and enhancement of the NMR signal assigned to IV was observed on addition of an authentic sample of IV⁹ 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 processes⁷ 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 CF₂BrCl (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.

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Observation of Secondary ¹³C Equilibrium Isotope Effect in the Degenerate Rearrangement of 2,3-Dimethyl-2-butyl Cation Using Natural Abundance ¹³C NMR Spectroscopy¹

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The deuterium isotope perturbation method, developed by Saunders and co-workers² 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 ¹³C NMR spectroscopy the σ -bridged nature of several carbocations have been demonstrated. Other

Table I.	Secondary 1	'C Equi	ilibrium	Isotope	Effect	i
2,2-Dime	ethyl-2-butyl	Cation,	in SO ₂	CIF/SbI	-	

temp (±2 °C)	chem shift splitting (±1 Hz), δ	K_2/K_1^a (±0.0004) (secondary ¹³ C equilibrium isotope effect)	K2 ^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 ¹³C equilibrium isotope effect in 2,3-dimethyl-2-butyl cation⁴ and secondary ¹³C equilibrium isotope effect in 1,2-dimethylcyclopentyl cation.5

The deuterium isotopic perturbation studies and the recent ¹³C equilibrium isotope effect study require preparation of specifically labeled precursors. Recently we have reported⁶ investigations on ¹³C-¹³C NMR coupling constants in a variety of neutral and electron-deficient systems measured with natural abundance ¹³C samples using the INADEQUATE⁷ pulse sequence.

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



Ion 1 (30% w/v) was prepared by the ionization of 2-chloro-2,3-dimethylbutane in SbF5/SO2ClF at -78 °C and studied at three different temperatures (-90, -100, and -110 °C). The ¹³C 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 $1a \Rightarrow 1b$ and $1c \Rightarrow 1d$.



Earlier study by Saunders et al. on the equilibrium $1a \Rightarrow 1b$ has shown that the equilibrium constant, i.e., primary ¹³C 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 $1c \Rightarrow 1d$ the unsymmetrically situated ¹³C-methyl group will perturb the equilibrium which can be detected by a shift in the ¹³C resonance frequency of the average cationicmethine carbon. Signals from the doubly labeled ion $(1c \Rightarrow 1d)$ at natural abundance can be detected by using the INADE-QUATE pulse sequence, while those from the mono labeled ion

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Figure 1. (a) ¹³C NMR spectrum of 1 in SbF₅/SO₂ClF at -90 °C. (b) ¹³C Satellite spectrum of 1 in SbF₅/SO₂ClF 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 ¹³C spectrum.

Figure 1 shows both the regular ¹³C NMR spectrum and ¹³C "satellite" spectrum of 1 obtained in SbF₅/SO₂ClF at -90 °C.⁸ In the satellite spectrum (using the INADEQUATE pulse sequence)⁹ both the signals appear as doublets¹⁰ 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 ¹³C 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 $1c \Rightarrow 1d$. The resonance frequency of the peak at δ_{DC} 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 ¹³C isotope effect on ¹³C chemical shift we also studied the tert-butyl cation. The difference in the cationic carbon chemical shift between the normal ¹³C spectrum (which represent the ${}^{13}C$ spectrum of 2a) and the ${}^{13}C$



(8) The spectra were recorded on a Varian XL-200 superconducting NMR spectrometer operating at 50-MHz $^{13}\mathrm{C}$ 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 ¹³C satellite spectra, based on Freeman et al.,⁷ is 90°(x)- τ -180°($\pm y$)- τ -90°(x)- Δ -90°(ϕ)- Δ cq(ψ), where $\tau \simeq (2n + 1)/4J_{CC}$, Δ is a very short delay (~10 μ s) needed to reset the radiofre-quency 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.

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

The secondary ¹³C 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 ¹³C satellite spectrum. The values of secondary ¹³C 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 earlier⁴) 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 ¹³C 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 ¹³C equilibrium isotope effect) range from 1.0203 to 1.0273.

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

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Registry No. 1a, 17603-18-8; (CH₃)₂CHCCl(CH₃)₂, 594-57-0; ¹³C, 14762-74-4.

Pentadienyl Compounds of Zirconium, Niobium, and Molybdenum: "U" vs. "S" η^5 -2,4-Dimethylpentadienyl Coordination¹

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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 η^5 , η^3 , and η^1 bonding modes for the pentadienyl ligand (I-III) is a key reason for its utility. As our initial studies



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