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(tri-fluoromethyl)ferrocene (3) in 43% yield.<sup>9</sup> ESCA measurements<sup>10</sup>



on 3 showed a Fe( $2p_{3/2}$ ) binding energy of 708.6 ± 0.1 eV. This can be compared to values of  $708.0 \pm 0.1$  and  $707.1 \pm 0.1$  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<sup>10</sup> of 3 gave an  $E^{\circ} = 0.95 \pm 0.02$  V, which can be compared to  $E^{\circ}$ = 0.31 and -0.23 V for ferrocene and decamethylferrocene, respectively.<sup>1a</sup> 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<sup>8</sup> in tetrahydrofuran with 1.1 equiv of 2 gave 84% of 4.<sup>11</sup> Examination of the ESCA spectrum of 4 showed a  $Ti(2p_{3/2})$ binding energy of  $457.3 \pm 0.1$  eV. This can be compared with

(10) For experimental conditions, see ref 1a.

a related value of 456.9  $\pm$  0.1 eV for titanocene dichloride.<sup>1a</sup> 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<sup>12</sup> with 2 in tetrahydrofuran for 2 h gave 71% of 6,<sup>14</sup> and reaction of chloro(1,5-cyclooctadiene)iridium(I) dimer<sup>12</sup> with 2 under similar conditions gave 76% of 7.15 These examples amply demonstrated the versatility of 2 as a reagent for preparing CF<sub>3</sub>Cp derivatives of transition metals.

In summary, we have prepared several examples of CF<sub>3</sub>Cp complexes of transition metals and have demonstrated that the trifluoromethyl group exercises a powerful electron-withdrawing effect. We believe that the CF<sub>3</sub>Cp 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.

(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<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  5.21 (d, 4 H), 3.82 (s, 4 H), 1.82 (m, 8 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  124.06 (q,  $J_{CF} = 26$ H), 532 (5, 4 H), 1.52 (1, 9 H), 1.52 (1, 9 H), 1.54 (1, 9 H), 1.54 (1, 9 H), 1.55 (1, 9 H), 1.

## Generation, Spectroscopic Detection, and Chemical Reactivity of Fluorinated Vinylcopper Reagents<sup>1</sup>

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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.<sup>2</sup> 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.<sup>3</sup>

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

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<sup>(9)</sup> Compound 3 showed the following properties: mp (sealed tube) 39-40 <sup>(6)</sup> Compound 3 showed the following properties: mp (sealed tube) 39-40<sup>o</sup>C; IR (KBr) 3020, 2975, 2840, 1733, 1489, 1456, 1388, 1305, 1230, 1146, 1125, 1111, 1030, 1020, 891, 831, 750, 727, 695 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ 4.58 (t, J = 2 Hz, 4 H), 4.40 (d, J = 2 Hz, 4 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  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<sub>12</sub>H<sub>8</sub>F<sub>6</sub>Fe, 321.9880; found, 321.9880. Anal. Calcd for C<sub>12</sub>H<sub>8</sub>F<sub>6</sub>Fe: C, 44.76; H, 2.50. Found: C, 44.95; H, 2.55. In addition, the tructure of  $\delta$  was established by single crystal V and pulsic (details to ba structure of 3 was established by single-crystal X-ray analysis (details to be published later).

<sup>(10)</sup> For experimental conditions, see ref 12. (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<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  6.97 (t, J = 2.9 Hz, 2 H), 6.69 (s, 5 H), 6.52 (t, J = 2.9 Hz, 2 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  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, 315.9593. Anal. Calcd for  $C_{11}H_9Cl_2F_3Ti$ : C 41.68; H 2.86 Equad: C 41.71; H 3.02 C, 41.68; H, 2.86. Found: C, 41.71; H, 3.02.

<sup>(12)</sup> 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<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  5.0 (brs, 2 H), 4.0 (brs, 2 H), <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  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<sub>9</sub>H<sub>4</sub>O<sub>3</sub>F<sub>3</sub>Mn, 271.9493; found, 271.9493. Anal. Calcd for C<sub>9</sub>H<sub>4</sub>O<sub>3</sub>F<sub>3</sub>Mn: C, 39.73; H, 1.48. Found: 98, 840, 733, 696 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 5.0 (brs, 2 H), 4.6 (brs, 2 H); C, 39.40; H, 1.47.

<sup>(14)</sup> Compound 6 had the following properties: mp (sealed tube) 45-46 °C; IR (KBr) 3000, 2945, 2880, 2835, 1735, 1495, 1458, 1436, 1395, 1332, <sup>1</sup>C; IR (KBF) 3000, 2943, 2860, 2853, 1735, 1495, 1438, 1436, 1436, 1395, 1392, 1392, 1307, 1246, 1235, 1147, 1121, 1094, 1065, 1055, 1031, 1025, 971, 895, 876, 835, 819, 786, 728, 700 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  4.16 (s, 4 H), 4.00 (s, 4 H), 2.00 (m, 8 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  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<sub>14</sub>H<sub>16</sub>F<sub>3</sub>Rh, 344.0259; found, 344.0258. Anal. Calcd for C<sub>14</sub>H<sub>16</sub>F<sub>3</sub>Rh; C, 48.85 (d, 4.92), 46.85 (d, 4.92), 46.95 (d, 4.92

<sup>(1)</sup> Presented in part at the 11th International Symposium on Fluorine Chemistry, East Berlin, Germany, Aug 1985, Abstract B-4.

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Table I. Preparation of Vinylcopper Reagents

			%
olefin	Μ	R <sub>F</sub> CF=CFCu	yield <sup>a</sup>
CF <sub>2</sub> =CFI	Cd	CF2=CFCu	99%
CF <sub>2</sub> =CFBr	Zn	CF <sub>2</sub> =CFCu	72%
(Z)-CF <sub>3</sub> CF=CFI	Cd	(Z)-CF <sub>3</sub> CF=CFCu	92%
(Z)-CF <sub>3</sub> CF=CFI	Zn	(Z)-CF <sub>3</sub> CF=CFCu	76%
(E)-CF <sub>3</sub> CF=CFI	Cd	(E)-CF <sub>3</sub> CF=CFCu	83%
(Z)-CF <sub>3</sub> (CF <sub>2</sub> ) <sub>4</sub> CF=CFI	Cd	(Z)-CF <sub>3</sub> (CF <sub>2</sub> ) <sub>4</sub> CF=CFCu	87%
(Z)-CF <sub>3</sub> CCl=CFI	Cd	(Z)-CF <sub>3</sub> CCl=CFCu	78%
CF <sub>3</sub> C(Ph)=CFBr	Zn	CF <sub>3</sub> C(Ph)=CFCu	84%
E/Z = 59/41		E/Z = 59/41	
CF <sub>3</sub> CF=C(Ph)CF=CFBr	Zn	CF <sub>3</sub> CF=C(Ph)CF=CFCu	63%
E/Z = 90/10		E/Z = 90/10	

<sup>a</sup>Overall <sup>19</sup>F NMR yield based on starting olefin.

## Scheme 17



Z-CF3CF=CFC(0)Ph(80%)

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

$$R_{F}CF = CFX + M$$

$$X = Br, I \qquad M = Cd, Zn$$

$$\xrightarrow{DMF} R_{F}CF = CFMX + (R_{F}CF = CF)_{2}M + MX_{2} \xrightarrow{Cu^{1}X} R_{F}CF = CFCu$$

$$68-99\%$$

The preparation of the vinylcadmium or -zinc precursors proceeds stereospecifically, and the metathesis with Cu<sup>I</sup>X occurs with retention of configuration.<sup>5</sup> 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<sub>3</sub>CF=CFCu.

The operational details of a typical experimental procedure for the pregeneration of (Z)-CF<sub>3</sub>CF=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<sub>3</sub>CF=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<sub>3</sub>CF=CFCdX was formed in 96% yield (mono/bis = 67/33) as determined by <sup>19</sup>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. <sup>19</sup>F NMR analysis<sup>8</sup> indicated a 96% yield of (Z)-CF<sub>3</sub>CF=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.

(7) Yields in Scheme I are based on <sup>19</sup>F NMR using PhCF<sub>3</sub> as the internal standard

(8) <sup>19</sup>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<sup>1-5</sup> (stability constants  $<\sim 10 \text{ M}^{-1}$ ). We report here that new cavitand 2, cryptophane E, can form inclusion complexes of comparatively very large

<sup>(4)</sup> Such reagents are prepared in 80-99% yield via direct reaction of cadmium or zinc powder with the corresponding vinyl iodide (at room tem-perature) or vinyl bromide (at 60 °C) in DMF.

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

<sup>(6)</sup> In 1979 Miller and co-workers reported the preparation of (E)-CF<sub>3</sub>CF=C(CF<sub>3</sub>)Cu from (E)-CF<sub>3</sub>CF=C(CF<sub>3</sub>)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.

<sup>&</sup>lt;sup>†</sup>Equipe de recherche du C.N.R.S. No 285

<sup>&</sup>lt;sup>†</sup>Equipe de recherche du C.N.R.S. No 285 (1) Very few complexes between uncharged host and guest partners in nonaqueous solvents have been reported; for relevant examples and general discussions, see ref 2-4 and the following papers: (a) Vögtle, F.; Müller, W. J. Incl. Phenomena 1984, I, 369-386. (b) Jarvi, E. T.; Whitlock, H. W. J. Am. Chem. Soc. 1982, 104, 7196. Whitlock, B. J.; Whitlock, H. W. J. Am. Chem. Soc. 1985, 107, 1325-1329. (c) Bauer, L. J.; Gutsche, C. D. J. Am. Chem. Soc. 1985, 107, 6063-6069. (d) Mossier-Boss, P.; Popov, A. I. J. Am. Chem. Soc. 1985, 107, 6168-6174. (e) O'Krongly, D.; Denmeade, R.; Chiang, M. Y.; Breslow, R. J. Am. Chem. Soc. 1985, 107, 5544-5545. (2) Moran, J. R.; Karbach, S.; Cram, D. J. J. Am. Chem. Soc. 1982, 104

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