magnetization curves were analyzed in terms of the Brillouin function.² The magnetization behaviors at the two temperatures were found not to be the same, and the saturation behavior at 4.5 K fits closely to that of $S = 4/2$, and that at 2.1 K is rather closer to $S = 8/2$ especially at the low H/T range. The results indicate that intermolecular magnetic interaction develops over a wider range at 2.1 than at 4.5 K, connecting four carbene molecules magnetically on the average.

In order to understand the magnetic interaction of the carbene species on the basis of their spacial arrangement in the crystals, an X-ray diffraction analysis was carried out on *p,p*-bis(octyloxy)benzophenone (**3**), at room temperature, as a model for diazo compound **1** and for the resulting carbene **2** in the crystals.⁸ The benzophenone crystallizes in the orthorhombic system and the unit cell dimensions are $a = 56.60$ (2) Å, $b = 7.395$ (2) Å, and $c = 6.332$ (2) Å, with a space group of *Pnca*; R value is 9.3% for 1616 independent reflections. The projections along a and b axes are depicted in Figure 2, showing the multilayered structure of the benzophenone units. Each layer is separated by the all-trans octyl

(6) The complex behavior in the $1/\chi_p$ vs. T plot could be rationalized by an orientational transition such as the change in the dihedral angle between two spin-distributed benzene rings of a carbene molecule.

(7) Effective paramagnetic species in this temperature range (80–150 K) is found by ESR spectroscopy to be a quintet species. The higher multiplet signals due to magnetic interaction among quintet species were observed to start at lower temperatures than 80 K.

(8) It was difficult to obtain a good crystal of **1** suitable for single-crystal analysis. An X-ray analysis on a thin crystal of the diazo compound **1** is under way. The crystals are orthorhombic and the unit cell dimensions are $a = 52.8$ Å, $b = 7.32$ Å, and $c = 7.05$ Å, with a space group of *Pnca*. Therefore the packing arrangement of **1** is supposed to be practically the same.

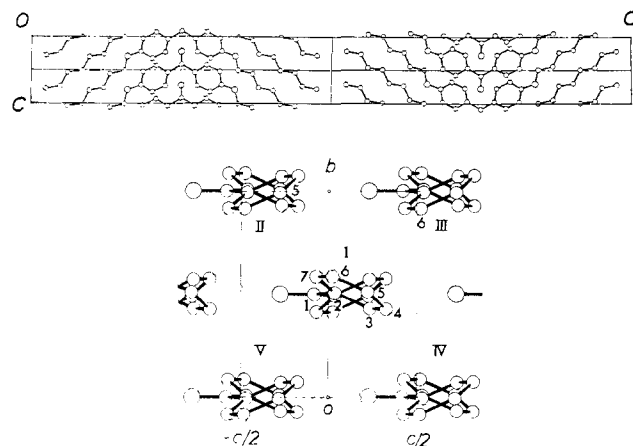


Figure 2. Crystal structure of **3** viewed along the b axis (top) and partial packing arrangement (chains and hydrogen atoms are omitted) viewed along the a axis (bottom).

chains which are aligned parallel to each other. One of the benzene rings in molecule **1** has four nearest neighbors (II–V), presenting a two-dimensional network with interactions satisfying McConnell's ferromagnetic condition.⁹ Thus if the molecules of **2** stack similarly in the crystals, ferromagnetic interaction would develop within the layer, which can be regarded as a domain in ferromagnets. Since magnetic interaction between the layers is insulated by long alkyl chains, the gross magnetic moment of the layers would align to the same direction under strong external field. If the magnetic anisotropy of the assembly of **2** within a layer is large enough, the sample may show macroscopic ferromagnetism.

Better overlap of spin-containing benzene rings and some additional force to support crystal structures should increase the magnetic interaction and would lead to organic ferromagnets. Investigation along this line is in progress in these laboratories.

(9) McConnell, H. M. *J. Chem. Phys.* **1963**, *39*, 1910. There are several important interactions among spin-containing benzene rings. When viewed along a axis, ferromagnetic interaction prevails among benzene rings II_f, II_f, and III_f in front (e.g., between C6 of II_f and C5 of III_f, and between C5 of II_f and C6 of III_f with an intermolecular distance of 3.55 Å) and among benzene rings I_r and IV_r or V_r in the rear.

Detection of the Static 1,2-Dimethyl-2-norbornyl Cation by Variable-Temperature ¹³C CPMAS NMR

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NMR studies of the 2-norbornyl cation show that the positive charge is equally distributed between C1 and C2 at temperatures as low as 5 K.¹ This result allows one to restrict the barrier for a hypothetical Wagner–Meerwein shift in the 2-norbornyl cation to about 0.2 kcal mol⁻¹, if tunneling by carbon is not important.^{1,2} Carbon tunneling has been invoked in order to account for differences between the calculated and observed rate of the automerization of cyclobutadiene.³ More detailed calculations indicate

(1) Yannoni, C. S.; Macho, V.; Myhre, P. C. *J. Am. Chem. Soc.* **1982**, *104*, 7380–7381.

(2) Fong, F. K. *J. Am. Chem. Soc.* **1974**, *96*, 7638–7646.

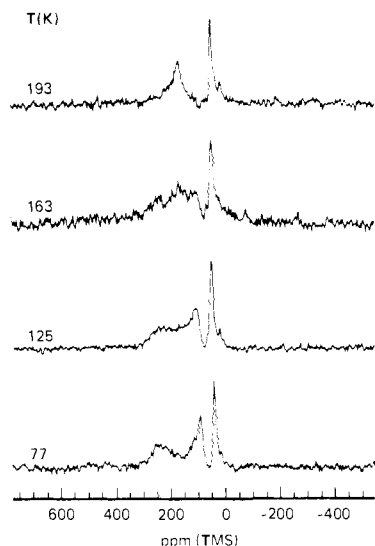


Figure 1. Representative low-temperature ^{13}C CPMAS spectra of **1**. The spectra were obtained with the use of 1-ms cross-polarization time and a 500-ms delay time between scans. The number of scans (in thousands) in order of decreasing temperature are 24.6, 11.6, 28.8, and 12.3.

the possible importance of carbon tunneling in this degenerate process which involves small changes in nuclear coordinates.^{4,5} Small changes in carbon coordinates may also apply to the norbornyl system.⁶ This consideration prompted us to design an experimental test for tunneling in a 2-norbornyl cation.

The 1,2-dimethyl-2-norbornyl cation (**1**) appeared to be a reasonable test case. There is no controversy concerning the chiral character of **1**.⁷ However, **1** yields average NMR spectra under all accessible solution-state conditions. Application of the isotopic perturbation of resonance test reveals this ion to be distinctly more delocalized than many rapidly equilibrating classical ions.^{8,9} Thus, **1** is an intrinsically attractive target for study by variable-temperature CPMAS NMR. The bicyclo[2.2.1]heptyl geometry of **1** and the minimal perturbation introduced by the methyl groups make it a good model for exploring the possibility of tunneling in the 2-norbornyl cation.

The most direct test of tunneling in **1** is whether or not a spectrum of the *static* 1,2-dimethyl-2-norbornyl cation can be obtained at a temperature above the limiting temperature of the spectrometer. If one can slow the degenerate rearrangement, a slightly more refined test involves comparison of the temperature required to freeze out **1** with temperatures required to freeze out a representative set of rapidly equilibrating classical ions.

We have prepared samples of **1** labeled with ^{13}C at carbons 1, 2, and 6 in solid SbF_5 matrices, and we have collected CPMAS NMR spectra of these samples from 200 to 77 K.^{10,11} The spectra

at relatively high temperature show resonances consonant with those reported in solution-state studies, with absorption at 47 ppm assigned to C6 and absorption at 165 ppm assigned to C1 and C2. As the temperature is lowered, the spectral pattern changes with the development of a downfield signal at 250 ppm and two signals at 93 and 50 ppm, assigned to C1, C2, and C6, respectively, Figure 1. Additional nonspinning spectra of this ion have been obtained down to 8 K. Spectra of nonspinning samples of **1** over the 80–8 K range show only small changes that are consistent with the further slowing of the 1,2-shift.

The changes in the spectra with temperature reflect clearly the slowing down of the Wagner–Meerwein bond shift on the NMR time scale and stand in marked contrast with the spectral behavior of the parent 2-norbornyl cation.¹ While the situation in solid SbF_5 matrices may be complicated by distributions of rates,¹² the temperature at which a near limiting spectrum of the static ion is observed appears to be only a few degrees lower than that required to freeze out the 2,3-dimethyl-2-butyl, 2,3,3-trimethyl-2-butyl, and 1,2-dimethyl-1-cyclopentyl cations,¹² ions that all show much larger isotopic perturbation splittings and in which the charge appears to be more localized.^{8,9,13}

Thus, we take the spectral behavior of **1** to be clear evidence of the unimportance of tunneling in the dynamic behavior of this ion. Further, we suggest on the basis of structural correspondence that tunneling would also be relatively unimportant in the hypothesized, classical 2-norbornyl cation.^{6,14}

The spectra of **1** observed in the intermediate temperature regions do not resemble those observed for the 2,3-dimethyl-2-butyl system,¹² where apparent coexistence of both rapidly equilibrating and static forms of the ion is found owing to a broad distribution of rearrangement rates in the amorphous solid. The spectra conform more closely to solution-like dynamic behavior of the type exhibited by solid samples of the 2-norbornyl cation in the temperature region where the 6,2,1-hydride shift slows.^{15,16}

The charged carbon in **1** is markedly less deshielded, 250 ppm, than normally observed for localized carbocations. Correspondingly, the adjacent uncharged quaternary carbon is more deshielded than normally observed. This supports the commonly held view that **1** is a rapidly equilibrating partially delocalized ion.^{9,17,18} It seems particularly significant that use of the solid-state NMR method allows the freezing out of a degenerate rearrangement in this kind of system.

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(11) Samples of labeled 1,2-dimethylnorbornyl cation were prepared in two ways: (1) by conversion of ^{13}C -labeled norbornyl acetate¹⁵ via a standard sequence to the equivalently labeled 1,2-dimethylnorbornyl chloride and subsequent codeposition;¹⁰ (2) by solvolytic ring closure of 2-(3-cyclopentenyl)-1,1-dimethylethanol- $1-^{13}\text{C}$ in a chloroform solution of trifluoroacetic acid/trifluoroacetic anhydride to yield 6,6-dimethyl-2-norbornyl- $6-^{13}\text{C}$ trifluoroacetate. Saponification of the ester and subsequent treatment of the alcohol with Lucas reagent afforded 6,6-dimethyl-2-norbornyl- $6-^{13}\text{C}$ chloride which was converted to the ion by long standing in a solution of SO_2ClF at 200 K followed by removal of SO_2ClF under high vacuum to leave the ion in a solid SbF_5 matrix.

(12) Myhre, P. C.; Kruger, J. D.; Hammond, B. L.; Lok, S. M.; Yannoni, C. S.; Macho, V.; Limbach, H. H.; Vieth, H. M. *J. Am. Chem. Soc.* **1984**, *106*, 6079–6080.

(13) Schleyer, P. v. R.; Lenior, D.; Mison, P.; Liang, G.; Prakash, G. K. S.; Olah, G. A. *J. Am. Chem. Soc.* **1980**, *102*, 683–691.

(14) It should be noted that Fong's analysis of tunneling, based on a "concerted intramolecular twist vibration" as the promoting mode, led him to predict that the intrinsic barrier to interconversion of chiral forms in **1** would be significantly greater than interconversion of possible chiral forms of the 2-norbornyl cation; see ref 2. The strength of this argument will be considered in more detail in the full account.

(15) Yannoni, C. S.; Macho, V.; Myhre, P. C. *J. Am. Chem. Soc.* **1981**, *104*, 907–909.

(16) The present data are not sufficient to evaluate adequately the issue of a single rate vs. a distribution of rates. It is clear, however, that if a distribution of rates exists, this distribution is significantly narrower than the one required to explain the spectral behavior of the 2,3-dimethyl-2-butyl cation as a function of temperature. See ref 12.

(17) Olah, G. A.; DeMember, J. R.; Lui, C. Y.; Porter, R. D. *J. Am. Chem. Soc.* **1971**, *93*, 1442–1446.

(18) Haseltine, R.; Wong, N.; Sorensen, T. S. *Can. J. Chem.* **1975**, *53*, 1891–1900.

(3) Carpenter, B. K. *J. Am. Chem. Soc.* **1983**, *105*, 1700–1701.

(4) Huang, M.-J.; Wolfsberg, M. *J. Am. Chem. Soc.* **1984**, *106*, 4039–4040.

(5) Dewar, M. J. S.; Merz, K. M., Jr.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1984**, *106*, 4040–4041.

(6) Schaefer's calculations suggest that rather small changes in nuclear coordinates would be required to interconvert chiral, partially delocalized structures of the 2-norbornyl cation: Goddard, J. D.; Osamura, Y.; Schaefer, H. F. *J. Am. Chem. Soc.* **1982**, *104*, 3258–3262. Note, however, that more recent calculations at higher levels do not find minima for any classical 2-norbornyl structure. See: (a) Yoshimine, M.; McLean, A. D.; Liu, B.; DeFrees, D. J.; Binkley, J. S. *J. Am. Chem. Soc.* **1983**, *105*, 6185–6186. (b) Raghavachari, K.; Haddon, R. C.; Schleyer, P. v. R.; Schaefer, H. F. *J. Am. Chem. Soc.* **1983**, *105*, 5915–5917.

(7) Goering, H.; Humski, K. *J. Am. Chem. Soc.* **1968**, *90*, 6213–6214.

(8) Saunders, M.; Telkowski, L.; Kates, M. R. *J. Am. Chem. Soc.* **1977**, *99*, 8071–8072.

(9) Saunders, M.; Kates, M. R.; Wiberg, K. B.; Pratt, W. *J. Am. Chem. Soc.* **1977**, *99*, 8072–8073.

(10) Myhre, P. C.; Yannoni, C. S. *J. Am. Chem. Soc.* **1981**, *103*, 230–232.

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Condensation of Aldehydes with μ -Alkylidyne Diiron Complexes: A New Synthesis of μ -Vinylcarbyne Complexes

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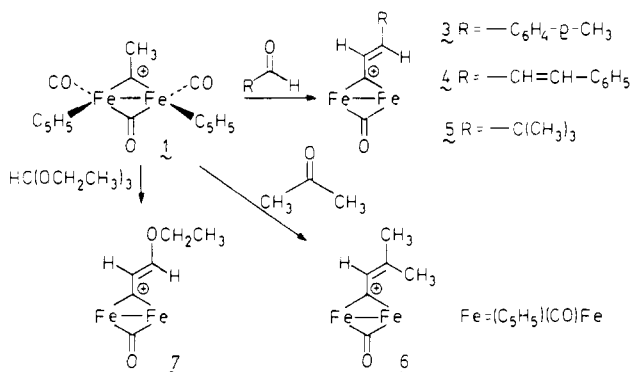
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Cationic bridging alkylidyne diiron complexes were first prepared by Rosenblum by the reaction of RLi with $[\text{C}_5\text{H}_5(\text{CO})\text{Fe}(\mu\text{-CO})_2]$ followed by strong acid workup.¹ Recently, we developed a new synthesis of μ -alkylidyne diiron complexes by addition of the C—H bond of μ -methylidyne complex **2**² across the C=C double bond of alkenes.^{3,4} A wide range of μ -alkylidyne complexes are readily available by this new hydrocarbonation procedure.

μ -Alkylidyne complexes can be reversibly deprotonated to give μ -alkenylidene complexes.⁵ The ease with which μ -alkenylidene complexes can be protonated to give cationic μ -alkylidyne complexes prompted us to study their reactions with carbon electrophiles. Here we report that μ -alkylidyne complexes react with aldehydes and related substrates to produce new cationic vinylcarbyne complexes in a reaction that involves attack of a μ -alkenylidene complex on a protonated aldehyde.

When a suspension of μ -ethylidyne complex **1** (630 mg, 1.43 mmol) was stirred with *p*-tolualdehyde (3 equiv) in THF for 26 h at 35 °C, the μ -(3-*p*-tolylprop-2-enylidyne)diiron complex **3**⁶



was formed in 93% yield as analytically pure purple microcrystals. The key ^1H NMR spectral features of **3** are the low-field chemical shifts of the vinylcarbyne protons at δ 10.26 ($\mu\text{-CCH}=\text{CHR}$) and

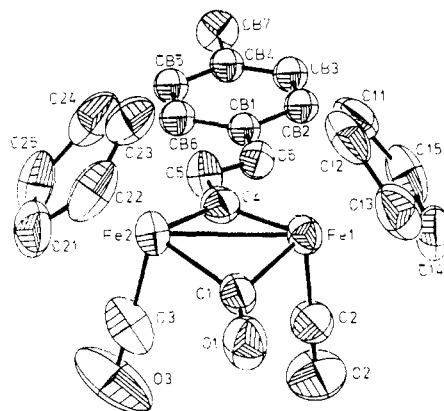
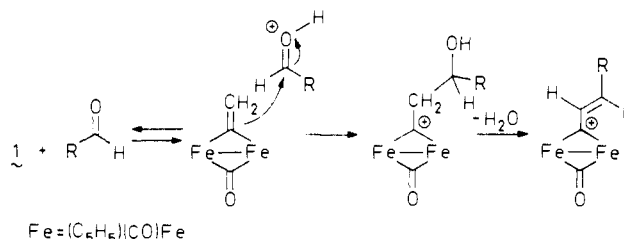


Figure 1. Structure of **3**, BF_4^- omitted for clarity.

8.09 ($\mu\text{-CCH}=\text{CHR}$). In the X-ray structure of **3** (Figure 1),⁷ the two iron centers and the entire vinylcarbyne ligand lie approximately in the same plane. The dihedral angles between the vinyl group and *p*-tolyl ring and between the vinyl group and the $\mu\text{-CFe}_2$ unit are 11.0° and 1.5°, respectively. The vinylcarbyne ligand is best described as having a single bond between the μ -alkylidyne carbon and the vinyl group (1.422 (8) Å) and a localized double bond in the vinyl unit (1.335 (8) Å).

Similar condensation reactions of μ -ethylidyne complex **1** with other aldehydes, ketones, and ortho esters have been observed. Reaction of 3 equiv of cinnamaldehyde with a suspension of **1** in THF occurred over 10 h at 35 °C to give vinylcarbyne complex **4**⁷ in 98% yield. Condensation of a large excess of pivalaldehyde with a suspension of **1** in THF occurred over 20 h at 50 °C to produce vinylcarbyne complex **5**⁷ in 74% yield. When an acetone solution of **1** was stirred for 20 h at 35 °C, condensation occurred to produce the known vinylcarbyne cation **6**⁸ in 83% yield. Reaction of a large excess of triethyl orthoformate with a suspension of **1** in THF led to the isolation of the vinyl ether carbyne complex **7**⁷ in 90% yield.

μ -Propylidyne complex **8** was prepared from μ -methylidyne complex **2** and ethylene in a hydrocarbonation reaction.^{3,4} When a suspension of **8** was stirred in neat *p*-tolualdehyde at ambient temperature, **8** slowly dissolved and a more highly substituted vinylcarbyne complex **9**⁷ was isolated in 83% yield after 20 h.



We believe that the formation of vinylcarbyne complexes can best be explained by the mechanism shown above. μ -Alkylidyne complexes and aldehydes are proposed to be in equilibrium with μ -alkenylidene complexes and protonated aldehydes. The μ -alkenylidene complex can act as a carbon nucleophile to attack the protonated aldehyde in the key carbon-carbon bond-forming step. The driving force for this reaction is the formation of a carbon-carbon bond and of a cationic carbon center stabilized by two strongly electron donating iron atoms. Subsequent acid-catalyzed dehydration produces the vinylcarbyne complex.

Diiron vinylcarbyne complexes are now readily available either by the new condensation reaction reported here or by hydride abstraction from μ -alkenylidene complexes.⁸ These crystalline materials are easily handled at room temperature in air. We are currently studying reactions of these new vinylcarbyne complexes with carbon nucleophiles to exploit their potential for synthesis.

(7) See supplementary material.

(8) Casey, C. P.; Marder, S. R. *Organometallics* 1985, 4, 411.

(1) Nitay, M.; Priester, W.; Rosenblum, M. *J. Am. Chem. Soc.* 1978, 100, 3620.

(2) Casey, C. P.; Fagan, P. J.; Miles, W. H. *J. Am. Chem. Soc.* 1982, 104, 1134.

(3) Casey, C. P.; Fagan, P. J. *J. Am. Chem. Soc.* 1982, 104, 4950.

(4) Casey, C. P.; Fagan, P. J.; Miles, W. H.; Marder, S. R. *J. Mol. Catal.* 1983, 21, 173.

(5) Kao, S. C.; Lu, P. P. Y.; Pettit, R. *Organometallics* 1982, 1, 911.

(6) **3**: ^1H NMR (270 MHz, acetone- d_6) δ 10.26 (d, $J = 14.9$ Hz, 1 H, $\text{CCH}=\text{CH}$), 8.20 (d, $J = 8.2$ Hz, 2 H, C_6H_4), 8.09 (d, $J = 14.9$ Hz, 1 H, $\text{CCH}=\text{CH}$), 7.48 (d, $J = 8.1$ Hz, 2 H, C_6H_4), 5.67 (s, 10 H, C_5H_5), 2.45 (s, 3 H, CH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (50.10 MHz, acetone- d_6 , 0.07 M $\text{Cr}(\text{acac})_3$) δ 439.9 ($\mu\text{-CCH}$), 254.3 ($\mu\text{-C}=\text{O}$), 208.9 (terminal CO), 153.4, 152.4 ($\text{CCH}=\text{CH}$), 146.8 ($\text{CH}=\text{CHC}$), 133.5, 131.6 (ortho, meta), 132.8 (CCH_3), 93.1 (C_5H_5), 22.2 (CH_3); IR (CH_2Cl_2) $\nu(\text{CO})$ 2033 (s), 2000 (m), 1848 (m) cm^{-1} . Anal. Calcd for $\text{C}_{23}\text{H}_{19}\text{BF}_4\text{Fe}_2\text{O}_3$: C, 50.98; H, 3.53. Found: C, 51.06; H, 3.76.