Journal of Fluorine Chemistry, 66 (1994) 23–24

Preliminary Note

The preparation, stability and reactivity of perfluorobenzyl-cadmium and -copper reagents

Donald J. Burton*, Zhen-Yu Yang and V. Platonov

Department of Chemistry, University of Iowa, Iowa City, IA 52242 (USA)

(Received March 2, 1993; accepted April 18, 1993)

Abstract

Perfluorobenzyl bromide reacts readily with acid-washed cadmium powder in DMF at room temperature to give the *F*-benzylcadmium reagent. Metathesis of the *F*-benzylcadmium reagent with Cu(I)Br at −40 °C to −35 °C in DMF affords the *F*-benzylcopper reagent. The formation of the *F*-benzylcadmium and -copper reagents was confirmed by ^{19}F NMR spectral analysis of the reaction mixture and chemical transformations.

The limited thermal stability of fluorinated organolithium and Grignard reagents has restricted their synthetic utility. For this reason, we have explored new methodologies for the preparation and application of thermally stable fluoro-organometallic reagents. Recent work in our laboratory has been directed toward the preparation of stable *F*-alkyl [1–4], difluoromethyl [5], *F*-allyl [6], *F*-vinyl [7, 8], *F*-acetylenic [9] and *F*-aryl [10, 11] organometallic reagents, as well as functionalized [12–14] cadmium, zinc and copper reagents. These reagents have been found to be invaluable in the synthesis of organofluorine compounds [15–27]. We now wish to report the preparation of the *F*-benzylcadmium reagent and the corresponding copper reagent.

When perfluorobenzyl bromide was added to a suspension of acid-washed cadmium powder in DMF at room temperature, an exothermic reaction occurred and resulted in the formation of the *F*-benzylcadmium reagent. The overall ^{19}F NMR yield of the cadmium reagents, existing as a mixture of mono and bis reagents in a ratio of 69:31, was 85%–90%. Only a trace of α-hydroperfluorotoluene was observed.

$$C_6F_5CF_2Br + Cd \xrightarrow[\text{R.T.}]{\text{DMF}} C_6F_5CF_2CdBr + (C_6F_5CF_2)_2Cd$$

The formation of the *F*-benzylcadmium reagents was confirmed via analysis of the ^{19}F NMR and ^{113}Cd spectra of the reaction mixture. The ^{19}F NMR spectrum exhibited distinct resonances for three types of aromatic fluorines and one difluoromethylene group. Fluorine atoms on the carbon α to cadmium showed the expected satellite peaks due to coupling with $^{111}Cd/^{113}Cd$ isotopes. Although it was difficult to distinguish between the mono and bis cadmium reagents in the ^{19}F NMR spectrum, the ratio could be readily determined via analysis of the ^{113}Cd NMR spectrum. The mono cadmium reagent exhibited a triplet signal, while a pentet was observed for the bis reagent due to the four α-fluorines.

$C_6F_5CF_2CdBr$: ^{19}F NMR (DMF, $C_6H_5CF_3$): δ −32.0 (dt, J=274.0 Hz, J=24.0 Hz, 2F); −82.5 (dt, J=22.6 Hz, J=22.6 Hz, 2F); −97.7 (t, J=22.0 Hz, 1F); −103.1 (m, 2F) ppm. ^{113}Cd NMR (DMF, $CdSO_4$) δ: 241.2 (t, J=274.5 Hz) ppm.

$(C_6F_5CF_2)_2Cd$: ^{19}F NMR (DMF, $C_6H_5CF_3$) δ: −31.9 (dt, J=236.7 Hz, J=26.0 Hz, 2F); −82.0 (dt, J=23.1 Hz, J=26.0 Hz, 2F); −97.6 (t, J=22.3 Hz, 1F); −103.0 (m, 2F) ppm. ^{113}Cd NMR (DMF, $CdSO_4$) δ: 218.3 (pent, J=236.8 Hz) ppm.

Consistent with the formation of the *F*-benzylcadmium reagents, hydrolysis of the solution of the cadmium reagents with dilute HCl gave α-hydroperfluorotoluene in quantitative yield. Treatment with iodine gave a 75% isolated yield of perfluorobenzyl iodide.

$$C_6F_5CF_2CdX + HCl\ (aq.) \longrightarrow C_6F_5CF_2H$$

[100% (^{19}F NMR spectroscopy)]

$$C_6F_5CF_2CdX + I_2 \longrightarrow \underset{(75\%)}{C_6F_5CF_2I}$$

In DMF, the *F*-benzylcadmium reagent was thermally stable at room temperature for several days, and showed little decomposition at 50 °C overnight. However, decomposition became rapid above 70 °C.

Like the *F*-allylcadmium reagent [6], the *F*-benzylcadmium reagent readily undergoes allylation at room temperature. Upon reaction with allyl bromide, 4,4-difluoro-4-pentafluorophenyl-1-butene was obtained in 75% isolated yield.

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*Author to whom correspondence should be addressed.

SSDI 0022-1139(93)02919-6

$$C_6F_5CF_2CdX + CH_2{=}CHCH_2Br \xrightarrow[\text{R.T.}]{\text{DMF}} \underset{(75\%)}{C_6F_5CF_2CH_2CH{=}CH_2}$$

Attempts to prepare the *F*-benzylcopper reagent failed at room temperature. When the cadmium reagent was treated with cuprous bromide at room temperature, only decomposition products were observed. However, upon addition of the solution of the cadmium reagent to CuBr in DMF at -35 °C to -40 °C, the metathesis reaction occurred rapidly and the corresponding copper reagent was formed in almost quantitative yield.

$$C_6F_5CF_2CdX + CuBr \xrightarrow[-40\ ^\circ\text{C to } -35\ ^\circ\text{C}]{\text{DMF}} C_6F_5CF_2Cu$$

$$[\sim 100\%\ (^{19}\text{F NMR spectroscopy})]$$

The resonance for the copper reagent in the ^{19}F NMR spectrum exhibited typical aromatic fluorines. The CF_2Cu signals appeared at δ -24.1 ppm (t, $J = 22$ Hz) and -28.0 ppm (t, $J = 22.0$ Hz) versus $C_6H_5CF_3$ in a 7:1 ratio, indicating two different copper species, which had been previously observed in several *F*-alkyl- and *F*-allyl-copper reagents in our laboratory [6, 15]. In addition, the $^{111/113}$Cd satellite couplings had disappeared.

Further evidence for the formation of the copper reagent was chemical transformation. Upon addition of allyl bromide to the copper reagent solution at low temperature, the signals assigned to CF_2Cu disappeared and the allylated product was observed within 15 min.

$$C_6F_5CF_2Cu + CH_2{=}CHCH_2Br \xrightarrow[-35\ ^\circ\text{C}]{\text{DMF}} C_6F_5CF_2CH_2CH{=}CH_2$$

In conclusion, stable *F*-benzyl-cadmium and -copper reagents have been prepared and their structures confirmed by chemical transformation and ^{19}F and $^{111/113}$Cd NMR analysis. Both exhibit high reactivity with allyl bromide and further applications of these reagents in organic synthesis are in progress.

Acknowledgement

We thank the National Science Foundation for generous support of this work and Dr Peter A. Morken for assistance with the low-temperature NMR spectra.

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