and enhancement of the NMR signal assigned to IV was observed on addition of an authentic sample of IV[9] to the reaction mixture. The infrared spectrum of the exit gas from the reaction mixture was identical with the infrared spectrum of carbon monoxide.[10]

The amine IV has been demonstrated to be an excellent source of fluoride ion.[11] Thus, we propose that trifluoromethide (V) is produced via capture of III by fluoride and that VI and VII result from attack of V on the in situ formed metal halide.

This novel method avoids the prior formation of mercurial, cadmium, or zinc reagents for ligand exchange processes[7] and it also avoids the use of the expensive trifluoromethyl iodide or trifluoroacetic acid precursors. In our process the reagent is produced in situ from readily available, cheap, commercial precursors and readily scaled up and can be directly utilized for the preparation of useful quantities of trifluoromethylated derivatives. Our future work will be directed toward the elucidation of the full scope of this unusual transformation.

The operational details of the experimental procedure for the preparation of the cadmium reagent are outlined below: A three-neck 250-mL round-bottom flask equipped with stopper, septum, magnetic stirring bar, and dry ice condenser under a nitrogen atmosphere was charged with 50 mL of dry dimethylformamide and 22.4 g (0.2 mol) of activated cadmium. The CF_2BrCl (8.6 mL, 0.10 mol) was condensed into the mixture of the solvent and metal. An exotherm resulted which gave a dark brown solution with precipitate. The reaction mixture was stirred for 2 h at room temperature and then filtered through a medium-fritted Schlenk funnel under nitrogen pressure. The precipitate was washed with 10–15 mL of dry DMF. The resulting solution (approximately 1 M) was utilized in subsequent reactions.

(9) Fawcett, F. S.; Tullock, C. W.; Coffman, D. D. *J. Am. Chem. Soc.* **1962**, *84*, 4275.
(10) The average of four experiments showed that the volume of CO formed equaled or slightly exceeded the percent of CF_3CdX formed.
(11) Knunyants, I. L.; Delyagina, N. I.; Igumnov, S. M. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1981**, *4*, 857.

Observation of Secondary ^{13}C Equilibrium Isotope Effect in the Degenerate Rearrangement of 2,3-Dimethyl-2-butyl Cation Using Natural Abundance ^{13}C NMR Spectroscopy[1]

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The deuterium isotope perturbation method, developed by Saunders and co-workers[2] to distinguish rapidly equilibrating systems with low energy barriers (double minima) from symmetric systems (single minimum), has become a versatile tool to study degenerate carbocation rearrangements.[3] By asymmetric deuterium substitution, by use of ^{13}C NMR spectroscopy the σ-bridged nature of several carbocations have been demonstrated. Other

(1) Considered Stable Carbocations. 264. For part 263, see: Prakash, G. K. S.; Krishnamurthy, V. V.; Arvanaghi, M.; Olah, G. A. *J. Org. Chem.*, in press.
(2) Saunders, M. in "Stereodynamics of Molecular Systems"; Sarma, Ed.; Pergamon Press: Oxford, 1979; p 171.
(3) Olah, G. A.; Prakash, G. K. S.; Sommer, J. "Superacids"; Wiley Interscience: New York, 1985; Chapter 3.

Table I. Secondary ^{13}C Equilibrium Isotope Effect in 2,2-Dimethyl-2-butyl Cation, in SO_2ClF/SbF_5

temp (± 2 °C)	chem shift splitting (± 1 Hz), δ	$K_2/K_1{}^a$ (± 0.0004) (secondary ^{13}C equilibrium isotope effect)	$K_2{}^b$
−90 °C	23	1.0066	1.0203
−100 °C	29	1.0084	1.0232
−110 °C	39	1.0113	1.0273

$^a K_2/K_1 = (\Delta + 2\delta)/(\Delta - 2\delta)$ where $\Delta = 13\,941$ (277 ppm[11,12] at 50.33 MHz). $^b K_1$ values are taken from ref 4.

rapidly equilibrating carbocationic systems which are degenerate in solution even at −140 °C were shown to be regular trivalent carbenium ions by this method. Saunders and co-workers recently studied the primary ^{13}C equilibrium isotope effect in 2,3-dimethyl-2-butyl cation[4] and secondary ^{13}C equilibrium isotope effect in 1,2-dimethylcyclopentyl cation.[5]

The deuterium isotopic perturbation studies and the recent ^{13}C equilibrium isotope effect study require preparation of specifically labeled precursors. Recently we have reported[6] investigations on $^{13}C-^{13}C$ NMR coupling constants in a variety of neutral and electron-deficient systems measured with natural abundance ^{13}C samples using the INADEQUATE[7] pulse sequence.

This versatile method of observing only molecules with two ^{13}C isotopes at natural abundance prompted us to investigate ^{13}C isotopic perturbation of a degenerate carbocation rearrangement. We chose to study 2,3-dimethyl-2-butyl cation (1), which undergoes rapid degenerate equilibration.

1
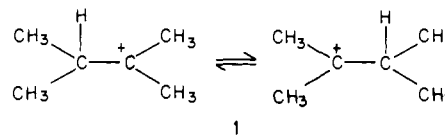
Ion 1 (30% w/v) was prepared by the ionization of 2-chloro-2,3-dimethylbutane in SbF_5/SO_2ClF at −78 °C and studied at three different temperatures (−90, −100, and −110 °C). The ^{13}C NMR spectrum shows two peaks, one average resonance for the methine and the cationic carbon ($\delta_{^{13}C}$ 181.0) and another resonance for the methyl groups ($\delta_{^{13}C}$ 15.7). The equilibria of interest in the present study are **1a ⇌ 1b** and **1c ⇌ 1d**.
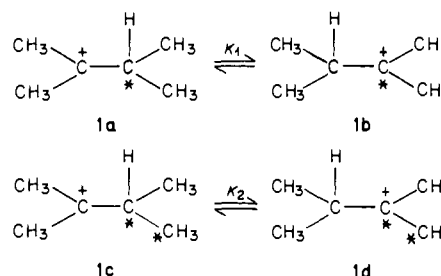

Earlier study by Saunders et al. on the equilibrium **1a ⇌ 1b** has shown that the equilibrium constant, i.e., primary ^{13}C isotope effect (K_1), is 1.0136, 1.0147, and 1.0159 at −90, −101, and −111 °C, respectively, with the positive charge being favored on the carbon-13. In **1c ⇌ 1d** the unsymmetrically situated ^{13}C-methyl group will perturb the equilibrium which can be detected by a shift in the ^{13}C resonance frequency of the average cationic-methine carbon. Signals from the doubly labeled ion (**1c ⇌ 1d**) at natural abundance can be detected by using the INADEQUATE pulse sequence, while those from the mono labeled ion

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(5) Saunders, M.; Telkowski, L.; Kates, M. R. *J. Am. Chem. Soc.* **1977**, *99*, 8070.
(6) Olah, G. A.; Iyer, P. S.; Prakash, G. K. S.; Krishnamurthy, V. V. *J. Am. Chem. Soc.* **1984**, *106*, 7073 and references therein.
(7) (a) Bax, A.; Freeman, R.; Kempsell, S. P. *J. Am. Chem. Soc.* **1980**, *102*, 4849. (b) Bax, A.; Freeman, R.; Kempsell, S. P. *J. Magn. Reson.* **1980**, *41*, 349. (c) Bax, A.; Freeman, R. *J. Magn. Reson.* **1980**, *41*, 507.
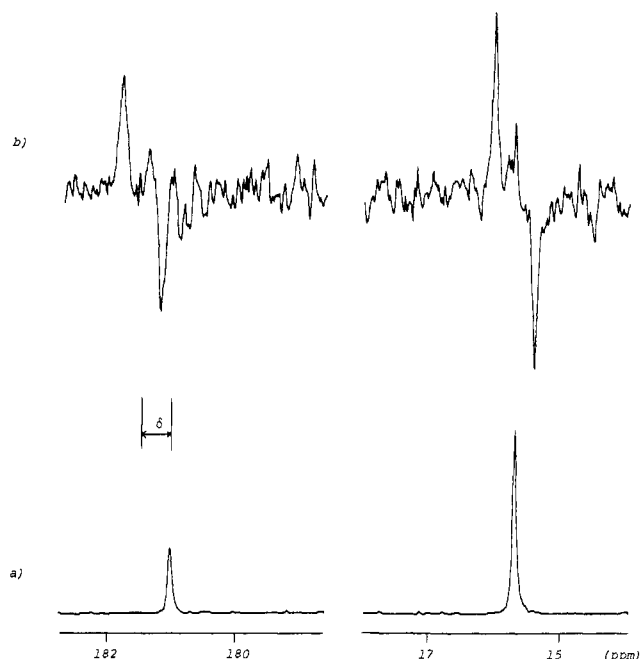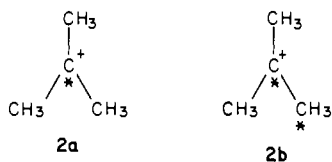
Figure 1. (a) ^{13}C NMR spectrum of **1** in SbF$_5$/SO$_2$ClF at –90 °C. (b) ^{13}C Satellite spectrum of **1** in SbF$_5$/SO$_2$ClF at –90 °C; δ, equilibrium ^{13}C isotope effect on ^{13}C chemical shift of the averaged methine and cationic carbons.

(**1a** $\rightleftharpoons$ **1b**) can be obtained by regular natural abundance ^{13}C spectrum.

Figure 1 shows both the regular ^{13}C NMR spectrum and ^{13}C "satellite" spectrum of **1** obtained in SbF$_5$/SO$_2$ClF at –90 °C.[8] In the satellite spectrum (using the INADEQUATE pulse sequence)[9] both the signals appear as doublets[10] with 180° phase shift in one component of each doublet. The resonance frequency of the carbons in the satellite spectrum can be calculated as the average of the AX doublets. The regular ^{13}C NMR spectrum (Figure 1a) represent the signal from the ion **1a** $\rightleftharpoons$ **1b** while the satellite spectrum (Figure 1b) represent the signal from the ion **1c** $\rightleftharpoons$ **1d**. The resonance frequency of the peak at $\delta_{^{13}C}$ 181 is shifted downfield in the satellite spectrum (Figure 1b) compared to that in the regular spectrum (Figure 1a). The magnitude of the shift is temperature dependent and the values are listed in Table I for the temperature range studied.

In order to determine the intrinsic ^{13}C isotope effect on ^{13}C chemical shift we also studied the *tert*-butyl cation. The difference in the cationic carbon chemical shift between the normal ^{13}C spectrum (which represent the ^{13}C spectrum of **2a**) and the ^{13}C

satellite spectrum (which represent the ^{13}C spectrum of **2b**) is less than 2 Hz. Thus the relatively large (23–39-Hz deshielding) ^{13}C isotope effect observed in **1** between –90 and –110 °C is due to the perturbation of the equilibrium due to ^{13}C isotopic substitution. The deshielding of the average peak at $\delta_{^{13}C}$ 181 in **1c** $\rightleftharpoons$ **1d** compared to that in **1a** $\rightleftharpoons$ **1b** indicates that the secondary ^{13}C isotope perturbs the equilibrium toward **1d**. In other words, the positive charge is favored on a carbon next to a ^{13}C isotope (as in **1c**) as opposed to next to a ^{12}C isotope (as in **1d**).

The secondary ^{13}C equilibrium isotope effect (i.e., K_2/K_1) can be determined by $(\Delta + 2\delta)/(\Delta - 2\delta)$ where Δ is the chemical shift difference between the cationic carbon and the methine carbon in the "frozen out" structure and δ is the chemical shift difference of the average cationic and methine carbon signals between the "normal" spectrum and the ^{13}C satellite spectrum. The values of secondary ^{13}C equilibrium isotope effects (i.e., K_2/K_1) and those of K_2 (calculated using the K_2/K_1 values obtained in this study and K_1 values reported earlier[4]) are listed in Table I. However, to calculate K_2 one need to know K_1, which can be determined only by labeling. The secondary ^{13}C isotope effects (K_2/K_1) range from 1.0066 to 1.0113 over the temperature range studied while K_2 (product of primary and secondary ^{13}C equilibrium isotope effect) range from 1.0203 to 1.0273.

Thus for the first time we have observed the secondary ^{13}C isotopic perturbation of a degenerate equilibrium using natural abundance sample. We have shown that the unsymmetrically positioned ^{13}C isotope does, indeed, produce significant perturbation of the equilibrium which can be conveniently monitored by a change in the ^{13}C chemical shift in the ^{13}C satellite spectrum. These isotope effects are significantly larger compared to intrinsic ^{13}C isotope effect on ^{13}C chemical shift as observed in the *tert*-butyl cation. Our studies are continuing to determine the feasibility of using such secondary ^{13}C isotope effects to distinguish equilibrating systems from bridged ones.

2a   2b

(8) The spectra were recorded on a Varian XL-200 superconducting NMR spectrometer operating at 50-MHz ^{13}C resonance frequency. The field frequency lock was held for the entire duration of the experiment using a coaxial insert containing acetone-d_6. Thus, the "normal" and the "satillite" spectrum can be compared with respect to the transmitter frequency.

(9) The pulse sequence used for the ^{13}C satellite spectra, based on Freeman et al.,[7] is 90°(x)–τ–180°(±y)–τ–90°(x)–Δ–90°(φ)–Acq(ψ), where τ ≃ (2n + 1)/4J_{CC}, Δ is a very short delay (~10 μs) needed to reset the radiofrequency phase, and φ and ψ are the phase of the last 90° "read" pulse and the receiver, respectively. Optimum setting of τ for direct coupling is when n = 0 and thus set a 7.0 ms (corresponding to a J_{CC} value of ~36 Hz). The repetition rate of this sequence is ~6 s, and reasonable signal to noise ratio was achieved in 8 h of acquisition.

(10) J_{C,CH_3} = 30 ± 1 Hz.

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Pentadienyl Compounds of Zirconium, Niobium, and Molybdenum: "U" vs. "S" η⁵-2,4-Dimethylpentadienyl Coordination[1]

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While metal–pentadienyl compounds have been known since at least 1962,[3] it has only been recently that the utility of these compounds has been appreciated.[4] From a reactivity standpoint, the accessibility of η⁵, η³, and η¹ bonding modes for the pentadienyl ligand (I–III) is a key reason for its utility. As our initial studies

I   II   III
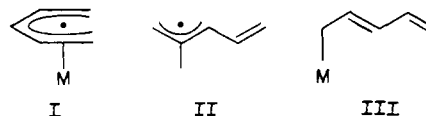
(1) A partial account has been presented: Stahl, L.; Ernst, R. D. "Abstracts of Papers", 40th Southwest Regional Meeting of the American Chemical Society, Lubbock, TX, Dec. 7, 1984; American Chemical Society: Washington, DC, 1984; No. 73.

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(3) Mahler, J. E.; Pettit, R. *J. Am. Chem. Soc.* **1962**, *84*, 1511.

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