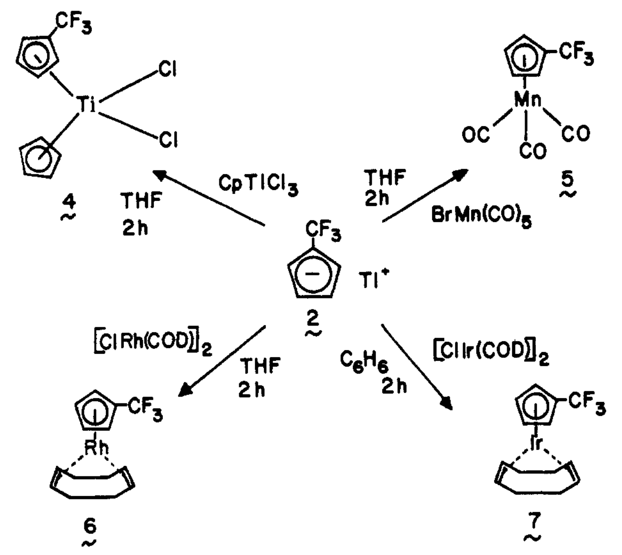
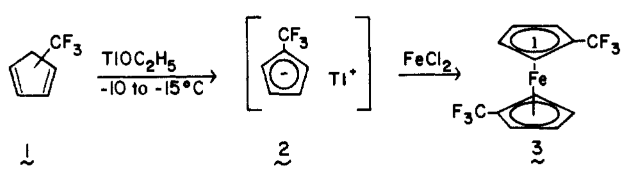
Scheme I



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 ± 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}; ^{1}H 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}; ^{1}H 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}; ^{1}H 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}; ^{1}H 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}; ^{1}H 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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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.

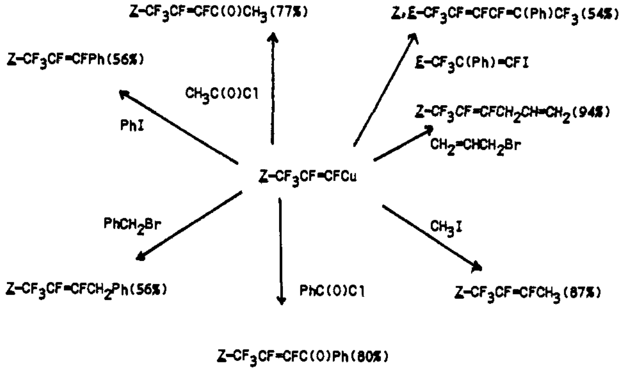
(3) Filler, R., Ed. *ACS Symp. Ser.* **1976**, *No. 28*. *Biomedicinal Aspects of Fluorine Chemistry*; Filler, R., Kobayashi, Y., Eds.; Kodasha/Elsevier: New York, 1982. *Organofluorine Chemicals and Their Industrial Applications*; Banks, R. E., Ed.; Ellis Harwood Ltd.: Chichester, 1979.

Table I. Preparation of Vinylcopper Reagents

olefin	M	$R_FCF{=}CFCu$	% yield[a]
$CF_2{=}CFI$	Cd	$CF_2{=}CFCu$	99%
$CF_2{=}CFBr$	Zn	$CF_2{=}CFCu$	72%
(*Z*)-$CF_3CF{=}CFI$	Cd	(*Z*)-$CF_3CF{=}CFCu$	92%
(*Z*)-$CF_3CF{=}CFI$	Zn	(*Z*)-$CF_3CF{=}CFCu$	76%
(*E*)-$CF_3CF{=}CFI$	Cd	(*E*)-$CF_3CF{=}CFCu$	83%
(*Z*)-$CF_3(CF_2)_4CF{=}CFI$	Cd	(*Z*)-$CF_3(CF_2)_4CF{=}CFCu$	87%
(*Z*)-$CF_3CCl{=}CFI$	Cd	(*Z*)-$CF_3CCl{=}CFCu$	78%
$CF_3C(Ph){=}CFBr$ $E/Z = 59/41$	Zn	$CF_3C(Ph){=}CFCu$ $E/Z = 59/41$	84%
$CF_3CF{=}C(Ph)CF{=}CFBr$ $E/Z = 90/10$	Zn	$CF_3CF{=}C(Ph)CF{=}CFCu$ $E/Z = 90/10$	63%

[a] Overall ^{19}F NMR yield based on starting olefin.

Scheme I[7]



a copper(I) halide metathesis reaction of the corresponding vinylcadmium and/or zinc reagents.[4] Table I summarizes these preliminary results.

$$\underset{X\,=\,Br,\ I}{R_FCF{=}CFX} + \underset{M\,=\,Cd,\ Zn}{M} \xrightarrow[\text{room temperature–60 °C}]{\text{DMF}} R_FCF{=}CFMX + (R_FCF{=}CF)_2M + MX_2 \xrightarrow[\text{room temperature}]{Cu^IX} \underset{68–99\%}{R_FCF{=}CFCu}$$

The preparation of the vinylcadmium or -zinc precursors proceeds stereospecifically, and the metathesis with Cu^IX occurs with retention of configuration.[5] Consequently, stereochemical integrity is retained throughout the synthetic sequence and one can confidently prepare either isomeric copper reagent with total stereochemical control by proper choice of the appropriate vinyl halide.[6]

The vinylcopper reagents exhibit excellent stability at room temperature in the absence of oxygen and/or moisture. At higher temperature (>50 °C) they undergo rapid decomposition.

The vinylcopper reagents participate in a variety of alkylation, coupling, and acylation reactions as illustrated in Scheme I with (*Z*)-$CF_3CF{=}CFCu$.

The operational details of a typical experimental procedure for the pregeneration of (*Z*)-$CF_3CF{=}CFCu$ are outlined below: A two-necked 50-mL round bottom flask equipped with thermometer, magnetic stir bar, septum port, and condenser was charged under a nitrogen atmosphere with 6.5 g (0.025 mol) of (*Z*)-$CF_3CF{=}CFI$ and 25 mL of dry DMF. To this solution was added 3.5 g (0.031 mol) of acid-washed cadmium powder. After a short induction period, a mild exotherm resulted and a mixture of mono and bis (*Z*)-$CF_3CF{=}CFCdX$ was formed in 96% yield (mono/bis = 67/33) as determined by ^{19}F NMR. The excess cadmium was removed by pressure filtration under dry nitrogen through a fine fritted glass filter (Schlenk funnel). Then 4.2 g (0.029 mol) of CuBr was added to this mixture at 0 °C and the mixture was stirred for $^1/_2$ h followed by warming to room temperature. ^{19}F NMR analysis[8] indicated a 96% yield of (*Z*)-$CF_3CF{=}CFCu$. This solution was employed for subsequent functionalization reactions.

In summary, this work describes an *unequivocal* route to fluorinated vinylcopper reagents. The reagent is readily produced in situ from vinylic halides under mild conditions, is easily scaled up, allows total stereochemical control, and can be directly utilized in a wide variety of synthetic transformations. Our work continues with these reagents and future efforts will focus on the elucidation of the full scope of these new organometallic reagents.

Acknowledgment. We thank the National Science Foundation (CHE-85-16380) and the Air Force Office of Scientific Research (AFOSR-85-0009) for financial support of this work.

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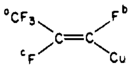
(4) Such reagents are prepared in 80–99% yield via direct reaction of cadmium or zinc powder with the corresponding vinyl iodide (at room temperature) or vinyl bromide (at 60 °C) in DMF.

(5) Stereochemical assignments are based on $J_{F,F}$ or J_{F,CF_3} in either the organometallic reagent or in the reduced olefin $R_FCF{=}CFH$, obtained on hydrolysis of the copper reagent.

(6) In 1979 Miller and co-workers reported the preparation of (*E*)-$CF_3CF{=}C(CF_3)Cu$ from (*E*)-$CF_3CF{=}C(CF_3)Ag$: Miller, W. T. *Abstracts of the 9th International Symposium on Fluorine Chemistry*; Avignon, France; p 027. Our method avoids the use of the expensive silver intermediates and the problem of regiospecificity in the addition of AgF to a perfluoroalkyne.

(7) Yields in Scheme I are based on ^{19}F NMR using $PhCF_3$ as the internal standard.

(8) ^{19}F NMR of



exhibits the following spectroscopic parameters: F_a (dd) −64.7, F_b (dq) −135.9, and F_c (dq) −180.0 ppm; $J_{ab} = 22.6$, $J_{ac} = 13.7$, and $J_{bc} = 100.2$ Hz.

New Cryptophane Forming Unusually Stable Inclusion Complexes with Neutral Guests in a Lipophilic Solvent

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In the absence of hydrophobic forces, host–guest complexes between uncharged species are usually weak[1–5] (stability constants <~10 M^{-1}). We report here that new cavitand **2**, cryptophane E, can form inclusion complexes of comparatively very large

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[†] Equipe de recherche du C.N.R.S. No 285

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