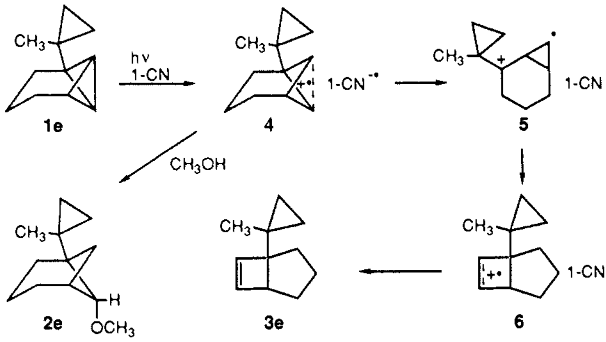
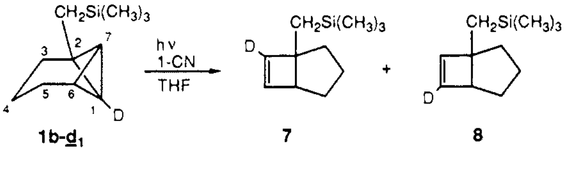
10^{-3} M **1e** and 2 × 10^{-3} M 1-CN gave 5% of **3e** and 22% of **2e**.[11] The relatively low yields obtained in this reaction could be traced to the destruction of both **2e** and **3e** under our reaction conditions in methanol. Addition of 1,4-cyclohexadiene as a free radical scavenger coupled with stopping the reaction at 15% conversion gave a 24% yield of **3e** and a 53% yield of **2e** based on unrecovered starting material.[12] This demonstrated that with a substituent which was intermediate in carbocation stabilizing ability, both products could be formed and that diverse reaction paths were followed from a single starting material.



Earlier, we suggested that the conversion of **1b** into **3b** proceeded by a stepwise process involving initial electron transfer from the C1–C7 bond of **1** to give a cation radical–anion radical pair analogous to that represented by **4**.[2d] Conversion of **4** into **5** followed by rearrangement to **6** and back electron transfer[13] to yield **3** would explain the formation of the rearranged product. The formation of only **3e** in tetrahydrofuran, benzene, or acetonitrile[14] coupled with the relatively low yield of **3e** and the formation of **2e** as the major product in the nucleophilic solvent methanol suggests to us that **4** is an intermediate in the formation of both **2e** and **3e**. The presence of methanol as a nucleophile resulted in the interception of **4** prior to rearrangement.[15]

The last question to be addressed was whether **4** might rearrange directly to **6** via migration of C5 from C6 to either C1 or C7 of **4**. This possibility was eliminated through a study of the photoinduced rearrangement of **1b**-d_1,[16] which gave **7** and **8** in the ratio of 1.24:1.[17] No **3b** deuterated at the bridge-head position was found, which ruled out the migration of C5 from C6 to either C1 or C7.



In summary, we have elucidated some of the factors which control the behavior of photogenerated cation radicals. Our findings support the concept that one-electron carbon–carbon bonds are subject to molecular rearrangement if suitably strong carbocation-stabilizing groups are properly situated. We are continuing our efforts in this study of photogenerated cation radicals.

Acknowledgment. We are indebted to the National Science Foundation for a grant which supported this investigation.

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[11] Compound **2e** showed the following properties: IR (neat) 3070, 2940, 2820, 1450, 1200, 1000 cm^{-1}; ^{1}H NMR (C_6D_6) δ 3.12 (1 H, d, J = 5.18 Hz), 3.02 (3 H, s), 2.28–2.19 (2 H, m), 1.85–1.78 (1 H, m), 1.70–1.50 (4 H, m), 1.24 (1 H, d, J = 9.62 Hz), 1.00 (3 H, s), 0.80 (1 H, d of d, J = 9.56, J = 6.21 Hz), 0.55 (1 H, m), 0.36 (1 H, m), 0.20–0.08 (2 H, m); ^{13}C NMR (C_6D_6) δ 79.26 (d), 55.34 (q), 50.20 (s), 33.39 (d), 26.41 (t), 22.65 (t), 21.89 (t), 21.40 (s), 21.16 (q), 16.55 (t), 10.63 (t), 10.13 (t); mass spectrum, m/e found 182.1669 (calcd for $C_{12}H_{20}O$ 182.1670). Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.93; H, 11.18.

[12] These relative yields were in agreement with the limiting quantum yields of 0.01 and 0.02 for the formation of **3e** and **2e**, respectively. In THF, with a 10^{-3} M 1-CN concentration and 1.7 × 10^{-2} M concentration of **1e**, the quantum yield for fluorescence quenching of 1-CN was 0.21.

[13] It should be noted that back electron transfer to **5** from the 1-CN anion radical, followed by rearrangement of the zwitterion, would also produce **3**.

[14] The yields of **3e** from **1e** in benzene and acetonitrile were 66% and 28%, respectively. In acetonitrile, a large amount of oligomeric material was formed.

[15] On the basis of presently available data, we cannot establish whether a highly delocalized cation radical, where the cation radical character is shared between the C1–C7 bond and the C1–C2 bond, is involved. However, we are reluctant to propose the intermediacy of such a "nonclassical" cation radical.

[16] Treatment of **1b** with n-butyllithium followed by quenching with deuterium oxide gave **1b**-d_1 which was 93% deuterated at C1 as determined by NMR and mass spectrometry.

[17] The ratio of **7** to **8** and the structural assignments were based on NMR analysis. This included extensive NOE studies.

(Trifluoromethyl)cyclopentadienide: A Powerful Electron-Withdrawing Ligand for Transition-Metal Complexes

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Received February 20, 1986

Recently, we have devoted considerable effort to the evaluation of the effects of substituents on the cyclopentadienyl moiety on the electronic character of complexed transition metals.[1] We have demonstrated through the use of X-ray photoelectron spectroscopy (XPS or ESCA) that methyl substitution can have a dramatic impact on the electronic properties of a series of complexed transition metals including titanium, zirconium, hafnium, and iron.[1a,2] In terms of substituents, most attention has been devoted to the use of the pentamethylcyclopentadienyl moiety.[3,4] By comparison, relatively little is known about cyclopentadienyl ligands bearing electron-withdrawing substituents.[5] In view of the desirability of cyclopentadienyl complexes bearing electron-withdrawing substituents for certain catalytic processes,[6] we found it surprising that the (trifluoromethyl)cyclopentadienyl group had not been developed as a transition-metal ligand. We now report the synthesis of a series of η^5-(trifluoromethyl)cyclopentadienyl (CF_3Cp) complexes. In addition, we have demonstrated through the use of ESCA that the CF_3Cp ligand exercises a powerful electron-withdrawing effect on the complexed transition metal.

(Trifluoromethyl)cyclopentadiene (**1**) was prepared according to the method of Olsson and Wennerström.[7] Since it was well established that **1** gave 6,6-disubstituted fulvenes on treatment with base, we chose to prepare the thallous salt **2**, through reaction of **1** with thallous ethoxide[8] at −10 to −15 °C in diethyl ether for 15 min. The very insoluble CF_3CpTl (**2**) was isolated by filtration,

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[1] (a) Gassman, P. G.; Macomber, D. W.; Hershberger, J. W. *Organometallics* **1983**, *2*, 1470. (b) Gassman, P. G; Macomber, D. W.; Willging, S. M. *J. Am. Chem. Soc.* **1985**, *107*, 2380. (c) Gassman, P. G.; Campbell, W. H.; Macomber, D. W. *Organometallics* **1984**, *3*, 385.

[2] See also: Calabro, D. C.; Hubbard, J. L.; Blevins, C. H., II; Campbell, A. C.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1981**, *103*, 6839 and references therein. Miller, E. J.; Landon, S. J.; Brill, T. B. *Organometallics* **1985**, *4*, 533.

[3] King, R. B.; Bisnette, M. B. *J. Organomet. Chem.* **1967**, *8*, 287.

[4] For general references, see: Maitlis, P. M. *Acc. Chem. Res.* **1978**, *11*, 301. Wolczanski, P. T.; Bercaw, J. E. *Ibid.* **1980**, *13*, 121. McLain, S. J.; Sancho, J.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 5451. Manriquez, J. M.; Fagan, P. J.; Marks, T. J. *Ibid.* **1978**, *100*, 3939. Sikora, D. J.; Rausch, M. D.; Rogers, R. D.; Atwood, J. L. *Ibid.* **1981**, *103*, 1265. Freyberg, D. P.; Robbins, J. L.; Raymond, K. N.; Smart, J. C. *Ibid.* **1979**, *101*, 892. King, R. B. *Coord. Chem. Rev.* **1976**, *20*, 155. Schmidt, G. F.; Brookhart, M. *J. Am. Chem. Soc.* **1985**, *107*, 1443. Gilbert, T. M.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 3508. Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. *Ibid.* **1985**, *107*, 8091.

[5] Macomber, D. W.; Hart, W. P.; Rausch, M. D. *Adv. Organomet. Chem.* **1982**, *21*, 1. Conway, B. G.; Rausch, M. D. *Organometallics* **1985**, *4*, 688.

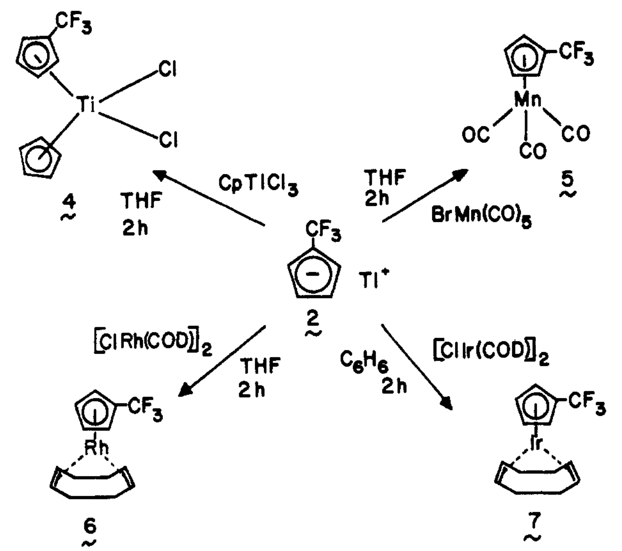
[6] Bönneman, H. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 248.

[7] Olsson, T.; Wennerström, O. *Acta Chem. Scand., Ser. B* **1978**, *B32*, 293.

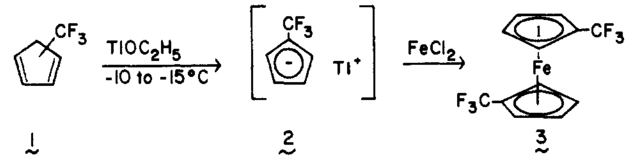
[8] Purchased from Aldrich Chemical Co. and used without purification.

0002-7863/86/1508-4228$01.50/0

Scheme I



washed with ether, and vacuum dried to afford 55–60% yields of **2**. Since this material was thermally labile (decomposed rapidly at room temperature) and very insoluble, it was not characterized further. Reaction of 2 equiv of **2** with ferrous chloride (1 equiv) in tetrahydrofuran at ambient temperature for 5 h gave bis(trifluoromethyl)ferrocene (3) in 43% yield.[9] ESCA measurements[10]



on **3** showed a Fe($2p_{3/2}$) binding energy of 708.6 ± 0.1 eV. This can be compared to values of 708.0 ± 0.1 and 707.1 ± 0.1 eV for ferrocene and decamethylferrocene, respectively.[1a] This illustrates the strong electron-withdrawing effect which the presence of the trifluoromethyl group exerts on the binding energy of the inner-shell electrons of iron. An analogous comparison can be made for the valence-shell electrons. Electrochemical oxidation[10] of **3** gave an $E° = 0.95 \pm 0.02$ V, which can be compared to $E° = 0.31$ and -0.23 V for ferrocene and decamethylferrocene, respectively.[1a] This illustrates that the trifluoromethyl group has an effect on the valence-shell electrons of ferrocene which shifts it by 0.64 V. This is opposite to and greater than the 0.54-V change observed for the addition of ten methyls to ferrocene. Thus, the trifluoromethyl group, while exerting relatively little steric effect, provides a significant electron-withdrawing electronic effect.

In order to illustrate the versatility of **2**, we carried out reactions with derivatives of titanium, rhodium, iridium, and manganese, as illustrated in Scheme I. Treatment of cyclopentadienyltitanium trichloride[8] in tetrahydrofuran with 1.1 equiv of **2** gave 84% of **4**.[11] Examination of the ESCA spectrum of **4** showed a Ti($2p_{3/2}$) binding energy of 457.3 ± 0.1 eV. This can be compared with a related value of 456.9 ± 0.1 eV for titanocene dichloride.[1a] Again, the strong electron-withdrawing characteristics of the trifluoromethyl group were demonstrated.

Reaction of manganese pentacarbonyl bromide[12] with **2** in tetrahydrofuran for 2 h gave a 70% yield of **5**.[13] Similarly, reaction of chloro(1,5-cyclooctadiene)rhodium(I) dimer[12] with **2** in tetrahydrofuran for 2 h gave 71% of **6**,[14] and reaction of chloro(1,5-cyclooctadiene)iridium(I) dimer[12] with **2** under similar conditions gave 76% of **7**.[15] These examples amply demonstrated the versatility of 2 as a reagent for preparing CF_3Cp derivatives of transition metals.

In summary, we have prepared several examples of CF_3Cp complexes of transition metals and have demonstrated that the trifluoromethyl group exercises a powerful electron-withdrawing effect. We believe that the CF_3Cp moiety will prove to be very useful in modifying the reactive properties of a variety of transition-metal complexes.

Acknowledgment. We are indebted to the National Science Foundation for a grant which partially supported this investigation.

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[9] Compound **3** showed the following properties: mp (sealed tube) 39–40 °C; IR (KBr) 3020, 2975, 2840, 1733, 1489, 1456, 1388, 1305, 1230, 1146, 1125, 1111, 1030, 1020, 891, 831, 750, 727, 695 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.58 (t, $J = 2$ Hz, 4 H), 4.40 (d, $J = 2$ Hz, 4 H); ^{13}C NMR ($CDCl_3$) δ 126.18 (q, $J_{CF} = 268$ Hz), 79.15 (q, $J_{CCF} = 39$ Hz), 71.14, 68.13; mass spectrum, *m/e* calcd for $C_{12}H_8F_6Fe$, 321.9880; found, 321.9880. Anal. Calcd for $C_{12}H_8F_6Fe$: C, 44.76; H, 2.50. Found: C, 44.95; H, 2.55. In addition, the structure of **3** was established by single-crystal X-ray analysis (details to be published later).

[10] For experimental conditions, see ref 1a.

[11] Compound **4** showed the following properties: mp (sealed tube) 141–142 °C; IR (KBr) 3115, 3035, 2930, 2855, 1736, 1512, 1502, 1450, 1392, 1335, 1249, 1170, 1137, 1122, 1074, 1059, 1020, 901, 821, 795, 735, 699, 680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.97 (t, $J = 2.9$ Hz, 2 H), 6.69 (s, 5 H), 6.52 (t, $J = 2.9$ Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 121.81, 121.68 (q, $J_{CF} = 270$ Hz), 121.49, 119.11, 116.33 (q, $J_{CCF} = 39$ Hz); mass spectrum, *m/e* calcd for $C_{11}H_9Cl_2F_3Ti$, 315.9513; found, 315.9539. Anal. Calcd for $C_{11}H_9Cl_2F_3Ti$: C, 41.68; H, 2.86. Found: C, 41.71; H, 3.02.

[12] Purchased from Strem Chemicals, Inc., and used without purification.

[13] Compound **5** was a liquid which was molecularly distilled (0.05 mm, ambient temperature): orange oil; IR (neat) 3130, 2030 (s), 2010 (sh), 1942 (vs), 1501, 1422, 1386, 1372, 1322, 1240, 1161, 1135, 1123, 1066, 1043, 1025, 898, 840, 733, 696 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.0 (brs, 2 H), 4.6 (brs, 2 H); ^{13}C NMR ($CDCl_3$) δ 222.67, 123.28 (q, $J_{CF} = 269$ Hz), 90.10 (q, $J_{CCF} = 40$ Hz), 84.08, 81.93; mass spectrum, *m/e* calcd for $C_9H_4O_3F_3Mn$, 271.9493; found, 271.9493. Anal. Calcd for $C_9H_4O_3F_3Mn$: C, 39.73; H, 1.48. Found: C, 39.40; H, 1.47.

[14] Compound **6** had the following properties: mp (sealed tube) 45–46 °C; IR (KBr) 3000, 2945, 2880, 2835, 1735, 1495, 1458, 1436, 1395, 1332, 1307, 1246, 1235, 1147, 1121, 1094, 1065, 1055, 1031, 1025, 971, 895, 876, 835, 819, 786, 728, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.16 (s, 4 H), 4.00 (s, 4 H), 2.00 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ 124.40 (q, $J_{CF} = 268$ Hz), 95.76 (d of q, $J_{CCF} = 38$, $J_{Rh-C} = 4.0$ Hz), 88.45 (d, $J_{Rh-C} = 3.4$ Hz), 84.85 (d, $J_{Rh-C} = 2.8$ Hz), 65.23 (d, $J_{Rh-C} = 4.2$ Hz), 32.17; mass spectrum, *m/e* calcd for $C_{14}H_{16}F_3Rh$, 344.0259; found, 344.0258. Anal. Calcd for $C_{14}H_{16}F_3Rh$: C, 48.86; H, 4.68. Found: C, 49.14; H, 4.83.

[15] Compound **7** had the following properties: mp (sealed tube) 43–44 °C; IR (KBr) 3110, 3085, 2950, 2920, 2915, 2820, 1491, 1395, 1304, 1164, 1155, 1120, 1106, 1032, 921, 806, 729 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.21 (d, 4 H), 3.82 (s, 4 H), 1.82 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ 124.06 (q, $J_{CF} = 268$ Hz), 89.26 (q, $J_{CCF} = 38$ Hz), 84.59, 79.46, 48.82, 33.57; mass spectrum, *m/e* calcd for $C_{14}H_{16}F_3Ir$, 434.0834; found, 434.0839. Anal. Calcd for $C_{14}H_{16}F_3Ir$: C, 38.79; H, 3.72. Found: C, 38.95; H, 3.72.

Generation, Spectroscopic Detection, and Chemical Reactivity of Fluorinated Vinylcopper Reagents[1]

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Received February 10, 1986

The utility of alkenyl copper and/or alkenyl cuprate reagents for regio- and stereochemical control in organic synthesis is well documented, and the addition of these organometallic compounds to the organic chemist's arsenal of reagents has permitted synthetic transformations which were difficult or impossible to accomplish effectively with any other reagent.[2] A notable omission, however, from the list of known copper species is the complete absence of any fluorinated vinyl copper reagent, although such moieties could be invaluable in the construction of fluorine-containing bioactive drugs, polymers, and agricultural chemicals.[3]

We report herein the preliminary results of a novel, high-yield preparation of stable polyfluorinated vinyl copper reagents via

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[1] Presented in part at the 11th International Symposium on Fluorine Chemistry, East Berlin, Germany, Aug 1985, Abstract B-4.

[2] *An Introduction To Synthesis Using Organocopper Reagents*; Posner, G. H., Ed.; Wiley-Interscience; New York, 1980.

[3] Filler, R., Ed. *ACS Symp. Ser.* **1976**, *No. 28*. *Biomedicinal Aspects of Fluorine Chemistry*; Filler, R., Kobayashi, Y., Eds.; Kodasha/Elsevier: New York, 1982. *Organofluorine Chemicals and Their Industrial Applications*; Banks, R. E., Ed.; Ellis Harwood Ltd.: Chichester, 1979.