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PRELIMINARY NOTE

The Preparation and Reaction of Fluorinated Phenyl Mono- or Bis- Cadmium and Copper Reagents

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SUMMARY

Tetrafluorodibromobenzenes react readily with acid-washed cadmium in DMF at temperatures ranging from 25°C to 60°C to give bromotetrafluorophenylcadmium reagents in excellent yields. Treatment of the mono- cadmium reagent solution with excess cadmium at 100°C affords the tetrafluorophenylbiscadmium reagents. The mono- and bis- copper reagents are obtained *via* metathesis of the corresponding cadmium reagents with cuprous bromide at room temperature. Allylation and acylation of the biscopper reagents give the corresponding allylated and acylated tetrafluoro-benzenes, respectively.

The limited thermal stability of fluorinated organolithium and Grignard reagents has restricted their synthetic utility. Therefore, we have explored new methodologies for the preparation and application of thermally stable fluoroorganometallic reagents. Recent work in our laboratory has been directed toward the preparation of stable F-alkyl[1,2], difluoromethyl[3], F-allyl[4], F-vinyl[5,6], and F-acetylenic[7] cadmium, zinc and copper reagents[8-11]. These reagents have been found to be invaluable in the synthesis of organofluorine compounds[12-21]. We now wish to report the preparation of polyfluorophenyl mono- and bis- cadmium as well as the corresponding copper reagents.

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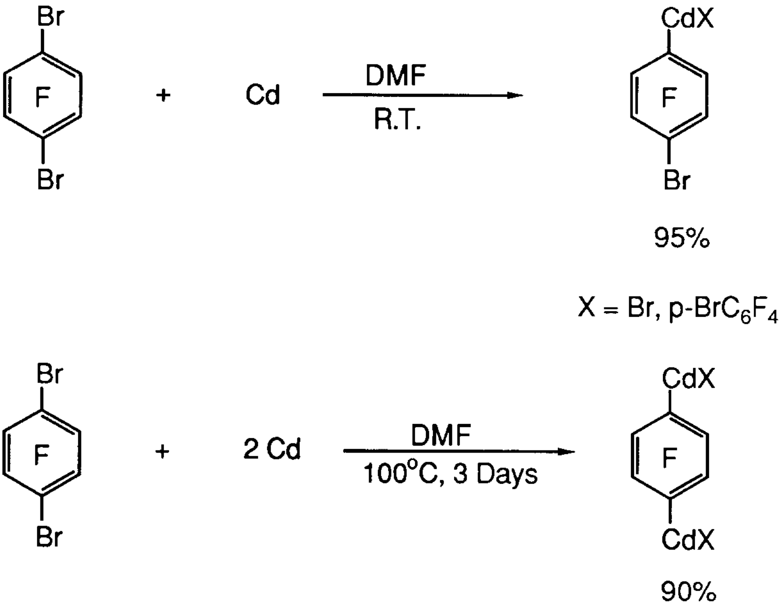
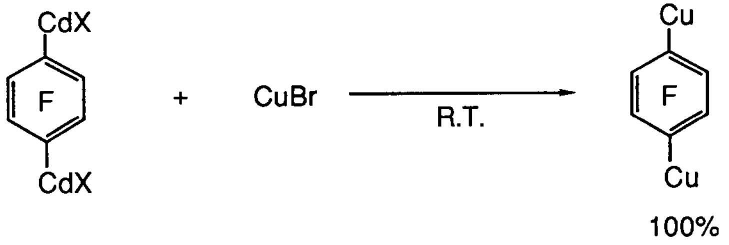
Pentafluorophenylcadmium[22] and copper[23-26] were prepared from the metathesis of pentafluorophenyllithium and Grignard reagents with cadmium chloride or copper halides twenty years ago. More recently, a similar approach to the 1,4-tetrafluorophenyl bis-copper reagent[27] has been reported.

In contrast to the lithium and Grignard reagents, the pentafluorophenylcadmium reagents are remarkably stable[1]. When 1,4-dibromotetrafluorobenzene reacted with acid-washed cadmium powder in DMF at room temperature for five hours, a mixture of 4-bromotetrafluorophenylcadmium bromide and bis(4-bromotetrafluorophenyl)cadmium[1] was formed in 95% yield. The 1,4-dibromotetrafluorobenzene reacted with excess cadmium on prolonged heating at 100°C to give the 1,4-bis-cadmiumtetrafluorobenzene in 90% yield.

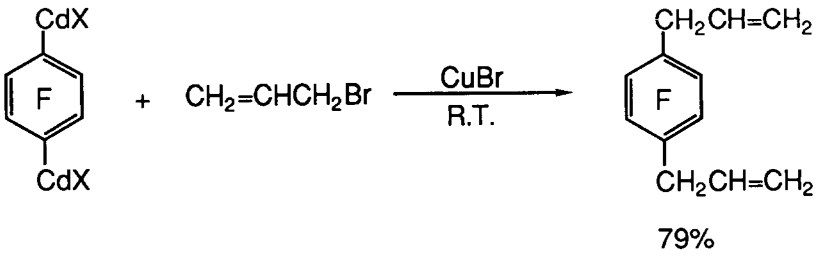


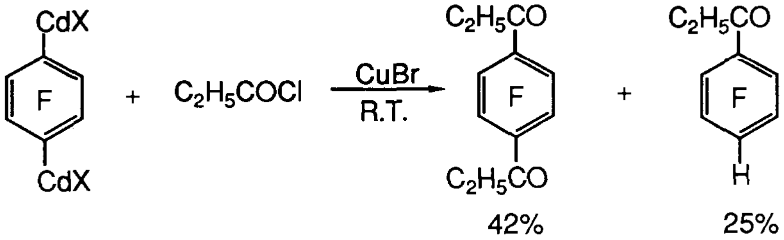
The formation of the bis-cadmium reagent was confirmed by chemical transformations and ^{19}F NMR analysis of the reaction mixture. The ^{19}F NMR spectrum of the bis-cadmium reagent showed one broad singlet at -116.6 ppm *versus* internal $CFCl_3$. Treatment of the bis- cadmium reagent with iodine gave 1,4-diiodo-tetrafluorobenzene in 80% isolated yield.

The corresponding 1-bromo-4-coppertetrafluorobenzene and 1,4-bis-coppertetrafluorobenzene can be obtained in quantitative yields *via* metathesis of the mono- and bis- cadmium reagents, respectively, with cuprous bromide at room temperature. The mono copper reagent exhibited two sets of doublets of doublets at -111.0 ppm and -138.3 ppm *versus* $CFCl_3$, with coupling constants of 35 Hz and 15 Hz. A sharp singlet at -115.6 ppm *versus* $CFCl_3$ was observed in the ^{19}F NMR spectrum of the bis- copper reagent.



The bis-copper reagent readily undergoes allylation and acylation at room temperature. For example, when the bis- copper reagent reacted with allyl bromide, the 1,4-diallyltetrafluorobenzene was obtained in 79% isolated yield. With propionyl chloride, 1,4-dipropionyltetrafluorobenzene and 4-hydro-1-propionyltetrafluorobenzene were formed in 42% and 25% yields, respectively.





Similarly, 1,2- and 1,3-dibromotetrafluorobenzene reacted with cadmium in DMF from room temperature to 60°C to give the corresponding mono-cadmium reagents in 85-90% yield. When the reaction of 1,2-dibromo-tetrafluorobenzene with excess cadmium was conducted at 100°C for 3 days, the 1,2-bis-cadmium reagent was formed in 53% yield with 5% mono-cadmium reagent. However, upon the reaction of 1,3-dibromotetrafluoro-benzene with excess cadmium at 100°C for four days, no bis- cadmium reagent was observed in the ^{19}F NMR spectrum, and 80% of the mono-cadmium reagent still remained.

Metathesis of the 3-bromotetrafluorophenylcadmium reagent with cuprous bromide gave the corresponding copper reagent in quantitative yield. However, upon treatment of 2-bromotetrafluorophenylcadmium and the 1,2-bis- cadmium reagent with cuprous bromide in DMF at room temperature, only decomposition products were observed, and no fluorinated phenyl copper reagents could be detected by ^{19}F NMR.

In summary, a simple, straightforward, mild, and high-yield preparation of several polyfluorophenyl mono- or bis- cadmium and copper reagents from the polyfluorophenyl bromide is described. The bis-copper reagent exhibits high reactivity with allyl bromide and propionyl chloride. Further applications of these reagents are in progress.

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