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PRELIMINARY NOTE

The Preparation of F-Cadmium Reagents Directly From F-alkyl Iodides and F-aryl Bromide and Cadmium Metal[†]

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SUMMARY

F-alkyl cadmium reagents can be readily prepared via the direct reaction of F-alkyl iodides with cadmium powder in DMF at room temperature. Similar reaction of bromopentafluorobenzene with cadmium powder in DMF at room temperature affords the F-aryl cadmium reagent in excellent yield. This approach provides a rapid, easily scaled up, one-pot procedure to these valuable synthetic reagents from commercially available precursors.

The preparation and synthetic utility of F-alkyl cadmium reagents has been of current interest in a number of laboratories. These reagents have been typically prepared via metathesis between dialkyl cadmiums and bis-F-alkyl mercurials [1,2] or by the reaction of dialkyl cadmiums with F-alkyl iodides [3], as summarized below:

$$R_2Cd + (R_F)_2Hg \longrightarrow R_2Hg + (R_F)_2Cd$$

$$R_2Cd + 2\ R_FI \longrightarrow (R_F)_2Cd + 2\ RI$$

Alternatively, trifluoromethyl cadmium reagents can be directly prepared from cadmium metal and difluorodihalomethanes [4].

$$CF_2XY + Cd \longrightarrow CF_3CdX + (CF_3)_2Cd + CdXY$$

X, Y = Cl or Br

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We now wish to report a general route to these reagents via the direct reaction of cadmium powder (acid-washed) with F-alkyl iodides in DMF at room temperature. The reaction is exothermic (after a short induction period) and is generally complete in one hour. A mixture of

$$R_FI + Cd \xrightarrow{DMF} R_FCdI + (R_F)_2Cd + CdI_2$$

mono- and bis-F-alkyl cadmium reagents is obtained - identified by ^{19}F and ^{113}Cd NMR and hydrolysis to R_FH. The results of this direct preparation are summarized in Table I.

The yields are good to excellent when $R_F = CF_3$, C_2F_5, and C_3F_7. With longer R_F chains (C_4, C_6, C_7, C_8) the yields are moderate, as elimination products are formed as by-products. These by-products, however, form a separate lower layer from the $[R_FCdX]$-DMF solution and are readily separated from the F-cadmium reagent solution in a separatory funnel under an inert atmosphere (to exclude moisture and prevent hydrolysis). The by-product formation occurs during the formation of the F-cadmium reagent, since the F-cadmium reagent is stable, once formed, and the by-products do not increase after the preparative sequence is completed.

TABLE I

Data of the F-cadmium reagents

$$R_FI + Cd \xrightarrow[RT]{DMF} R_FCdI + (R_F)_2Cd$$

R_FI	% $[R_FCdX + (R_F)_2Cd]$[a]	mono/bis ratio
CF_3	65	62/38
C_2F_5	68	b
n-C_3F_7	93	60/40
n-C_4F_9	43	68/32
n-C_6F_{13}	46	46/54
n-C_7F_{15}	25	48/52
n-C_8F_{17}	47	43/57

a) ^{19}F NMR yield of F-alkyl cadmium reagents vs. $PhCF_3$.

b) Signals overlapped and ratio could not be determined.

Similarly, bromopentafluorobenzene reacts under similar conditions to give a 90% yield of the *F*-aryl cadmium reagent. Evans and Phillips [5] had utilized the more expensive iodopentafluorobenzene in an earlier

$$C_6F_5Br + Cd \xrightarrow[RT]{DMF} [C_6F_5CdX],\ 90\% \qquad \text{mono/bis} = 85/15$$

$$X = Br,\ C_6F_5$$

preparation of this reagent.

In conclusion, a simple, straightforward, mild preparation of *F*-alkyl and *F*-aryl cadmium reagents from *F*-alkyl iodides and *F*-aryl bromide is described. The reagents are readily prepared in moderate to excellent yields from commercially available materials, easily scaled up (to 50-100 mmoles), and easily separated from by-products. No prior formation of dialkyl cadmium or mercurials is required, and no equilibrium processes are involved. This direct approach should find extensive synthetic utility, and we recommend this approach to researchers interested in *F*-alkyl and/or *F*-aryl cadmium reagents.

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