higher level (MP2/6-31G*).[12] The C–C–C bond angle calculated by using 1.46 and 2.51 Å for the central-methyl and methyl–methyl distances is 120° within experimental error, providing a clear experimental verification of the traditional bonding model. Thus, nutation NMR shows that the structure of the *tert*-butyl cation is trigonal with a short (1.46 Å) central carbon–methyl carbon bond length.

We have demonstrated a general methodology for measuring the molecular geometry (bond lengths and angles) of carbocations by using nutation NMR spectroscopy. It should be possible, by using nutation NMR, to obtain the localized geometry of many reactive intermediates that can be stabilized in a matrix. Preparation of doubly-^{13}C labeled isomers of several other interesting carbocations is in progress.

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Registry No. *tert*-Butyl cation, 14804-25-2; *tert*-butyl chloride, 507-20-0.

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The Carbon-13 NMR Spectrum of Solid Iron Pentacarbonyl

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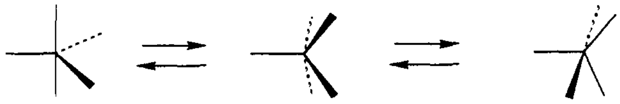
For the first time the carbon-13 NMR signals for the axial and equatorial carbonyls in iron pentacarbonyl have been observed. The detection of these signals in the solid suggests that axial–equatorial exchange in the solid state cannot occur at a rate greater than 10^2 s^{-1} at −38 °C or lower.

The first carbon-13 NMR spectrum of a metal carbonyl was reported in 1958 for iron pentacarbonyl by Cotton, Danti, Waugh, and Fessenden.[1] The result, a single resonance in the carbonyl region, has been shown to be correct by several subsequent investigations;[2-4] in fact the single resonance for $Fe(CO)_5$ persists to −160 °C.[4] Since the structure of iron pentacarbonyl in solution is trigonal-bipyramidal, the carbon-13 NMR spectrum for this complex should contain two signals of relative intensity 2 to 3. Of the possible explanations for the single resonance it is now accepted that the trigonal-bipyramidal structure undergoes a reorientation which is fast on the NMR time scale and exchanges equatorial and axial carbonyl resonances. The most likely mechanism for the exchange of carbonyls is the well-known Berry pseudorotation[5] shown schematically below.

Berry Rotation



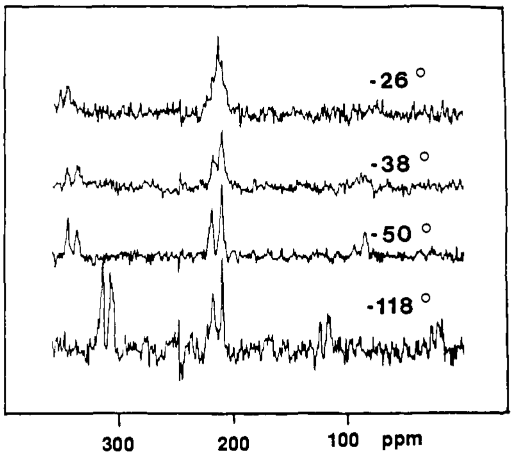


Figure 1. Magic angle spinning ^{13}C NMR spectra of solid $Fe(CO)_5$. The spinning rate varied from 2140 Hz at −118 to 2900 Hz at −26 °C.

Iron pentacarbonyl has been previously studied in the solid state by broadline NMR at temperatures from 4.2 to 213 K.[6] Evaluation of the spin lattice relaxation times over part of this temperature range and calculation of the expected line shapes led to the conclusion that a molecular rearrangement occurs in solid $Fe(CO)_5$. Two possible mechanisms for the motion were considered, a pseudorotation, as described above, and a rotation about the molecular 3-fold axis of the trigonal-bipyramidal molecule. The authors concluded that a Berry pseudorotation better described the experimental data.[6] The exchange frequency for the motion was measured to be 2.4×10^4 s^{-1} at −60 °C. From the reported variation of the rate with temperature an activation energy of 0.5 kcal mol^{-1} can be calculated. Although the activation energy is similar to what is estimated for axial–equatorial exchange of carbonyls in liquid $Fe(CO)_5$, the exchange frequency is much slower than the corresponding rate of molecular reorientation in liquid $Fe(CO)_5$ at −20 °C (1.1×10^{10} s^{-1}).[7,8] The rate estimated from the broadline studies in the solid state is sufficiently fast to exchange axial and equatorial carbonyl resonances on the NMR time scale provided the isotropic chemical shifts of the axial and equatorial carbonyl groups are within 1000 Hz. The expected chemical shift difference at 22.5 MHz for axial and equatorial carbonyls should be less than this since the typical range of chemical shifts observed for terminal carbonyl ligands in neutral iron carbonyl derivatives is ca. 208–220 ppm.[9]

Figure 1 shows the magic angle spinning ^{13}C NMR spectra for iron pentacarbonyl as a function of temperature.[10] At temperatures of −38 °C and lower, two signals at 216.0 and 208.1 ppm are observed. The relative integrated intensities, including spinning sidebands, are 2:3, respectively, for the two signals consistent with a trigonal-bipyramidal structure. This represents the first time that distinct axial and equatorial signals have been observed in a metal pentacarbonyl complex.

The melting point of $Fe(CO)_5$ is approximately −20 °C. All MAS spectra recorded between the temperatures −20 and −30 °C show three signals in the carbonyl region. These occur at 216.0, 208.1, and 211.6 ppm. The last of these corresponds to the isotropic shift of iron pentacarbonyl.[3] The presence of this signal however is not indicative of rapid axial–equatorial exchange in

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(10) The MAS spectra were recorded on a spectrometer consisting of a 2.1 superconducting magnet (Chemagnetics), a JEOL FX90Q consol, and a variable-temperature MAS probe tuned to 22.53 MHz (Chemagnetics). Iron pentacarbonyl was enriched to ca. 15% in ^{13}CO by stirring the neat liquid under ^{13}CO in the presence of Palladium black. The sample was distilled and then transferred to a standard delrin rotor at −78 °C. The probe was precooled prior to −30 °C before the sample was introduced. All spectra obtained are the result of a single 90° pulse (6 μs) at the temperature indicated. Prior to obtaining a spectrum the temperature, as indicated by a thermocouple in the drive gas stream, was held constant for 10 min. After recording a spectrum and before recording the next spectrum the sample was warmed to between −23 and −30 °C for 0.5 h to allow the carbon magnetization to relax. The sample was then recooled to the desired temperature.

the solid state. Rather the simultaneous observation of three signals indicates the presence of two phases, most likely a liquid and a solid phase, in the sample at these temperatures. Further evidence of this is seen in the first set of spinning sidebands in the spectrum at −26 °C; the sidebands corresponding to the solid phase are observed, but a sideband representing the average of axial and equatorial signals is not present.

Clearly it can be concluded from these results that axial–equatorial exchange of carbonyls is not rapid on the NMR time scale in solid Fe(CO)$_5$ at temperatures of −26 °C and lower. This is in contrast to the conclusion reached from broadline NMR.[6] We propose therefore that the motion indicated by broadline NMR in iron pentacarbonyl is best represented by a rotation about the 3-fold axis of the trigonal-bipyramidal and not a pseudorotation. Such a rotation does not exchange axial and equatorial carbonyls.

Further examination of the MAS NMR results for Fe(CO)$_5$ shows that the line widths of both peaks diminish as the temperature is lowered. Although in principle a plot of the log of the line width vs $1/T$ will yield an activation energy for the process responsible for the line narrowing, in the present case the data is not sufficiently good to put a great deal of faith in the result.[11] The line narrowing observed as the temperature is lowered may be due to rotation about the molecular 3-fold axis.

At temperatures above −50 °C the chemical shift anisotropy appears to diminish as judged by the relative intensity of the spinning side bands to the center band. This may be indicative of incipient axial–equatorial exchange but at a rate which is too slow to average signals on the NMR time scale. Work at high field in the slow spinning regime is necessary for the elucidation of the chemical shift parameters which may shed further light on the molecular motions in solid Fe(CO)$_5$.[12]

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(11) From five data points at −38 °C and lower an activation energy of 0.6 kcal mol^{-1} is calculated; however, the correlation coefficient from the least-squares fit is only 0.7.

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A Novel Intramolecular Cyclopropanation Using Iodonium Ylides

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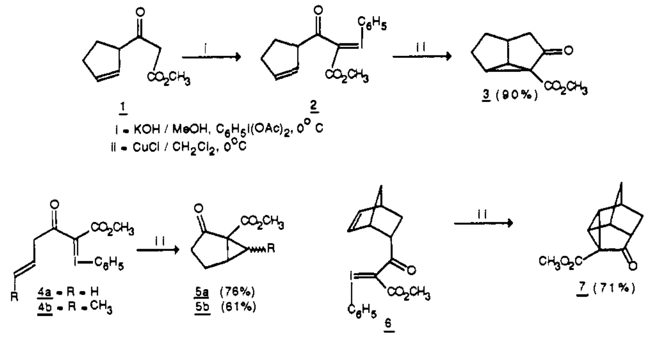
In 1961, Stork and Ficini reported intramolecular cyclopropanation in the Cu bronze decomposition of an unsaturated α-diazo ketone.[1] Since then, this reaction has emerged as a widely useful method in organic synthesis.[2,3] Particularly noteworthy are recent examples by Hudlicky et al.,[4] Taber et al.,[5] Chen,[6] and Kang et al.[7] Reasoning from a formal analogy between β-dicarbonyl iodonium ylides and the β-dicarbonyl α-diazo compound[8] and motivated to find a method that avoids the hazards of diazo compounds (explosive carcinogens)[9] for intramolecular cyclopropanation, we synthesized iodonium ylide **2** and carried out its decomposition in the presence of CuCl.[10] Indeed, a 90% yield of **3** was obtained.[10] Reactions **4a**,**b** → **5a**,**b** as well as **6** → **7** suggest the generality of the intramolecular cyclopropanation.



In the transition-metal-catalyzed decomposition of diazo compounds, a metal–carbene complex probably intervenes.[3] In the present reactions, we do not believe carbenoid intermediates are involved for the following reasons. First, iodonium ylides undergo a number of cycloaddition reactions leading to the formation of five-membered heterocycles. These include reactions with CS$_2$,[11] phenyl isothiocyanate,[11] acetonitrile,[11] alkenes,[11] and diphenylketene.[12] In the reaction of 2,4-dinitro-6-phenyliodonium phenolate with alkenes, alkynes, and aromatics, 2,3-dihydrobenzo[*b*]furans, benzo[*b*]furans, and 6-aryl-2,4-dinitrophenols are formed.[13] Secondly, no Wolff-type rearrangement products were formed in these reactions, although the analogous α-keto carbene

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(10) Ylide **2** was synthesized by the reaction of **1** with diacetoxyiodobenzene in KOH/MeOH at 0 °C (yield 80%): mp 113–115 °C (dec); IR (CHCl$_3$) 1726 (C═O stretching), 1655 (C═C stretching) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.46–2.37 (m, 4 H, CH_2CH_2 in cyclopentene), 3.04 (d, 2 H, CH_2CO), 3.12–3.22 (m, 1 H, CH in cyclopentene), 3.65 (s, 3 H, COOCH_3), 5.67–5.73 (m, 2 H, CH═CH), 7.33–7.78 (m, 5 H, aromatic protons). Ylide **4a**: mp 54–56 °C (dec); yield 78%; IR (CHCl$_3$) 1734 (C═O stretching), 1653 (C═C stretching) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.5 (t, 2 H, CH_2), 3.75 (s, 3 H, COOCH_3), 5.1 (m, 2 H, CH═CH_2), 6.0 (m, 1 H, CH), 7.4–7.9 (m, 5 H, aromatic protons). Ylide **4b**: mp 85–86 °C (dec); yield 85%; IR (CHCl$_3$) 1735 (C═O stretching), 1650 (C═C stretching) cm^{-1}; ^{1}H NMR δ 1.6 (d, 3 H, CH_3), 2.33 (m, 2 H, CH_2CH═), 3.03 (t, 2 H, CH_2CO), 3.65 (s, 3 H, COOCH_3), 5.45 (m, 2 H, CH═CH), 7.35–7.75 (m, 5 H, aromatic protons). Ylide **6**: mp 94–96 °C (dec); yield 91%; IR (CHCl$_3$) 1730 (C═O stretching), 1653 (C═C stretching) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.3–2.1 (m, 4 H, 2 × CH_2), 2.85 (m, 1 H, CH), 3.2 (m, 1 H, CH), 3.70 (s, 3 H, COOCH_3), 4.15 (m, 1 H, CH), 5.8 (m, 2 H, CH═CH), 6.2 (m, 2 H, CH═CH), 7.3–7.90 (m, 5 H, aromatic protons). In a typical experiment, cuprous chloride (10–20 mg) was added to a solution of **2** (3.70 g, 10 mmol) in dichloromethane (20 mL) under nitrogen at 0 °C. The reaction mixture was stirred at 0 °C for 10 min and then at room temperature for 1 h. The mixture was then filtered, evaporated to dryness in vacuo, and chromatographed on silica gel (9:1 (v/v) hexane–ethyl acetate) to remove C$_6$H$_5$I and gave pure **3** (1.60 g, 90%). The spectral properties (IR, ^{1}H NMR, MS) of product **3** were identical with those reported in ref 24. Product **5a**: yield 76%; this product had the same properties as those reported in ref 25. Product **5b**: yield 81%; IR (neat) 1740 (b, C═O stretching of COOMe), 1725 (C═O stretching) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.25 (d, 3 H, CH_3), 1.78–2.68 (m, 6 H), 3.78 (s, 3 H, COOCH_3) (the ^{1}H NMR of **5b** shows about a 70:30 mixture of two diastereomers; one diastereomer (30%) is reported[5]). Product **7**: yield 71%; IR (CHCl$_3$) 1754 (C═O stretching of COOMe), 1734 (C═O stretching) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.50 (d, 1 H, CH), 1.70 (m, 2 H, 2 × CH), 2.02 (d, 1 H, CH), 2.40 (dd, 1 H, CH), 2.63 (m, 1 H, CH), 2.75 (m, 1 H, CH), 3.05 (m, CH), 3.70 (s, 3 H, COOCH_3), 3.78 (m, CH); MS M$^+$ = 192 (12.49%), 77 (100%).

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