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Preparation and properties of (.eta.5-C5H5)Co(CO)(CF3)2. The reaction of (CF3)2Cd.cntdot.glyme with CpCo(CO)I2

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Preparation and Properties of (η^5-C_5H_5)Co(CO)(CF_3)$_2$. The Reaction of (CF_3)$_2$Cd·glyme with CpCo(CO)I_2

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The reaction of $(CF_3)_2Cd$·glyme, where glyme = $CH_3OCH_2CH_2OCH_3$, with (η^5-Cp)Co(CO)I_2 generates (η^5-Cp)Co(CO)$(CF_3)_2$ in 63% yield along with (η^5-Cp)Co(CO)(CF_3)I in 16% yield. The bis(trifluoromethyl) product is also obtained from the interaction of $(CF_3)_2Cd$·glyme with CpCo(CO)(CF_3)I in 73% yield. The disubstituted species is an air-stable, yellow compound which thermally decomposes only near 175 °C. In contrast to the results typically found for main-group element trifluoromethyl halides, CpCo(CO)$(CF_3)_2$ is more thermally stable than (η^5-Cp)Co(CO)(CF_3)I. The reaction of CpCo(CO)$(CF_3)_2$ with $(CH_3)_2Cd$ forms CpCo(CO)$(CH_3)_2$ which decomposes at ambient temperature; CpCo(CO)(CF_3)(CH_3) is unobserved. The reaction with Br_2 generates CpCo(CO)(CF_3)Br, while photolysis in the presence of PPh_3 results in CpCo(PPh_3)$(CF_3)_2$.

Introduction

Recently, we have been examining the ligand exchange reactions of $(CF_3)_2Hg$ and $(CF_3)_2Cd$·glyme (glyme = $CH_3OCH_2CH_2OCH_3$) with the halides of a variety of elements. Bis(trifluoromethyl)cadmium·glyme has been found to react readily with a number of main-group compounds like GeI_4 and $SnBr_4$ to generate the completely substituted $(CF_3)_4Ge$ and $(CF_3)_4Sn$ derivatives.[1] Similarly, typical d^8 coordination complexes, like $Br_2Pd(PEt_3)_2$, afford the trifluoromethylated compounds $(CF_3)BrPd(PEt_3)_2$ and $(CF_3)_2Pd(PEt_3)_2$.[2]

The objective of the present study was to examine the reactivity of $(CF_3)_2Hg$ and $(CF_3)_2Cd$·glyme toward a typical low-valent transition metal containing organometallic substrate. The reagent CpCo(CO)I_2, containing a d^6 metal ion, was selected because it contains both a Cp– and a CO–metal linkage and because the chemistry of the η^5-CpCo(CO) moiety has been exceptionally well documented.

The specific goals of this study were fourfold: to establish the relative efficiency of $(CF_3)_2Hg$ and $(CF_3)_2Cd$·glyme in ligand exchange reactions with a representative organometallic compound, CpCo(CO)I_2; to compare the results of these reactions with the results obtained from the reactions of typical main-group elements; to examine the thermal and chemical stability of the expected product, CpCo(CO)$(CF_3)_2$; to ascertain whether the organic substance(s) derived from the thermal decomposition of CpCo(CO)$(CF_3)_2$ might consist at least in part, of $(CF_3)_2CO$, the perfluorinated derivative of the compound arising from the thermal decomposition of CpCo(CO)$(CH_3)_2$.[3]

Table I. Fluorine NMR Data for Organometallic Compounds

	δ^a	J, Hz
$(CF_3)_2Hg$	41.6	1277^b
$(CF_3)HgI$	44.5	1880^b
$(CF_3)_2Cd$·glyme	42.7	$493/461^c$
CpCo(CO)$(CF_3)_2$	81.7	
CpCo(PPh_3)$(CF_3)_2$	82.0	
CpCo(CO)CF_3I	90.4	
CpCo(CO)(CF_3)Br	83.7	

[a] Vs. external TFA. [b] $^2J_{Hg-F}$. [c] $J_{^{119/117}Cd-F}$.

Experimental Section

General Procedures. Dimethyl cadmium was prepared from CH_3MgI and $CdBr_2$. Bis(trifluoromethyl)cadmium·glyme was synthesized from $(CF_3)_2Hg$[4] and $(CH_3)_2Cd$ in glyme ($CH_3OCH_2CH_2OCH_3$).[1] The reagents CpCo(CO)I_2 and CpCo(CO)CF_3I were generated by standard procedures.[5-7] The former was purified by recrystallization from CH_2Cl_2 and the latter by sublimation at 60 °C. Pentane, hexane, Br_2, I_2, CF_3I, PPh_3, and (η^5-Cp)Co(CO)$_2$ were all used as received. Methylene chloride and $CDCl_3$ were dried over P_2O_5; C_6H_6, C_6D_6, *n*-butyl ether, glyme, and petroleum ether were dried over sodium benzophenone ketyl.

NMR data were recorded on Bruker HFX-90 and IBM WP-200-SY instruments; resonances deshielded from the standards are positive. Mass spectra were obtained from an AEI MS-30 spectrometer operating at 70 eV and ambient temperature. The infrared spectra are from an IBM IR-32 spectrophotometer. Uncorrected melting points were determined on samples which had been sealed into capillary tubes. The elemental analysis was carried out by Schwarzkopf, Woodside, N.Y.

Typically, the reactions and separations described below utilized standard vacuum lines and gloveboxes. However, since (η^5-Cp)Co(CO)$(CF_3)_2$ is essentially unaffected by the atmosphere, all manipulations of this material were routinely carried out on the bench top.

Interaction of $(CF_3)_2Hg$ with CpCo(CO)I_2 and CpCo(CO)(CF_3)I at Ambient Temperature. Bis(trifluoromethyl)mercury (0.043 mmol) and CpCo(CO)I_2 (0.019 mmol) were placed into a 4-mm tube, and, after evacuation, *n*-butyl ether was added. Similarly $(CF_3)_2Hg$ (0.12 mmol), CpCo(CO)(CF_3)I (0.02 mmol), and *n*-butyl ether were introduced into a second reactor. The vessels were then sealed and maintained at ambient temperature for 30 days. The only ^{19}F resonances observed were due to the $(CF_3)_2Hg$ and CpCo(CO)(CF_3)I; see Table I.

Interaction of $(CF_3)_2Hg$ with CpCo(CO)I_2 and CpCo(CO)(CF_3)I at 115 °C. The reaction of $(CF_3)_2Hg$ (0.074 mmol) with CpCo(CO)I_2 (0.037 mmol) in *n*-Bu_2O at 115 ± 2 °C was followed over a 65-h period during which time the formation of CF_3I and CF_3HgI was observed by ^{19}F NMR; see Table I. After 65 h the intensity of each resonance was ca. 10% of that due to the $(CF_3)_2Hg$ remaining. Aside from a very small amount of CF_3H (–0.3 ppm, $^2J_{HF}$ = 79 Hz) the only other resonance observed, δ 81.7, is ascribed to CpCo(CO)$(CF_3)_2$; see below. The maximum

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intensity at 81.7 ppm (45 h) was 2% of that due to $(CF_3)_2Hg$.

Bis(trifluoromethyl)mercury (0.055 g, 0.16 mmol) and CpCo(CO)(CF_3)I (0.0287 g, 0.082 mmol), in n-Bu_2O, were maintained at 115 °C for 238 h. Fluorine NMR indicated that CF_3H and CF_3HgI were generated in addition to small amounts of CpCo(CO)$(CF_3)_2$. The maximum amount of CpCo(CO)$(CF_3)_2$, (96 h) corresponded to a yield of 8%.

Interaction of $(CF_3)_2$Cd·glyme with CpCo(CO)I_2 and CpCo(CO)(CF_3)I. At ambient temperature, $(CF_3)_2$Cd·glyme (0.147 mmol) and CpCo(CO)I_2 (0.047 mmol) were allowed to react in CH_2Cl_2. After 94 h, CpCo(CO)$(CF_3)_2$, CF_3H, CF_3I (73.2 ppm), and $(CF_3)_2$Cd·glyme were present in the relative molar ratios 1.00:2.00:0.54:0.44; CpCo(CO)(CF_3)I was unobserved.

After 2 h at ambient temperature, fluorine NMR of the mixture originally containing $(CF_3)_2$Cd·glyme (0.09 mmol) and CpCo(CO)(CF_3)I (0.03 mmol) in CH_2Cl_2 indicated the presence of CpCo(CO)$(CF_3)_2$ and CpCo(CO)(CF_3)I in the molar ratio of 0.31:1.00. After 14 h the only resonances in the spectra were those due to CpCo(CO)$(CF_3)_2$ and $(CF_3)_2$Cd·glyme.

Preparation of CpCo(CO)$(CF_3)_2$ by Reaction of $(CF_3)_2$Cd·glyme with CpCo(CO)I_2. Under N_2 CpCo(CO)I_2 (0.229 g, 0.564 mmol) and $(CF_3)_2$Cd·glyme (0.554 g, 1.63 mmol) were dissolved in 10 mL of CH_2Cl_2 contained in a 50-mL round-bottom flask. The solution was magnetically stirred for 75 h during which time the color progressively lightened from a very dark green to a yellow-green. The solvent was removed under reduced pressure leaving a light brown solid. Column chromatography (120 × 10 mm column; 60–200 mesh silica gel; benzene) resulted in a bright yellow band and a dark purple band. Recrystallization from benzene–hexane (1:4 v/v) gave yellow CpCo(CO)$(CF_3)_2$ (0.103 g, 63%). After solvent removal 0.030 g (0.087 mmol) of CpCo(CO)(CF_3)I was recovered from the dark purple band. The yield was 16%.

Carbonyl(η^5-cyclopentadienyl)bis(trifluoromethyl)cobalt(III) is a volatile, air-stable material which in the absence of solvent thermally decomposes only near 175 °C; in sealed capillaries melting is not observed. The ^{19}F chemical shift (C_6D_6) is 81.7 ppm vs. TFA while that of the ^1H resonance is 4.50 ppm vs. Me_4Si. In $CDCl_3$, ^{13}C resonances are observed at 208 (CO) and 92.9 ppm (Cp, $^1J_{C-H}$ = 183 Hz) vs. Me_4Si, respectively. Although all of the resonances are slightly broadened, coupling to ^{59}Co (100%, I = $^7/_2$) is unresolved.

The low-resolution mass spectrum of CpCo(CO)$(CF_3)_2$ contains the following (m/e, ion, ion intensity): 290, $(CF_3)_2$CpCo(CO), 18; 271, (CF_3)(CF_2)CpCo(CO), 9; 262, $(CF_3)_2$CpCo, 10; 221, CF_3CpCo(CO), 22; 193, CF_3CpCo, 24; 143, FCpCo, 100; 128, CF_3Co, 24; 124, CpCo, 35; 78, FCo, 18; 69, CF_3, 26; 59, Co, 32. The measured exact mass of the molecular ion is 289.9565 (calculated 289.9576); $\Delta m/m$ = 3.8 ppm. Infrared absorptions (KBr) are found at 3132 (m), 2083 (s), 1632 (m), 1092 (s), 1065 (s), 1034 (s), 999 (s), 853 (w), and 710 (w) cm^{-1}. Anal. Calcd for $C_8H_5F_6OCo$: C, 33.10; H, 1.73; Found: C, 33.10; H, 1.68.

By Reaction of $(CF_3)_2$Cd·glyme with CpCo(CO)(CF_3)I. Under N_2, 1.59 g (4.69 mmol) of $(CF_3)_2$Cd·glyme and 0.54 g (1.56 mmol) of freshly sublimed, dark purple CpCo(CO)(CF_3)I were dissolved in 20 mL of CH_2Cl_2; the solution was magnetically stirred at ambient temperature for 12 h. After filtration and then solvent removal under reduced pressure, the resulting light brown solid was chromatographed as above. Recrystallization from benzene/hexane (1:4, v/v) yielded CpCo(CO)$(CF_3)_2$, 0.329 g (73%). The identity of the light yellow product was confirmed by mass and NMR spectra; see above.

Thermal Stability of (Trifluoromethyl)cyclopentadienylcobalt Carbonyl Compounds. An 0.03 M solution of CpCo(CO)$(CF_3)_2$ in n-Bu_2O was sealed into a 4-mm reactor and then maintained at 115 ± 2 °C. Until 57 h had elapsed, no change was evident. During the next 200 h, fluorine NMR indicated the slow formation of SiF_4 and c-C_3F_6 along with a transient species, δ 2.0. After 261 h at 115 °C, ca. 50% of the CpCo(CO)$(CF_3)_2$, originally utilized, remained.

The identity of the transient species was confirmed by a second experiment in which the reactor was opened after 124 h. When $(CF_3)_2CO$ was added to the material volatile at ambient temperature, the intensity of the resonance at 2.0 ppm increased.

An 0.030 M solution of CpCo(CO)(CF_3)I in Bu_2O was prepared and maintained at 115 °C. After 21 h at 115 °C, all of the CpCo(CO)(CF_3)I had decomposed. The only ^{19}F resonances present corresponded to SiF_4 and c-C_3F_6.

Reaction of CpCo(CO)$(CF_3)_2$ with Bromine. By means of the usual syringe techniques CpCo(CO)$(CF_3)_2$ (11.6 mg, 0.04 mmol) in 0.5 mL of CH_2Cl_2 and Br_2 (0.020 mmol) in 100 μL of CH_2Cl_2 were introduced into a 5-mm reactor. After being degassed, the tube was sealed and the contents were allowed to react at ambient temperature for 125 h.

Fluorine NMR of the dark red solution indicated the slow decrease in the amount of CpCo(CO)$(CF_3)_2$ present and the slow increase of CF_3Br (58.8 ppm) and CpCo(CO)(CF_3)Br (83.7 ppm). At the end of the experiment, the relative intensities of the resonances due to CpCo(CO)(CF_3)Br (83.7 ppm) and CpCo(CO)$(CF_3)_2$ (81.7 ppm) were 0.50:1.00.

The reactor was opened, and the material that was volatile was separated by fractionation. The identity of CF_3Br was confirmed by mass spectrometry and ^{19}F NMR. Column chromatography (benzene on silica gel) of the remaining material separated a yellow band of unreacted CpCo(CO)$(CF_3)_2$ and a red-brown band of CpCo(CO)(CF_3)Br (5.7 mg, 0.019 mmol), the latter isolated in 95% yield based upon the amount of Br_2 taken.

The new compound CpCo(CO)(CF_3)Br is a violet material which can be handled in air. NMR: ^{19}F, s, δ 83.7; ^1H ($CDCl_3$), 5.31 ppm. Mass spectrum (m/e, ion, intensity): 302, CF_3CpCo(CO)^{81}Br, 3.4; 283, CF_2CpCo(CO)^{81}Br, 2.4; 274, CF_3CpCo^{81}Br, 2.5; 252, FCpCo(CO)^{81}Br, 3.2; 233, CpCo(CO)^{81}Br 2.7; 221, CF_3CpCo(CO), 32.3; 205, CpCo^{81}Br, 10.2; 193, CF_3CpCo, 100. High-resolution mass spectrum: calcd, 301.8787; found, 301.8792; $\Delta m/m$ = 1.7 ppm.

Reaction of CpCo(CO)$(CF_3)_2$ with $(CH_3)_2$Cd. Dimethylcadmium (0.024 g, 0.168 mmol) was condensed onto a solution of CpCo(CO)$(CF_3)_2$ (0.026 g, 0.089 mmol) in C_6D_6 (2 mL). The vessel was sealed and then allowed to warm to ambient temperature. The solution immediately began to change from yellow to red-brown; simultaneously, a red precipitate formed. In addition to a resonance at 4.73 indicative of CpCo(CO)$(CF_3)_2$, proton NMR spectra contained extremely small resonances (singlets) at 4.40 (5 H) and 0.67 (6 H) ppm (CpCo(CO)$(CH_3)_2$), as well as a larger resonance at 1.60 ppm; the last increased in intensity throughout the experiment. After 168 h the reactor was opened, and the presence of acetone in the volatile products was confirmed by addition of a small amount of an authentic sample of acetone.

Reaction of CpCo(CO)$(CF_3)_2$ with Triphenylphosphine. To 0.5 mL of an 0.05 M solution of CpCo(CO)$(CF_3)_2$ in C_6H_6 was added 0.1 mL of an 0.2 M solution of PPh_3, also in benzene. The Pyrex reactor was sealed, and the yellow solution was irradiated with a high-pressure Hg arc for 35 min. The ^{19}F spectrum of the now dark orange solution contained only one resonance, at 82.0 ppm. After the bulk of the solvent was removed petroleum ether was slowly added until orange crystals of CpCo(PPh_3)$(CF_3)_2$ separated in quantitative yield. Mass spectrum (m/e, ion, intensity): 524, $(CF_3)_2$CpCo(PPh_3), 3.8; 455, CF_3CpCo(PPh_3), 4.6; 405, FCpCo(PPh_3), 1.7; 390, CF_3Co(PPh_3), 8.0; 386, CpCo(PPh_3), 4.5; 340, FCo(PPh_3), 8.0; 262, $(CF_3)_2$CpCo, 100. High-resolution mass spectrum: calcd, 524.0539; found, 524.0563; $\Delta m/m$ = 4.6 ppm. CpCo(PPh_3)$(CF_3)_2$ decomposes without melting at 141–142 °C. NMR (C_6D_6): ^{19}F, br s, δ 82.1; $^{31}P\{^1H\}$, br m, δ 50.9 (vs. 85% H_3PO_4); ^1H, br m, δ 7.37, 7.04, s, δ 4.89.

Results and Discussion

Preparation of $(CF_3)_2$CpCo(CO). The synthesis of the bis(trifluoromethyl)cobalt complex CpCo(CO)$(CF_3)_2$ by ligand exchange between $(CF_3)_2$Cd·glyme and either CpCo(CO)I_2 or CF_3CpCo(CO)I is an exceptionally convenient preparation, one that does not involve any of the more specialized equipment like the metal atom reactors, discharge apparatus, or pressure vessels often employed in the formation of CF_3–metal bonds. The experimental conditions utilized are very similar to those employed in alkylations with methylmagnesium halides or methyllithium. In all three cases the reagents, CH_3MgX, CH_3Li, or $(CF_3)_2$Cd·glyme, are moderately sensitive to the atmosphere, but each can be readily handled in standard glassware.

The apparent synthesis of choice for $CpCo(CO)(CH_3)_2$ involves the carbonylation of dimeric $[CH_3CpCo(CO)]_2$[3] and a direct comparison of yield data is not available. However, the alkylation of the more stable phosphine complex $CpCo(PPh_3)I_2$ with methylmagnesium halides generates $CpCo(PPh_3)(CH_3)_2$ in 17–61% yields.[3,6,8] The dimethylated triphenylarsine complex $CpCo(AsPh_3)(CH_3)_2$ is afforded from the diiodide in 28% yield.[8] Thus the isolated yield of $CpCo(CO)(CF_3)_2$ (63%) obtained here compares favorably to the yields encountered in methylation reactions of related cyclopentadienylcobalt halides and to the yield of $(CF_3)_4Sn$ obtained from SnI_4 (66%).[1]

Under the conditions examined, the interaction of the cobalt iodides studied here with $(CF_3)_2Hg$ has not been found to be a synthetically useful source of the trifluoromethylated cobalt organometallic compounds since the trifluoromethylation reaction is accompanied by the extensive decomposition. Although $CpCo(CO)(CF_3)_2$ alone is reasonably stable, the decomposition of this compound proceeds much more readily in the presence of the mercurial. The thermal decomposition of (trifluoromethyl)germanium and (trifluoromethyl)tin compounds has previously been shown to be catalyzed by mercury salts.[4,9–11] At the present time the most fruitful employment of $(CF_3)_2Hg$ with transition-metal compounds is as a reagent in oxidative-addition reactions.[12]

Stability of (Trifluoromethyl)cobalt Compounds. In Bu_2O, the half-life of $CpCo(CO)(CF_3)_2$ is ca. 260 h (11 days) at 115 °C whereas the half-life of $(CH_3)_2CpCo(CO)$ in THF is reported to be only 11 h at ambient temperature.[3] The substitution of a single CF_3 group for a CH_3 ligand has often been observed to raise the thermal decomposition temperature of low-valent transition-metal organometallic species by 75–100 °C,[9] and the results obtained here suggest that the effect of a second substitution is to further enhance the stability of the complex. At the present time, the relative thermal stabilities of trifluoromethyl and methyl derivatives of high-valent transition-metal compounds are unknown.

In butyl ether the monosubstituted compound $CpCo(CO)CF_3I$ is clearly less thermally stable than $CpCo(CO)(CF_3)_2$. This is the opposite of the stability order encountered in main-group trifluoromethyl halides where increasing CF_3 substitution typically results in decreasing thermal stability.[4,9,10]

Chemically, the trifluoromethyl–cobalt linkages in this d^6 complex are robust, being unaffected by the atmosphere, even after months of exposure, or by Lewis base exchange, as demonstrated by the PPh_3 for CO interchange carried out under photolysis. Cleavage of the CF_3Co bond does occur with Br_2, forming CF_3Br and $CF_3CpCo(CO)Br$ quantitatively, and with the moderately reactive alkylating agent $(CH_3)_2Cd$, generating $CpCo(CO)(CH_3)_2$. In the last reaction the mixed-ligand compound $CpCo(CO)(CH_3)CF_3$ was unobserved.

One of the more interesting findings was that when $CpCo(CO)(CF_3)_2$ does decompose thermally, one of the products formed is $(CF_3)_2CO$, the fluorocarbon analogue of the $(CH_3)_2CO$ which arises from the thermal decomposition of $CpCo(CO)(CH_3)_2$. Thus in this chemical system the decomposition reactions of the hydrocarbon and the corresponding fluorocarbon organometallic compounds appear to be related which raises the interesting possibility that metal–mediated fluorocarbon reactions may eventually prove to be as synthetically useful as their hydrocarbon counterparts.

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Registry No. $CpCo(CO)(CO)(CF_3)_2$, 101916-50-1; $(CF_{32}Cd\cdot$glyme, 76256-47-8; $CpCo(CO)I_2$, 12012-77-0; $CpCo(CO)(CF_3)I$, 12078-24-9; $CpCo(CO)(CF_3)Br$, 101916-51-2; CF_3Br, 75-63-8; $CpCo(CO)(CH_3)_2$, 61156-12-5; $CpCo(PPh_3)(CF_3)_2$, 101916-52-3; CF_3H, 75-46-7; CF_3I, 2314-97-8; CF_3HgI, 421-11-4; $(CF_3)_2Hg$, 371-76-6; $(CH_3)_2Cd$, 506-82-1.

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