Bis(trifluoromethyl)cadmium·glyme (glyme = dimethoxyethane), a New, Powerful Fluoroalkylating Agent and Low-temperature Source of Difluorocarbene

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Summary The newly isolated reagent $(CF_3)_2Cd\cdot$glyme [glyme = $(MeOCH_2)_2$] readily exchanges ligands with, *e.g.*, GeI_4, SnI_4, or PI_3 to form the fully substituted compounds $(CF_3)_4Ge$, $(CF_3)_4Sn$, or $(CF_3)_3P$, within minutes at ambient temperature; reactions with acyl halides, like MeC(O)Br, form the acyl fluorides, like MeC(O)F, in excellent yields, 95%, at −25 °C and extrusion of CF_2 at −25 °C in this reaction is indicated by the formation of the expected difluorocyclopropane from tetramethylethylene in 53% yield.

INTEREST in trifluoromethyl or, in general, perfluoroalkyl substituted metals and metalloids has grown steadily since the first preparations of the Group 5A perfluoromethylorganometallics. To date, however, all syntheses of fully substituted compounds have required either fairly sophisticated methodology, like metal atom reactors and/or discharge techniques, or prolonged interaction of the reagents at elevated temperatures.[1] Formation of highly substituted derivatives of many of the more electropositive metals, *e.g.*, $(CF_3)_4Sn$, by ligand exchange reactions with the only reagent known to be effective, $(CF_3)_2Hg$, is precluded by the conditions required for the exchange (35 h, 110 °C).[2] We have recently isolated $(CF_3)_2Cd\cdot$glyme [glyme = $(MeOCH_2)_2$] and find it to be the most reactive reagent currently known for these reactions.

Bis(trifluoromethyl)cadmium·glyme was best formed from an excess of $(CF_3)_2Hg$ (7·28 mmol) and $CdMe_2$ (5·28 mmol) in dry glyme (5 ml). After 3 h all volatile material was removed by prolonged pumping under high vacuum. The white solid remaining was air stable and soluble in CH_2Cl_2, $BrCH_2CH_2Br$, and ethers. The ^{19}F n.m.r. spectrum (CH_2Cl_2) [singlet at −44.2 p.p.m. *vs.* external CF_3CO_2H, $^2J(^{113}Cd–F)$ = 493 Hz, $^2J(^{111}Cd–F)$ = 461 Hz], indicated that only $(CF_3)_2Cd\cdot$glyme (in 58% yield) was present in the nonvolatile fraction. The identity of the product was confirmed by hydrolysis and its i.r. and mass spectrum, the last containing $CF_3Cd\cdot glyme^+$, 65%; CF_3CdF^+, 14%; and Cd^+, 100% ions, each with the expected isotopic envelope, at *m/e* 273, 202, and 114, respectively. Neither mercurials nor the mixed CF_3CdCH_3 compound were observed in the solid.

Germanium tetraiodide (0·690 mmol) and $(CF_3)_2Cd\cdot$glyme (2·65 mmol), after 15 min at ambient temperature in 1,2-dibromoethane (5 ml) formed the fully substituted compound, $(CF_3)_4Ge$ (0·297 mmol) in 43% yield based upon GeI_4.† Tin(IV) tetrabromide (17·1 mmol) was dissolved in 7 ml of 1,6-dibromohexane to which the cadmium reagent (3·16 mmol), was slowly added; all volatile materials were continuously removed *in vacuo*. Tetrakis(trifluoromethyl)tin (1·04 mmol) was recovered in 66% yield based upon the cadmium reagent.† Phosphorus tri-iodide was allowed to react with the cadmium reagent as for GeI_4, resulting in the formation of $(CF_3)_3P$ and $(CF_3)_2PI$ in 20 and 30% yields, respectively. This reaction, still under study, was complicated by the formation of large amounts of $(CF_3)_2PH$ and other products.† Arsenic tri-iodide reacted similarly.

The following reactions of acyl halides were designed to determine if coupling of the reagents to form fluorinated ketones might occur. Benzoyl chloride (2·71 mmol) and the cadmium reagent (1·74 mmol) in 5 ml of CH_2Cl_2, formed benzoyl fluoride (2·33 mmol) and C_2F_4 in 86 and 50% yield, respectively, during 20 min at ambient temperature.† Acetyl bromide (2·10 mmol), when exposed to the cadmium reagent (1·94 mmol), similarly formed MeC(O)F and C_2F_4 in 91 and 64% yields within 5 min. Acetyl bromide (5·13 mmol) and $(CH_3)_2C{=}C(CH_3)_2$ (4·90 mmol) were cooled to −25 °C and 2·20 mmol of the cadmium reagent were added; $CH_3C(O)F$ (95%) and $(CH_3)_2\overline{C\cdot CF_2\cdot C}(CH_3)_2$ (53%) were recovered; C_2F_4 was not observed. At about −60 °C the same products were recovered in comparable yields. The reaction proceeded, slowly, at temperatures at least as low as −78 °C. The cyclopropane adduct

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† All products were identified by, *e.g.*, n.m.r., mass, and i.r. spectra.

was also formed in the reaction of benzoyl chloride with $(CF_3)_2Cd$·glyme in the presence of tetramethylethylene.

Thus bis(trifluoromethyl)cadmium·glyme is by far the most convenient reagent now known for the preparation of trifluoromethyl substituted metal compounds, as reactions require only minutes under ambient conditions. With the exception of discharge reactions the present yields for, *e.g.*, $(CF_3)_4Sn$, are far higher than for other methods reported and much higher than for ligand exchange reactions with $(CF_3)_2Hg$ (0%), metal atom reactions with CF_3 radicals (0·8%), or the direct fluorination of $Sn(CH_3)_4$ (0%).[1,2,3] The mechanism of the reaction with acyl halides is under further study, but the fluorides are very quickly formed in excellent yields at low temperatures. In the presence of the acyl halides, $(CF_3)_2Cd$·glyme is clearly a CF_2 transfer agent at temperatures much lower than required for the thermal generation of CF_2 in other systems.

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