two-electron alkynes.[4] We have also been able to confirm that the odd electron in the intermediate $1^-$ is in a primarily metal-centered orbital by examination of the room temperature ESR spectrum of 1[K(DBC)]·2THF in THF: the sharp signal at $\langle g \rangle$ = 2.001 has well-resolved $^{53}$Cr satellites from which we can calculate $a$ ($^{53}$Cr) = 13.3 G.[20]

There is one example in the literature of a complex in which the electronic flexibility of an alkyne ligand allows the metal to coordinate an additional donor ligand,[30] but to the best of our knowledge the reduction of 1 is the first case in which this flexibility has been observed to permit direct addition of two electrons to an alkyne complex.

**Registry No. 1**, 97487-55-3; 1⁻, 97487-56-4; 1²⁻, 97487-57-5; 1[K-(DBC)]·THF, 97487-59-7; [Cr(Me₃SiC≡CSiMe₃)₂(CO)₂], 83802-82-8; Cr(CO)₃(NCEt)3, 91513-88-1; diphenylacetylene, 501-65-5.

**Supplementary Material Available:** Tables of atomic positional and thermal parameters and intramolecular bond lengths (4 pages). Ordering information given on any current masthead page.

(20) Reported $a(^{53}$Cr) for anionic Cr complexes are less than 2 G if the electron is in a ligand-based orbital.[21] Values between 14 and 20 G have been observed for d⁷ cases.[22]

(21) Kaim, W. *Inorg. Chem.* **1984**, *23*, 3365.

(22) (a) Elsenbroich, Ch.; Koch, J. *J. Organomet. Chem.* **1982**, *229*, 139. (b) Elsenbroich, Ch.; Bilger, E.; Koch, J.; Weber, J. *J. Am. Chem. Soc.* **1984**, *106*, 4297.

# A Remarkably Simple Preparation of (Trifluoromethyl)cadmium and -zinc Reagents Directly from Difluorodihalomethanes[1]
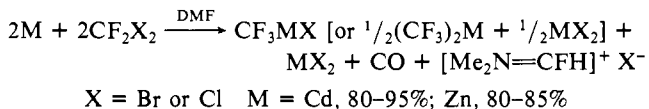
Donald J. Burton* and Denise M. Wiemers

*Department of Chemistry, University of Iowa Iowa City, Iowa 52242*

*Received April 1, 1985*

Bioactive drugs and agricultural chemicals that contain a trifluoromethyl group have been the subjects of increased research activity in recent years.[2] Concomitant with these applications has been renewed vigor in the design of a cheaper and more efficient synthetic methodology for the introduction of the trifluoromethyl group into organic compounds. An adjunct of this strategy has been a revival in the preparation of trifluoromethyl organometallic derivatives as potential transfer agents of the trifluoromethyl group.[3]

We report herein the preliminary results of a novel high-yield preparation of (trifluoromethyl)cadmium and -zinc reagents via reaction of difluorodihalomethanes, such as CF₂Cl₂, CF₂Br₂, and CF₂BrCl, with activated (acid-washed) cadmium and zinc powders[4] in dry dimethylformamide as outlined:

$$2M + 2CF_2X_2 \xrightarrow{DMF} CF_3MX \; [\text{or } {}^1/_2(CF_3)_2M + {}^1/_2MX_2] + MX_2 + CO + [Me_2N{=}CFH]^+ \; X^-$$

X = Br or Cl    M = Cd, 80–95%; Zn, 80–85%

(1) Presented in part at the ACS 7th Winter Fluorine Conference, Orlando, FL, Feb, 1985, Abstract 15.

(2) "Organofluorine Compounds and Their Industrial Applications"; Banks, R. E., Ed.; Ellis Horwood Ltd. Chichester, 1979. "Biomedicinal Aspects of Fluorine Chemistry"; Filler, R., Kobayashi, Y., Eds.; Kodasha/Elsevier: New York, 1982. "Biochemistry Involving Carbon-Fluorine Bonds"; Filler, R., Ed.; American Chemical Society: Washington, DC, 1976; ACS Symp. Ser., No. 28.

(3) Morrison, J. A. *Adv. Inorg. Chem. Radiochem.* **1983**, *27*, 293.

**Scheme I**
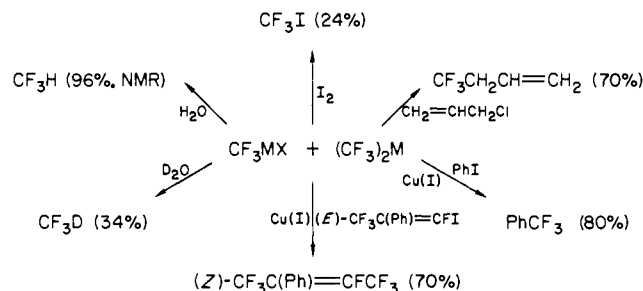


**Scheme II**
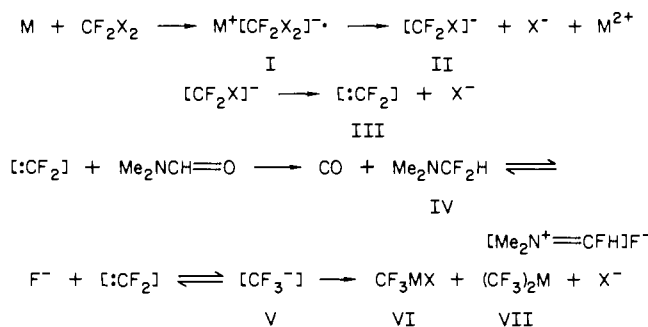


The reactions with CF₂Br₂ and CF₂BrCl are conveniently initiated at room temperature in standard glassware, whereas the preparation utilizing CF₂Cl₂ is carried out at 80 °C in a sealed ampule.[5] On mixing of the difluorodihalomethane with the metal powder, a short induction period ensues followed by an exothermic reaction. However, sequential addition of the methane permits ready scale-up, and the zinc reagent is routinely made in 0.5-mol preparations and the cadmium reagent in 0.1-mol preparations.

Confirmation of the remarkable transformation of a difluoromethylene carbon to a trifluoromethyl carbon was obtained via a combination of spectroscopic[6] and chemical evidence (Scheme I).

We propose the following mechanism (Scheme II) to explain this unprecedented difluoromethylene to trifluoromethyl transformation.

Electron-transfer between the metal and the difluorodihalomethane produces a radical anion I. A second electron-transfer produces the M²⁺ ion and the difluorohalomethide ion (II), which subsequently loses halide ion to give difluorocarbene (III).[8] Evidence consistent with the formation of I and III was obtained as follows: (a) When the reaction between CF₂X₂ and metal is carried out in the presence of *p*-dinitrobenzene (a known radical-anion inhibitor), total quenching of the reaction was observed; no trifluoromethyl organometallic was detected and no loss of methane was observed; (b) when the reaction was carried out in the presence of 2,3-dimethyl-2-butene, a 60% yield (NMR) of 1,1-difluoro-2,2,3,3-tetramethylcyclopropane was observed.

Subsequent capture of III by DMF ultimately gives the difluoromethyl amine IV and CO. The presence of IV was detected spectroscopically via ¹⁹F NMR analysis of the reaction mixture

(4) Acid-washed metal powders reduce the induction period.

(5) The reactions with CF₂Br₂ and CF₂BrCl initiate spontaneously; the reaction with CF₂Cl₂ is initiated by heating to 80 °C. Caution with the sealed ampule reaction is required because of pressure buildup due to the CO generated in the reaction.

(6) ¹⁹F NMR: CF₃ZnX, –44.5; (CF₃)₂Zn, –43.4; CF₃CdX, –35.7; (CF₃)₂CD, –36.1 ppm. ¹¹³Cd NMR: CF₃CdX, 459.3 (q); (CF₃)₂Cd, 409.8 (hept). *J*[(Cd-113)–(F-19)]: CF₃CdX, 438.2; (CF₃)₂Cd, 391.9 Hz. *J*-[(Cd-111)–(F-19)]: CF₃CdX, 256; (CF₃)₂Cd, 228 Hz. For simplicity the metal reagents are written as CF₃MX; however, they are probably coordinated with the DMF. These values are in good agreement with the literature values.[7]

(7) Krause, L. J.; Morrison, J. A. *J. Chem. Soc., Chem. Commun.* **1980**, 671. Naumann, D.; Lange, H. *J. Fluorine Chem.* **1984**, *26*, 1. Naumann, D.; Lange, H. *J. Fluorine Chem.* **1984**, *26*, 435.

(8) III may be formed via a concerted process. II is only shown for operational purposes.

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 CF₃CdX 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]

V. V. Krishnamurthy, G. K. Surya Prakash, Pradeep S. Iyer, and George A. Olah*

*The Donald P. and Katherine B. Loker Hydrocarbon Research Institute and Department of Chemistry University of Southern California Los Angeles, California 90089-1661*

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
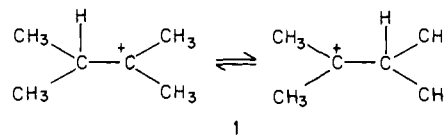
Ion 1 (30% w/v) was prepared by the ionization of 2-chloro-2,3-dimethylbutane in $SbF_5/SO_2ClF$ at −78 °C and studied at three different temperatures (−90, −100, and −110 °C). The $^{13}C$ NMR spectrum shows two peaks, one average resonance for the methine and the cationic carbon ($\delta_{^{13}C}$ 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**.
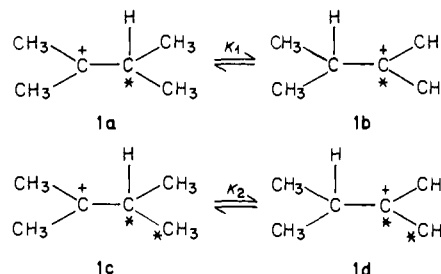


Earlier study by Saunders et al. on the equilibrium **1a ⇌ 1b** has shown that the equilibrium constant, i.e., primary $^{13}C$ isotope effect ($K_1$), is 1.0136, 1.0147, and 1.0159 at −90, −101, and −111 °C, respectively, with the positive charge being favored on the carbon-13. In **1c ⇌ 1d** the unsymmetrically 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

(4) Saunders, M.; Kates, M. R.; Walker, G. E. *J. Am. Chem. Soc.* **1981**, *103*, 4623.

(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.