

Synthesis and characterization of cadmiumbis(2,6-difluorobenzoate), $\text{Cd}[\text{OCO}(2,6\text{-F}_2\text{C}_6\text{H}_3)]_2$, and bis(2,6-difluorophenyl)cadmium, $\text{Cd}(2,6\text{-F}_2\text{C}_6\text{H}_3)_2$

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Abstract

The synthesis of $\text{Cd}(2,6\text{-F}_2\text{C}_6\text{H}_3)_2$ was successful via decarboxylation of the corresponding benzoate in 17% yield. The benzoate, $\text{Cd}[\text{OCO}(2,6\text{-F}_2\text{C}_6\text{H}_3)]_2$, was either prepared via metathesis reactions of the silver benzoate and CdCl_2 (75% yield) or by direct treatment of CdCO_3 with 2,6-difluorobenzoic acid (85% yield). © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Bis(2,6-difluorobenzoate)cadmium; Bis(2,6-difluorophenyl)cadmium; Synthesis; Decarboxylation

1. Introduction

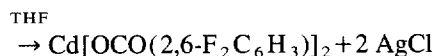
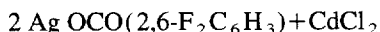
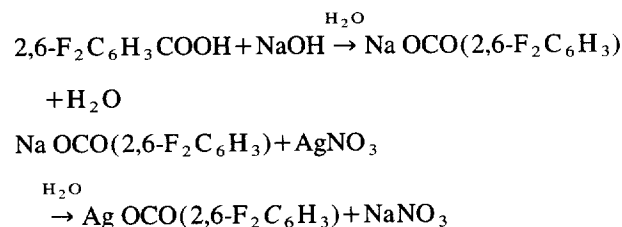
The synthesis of organomercury derivatives with fluorinated or partially fluorinated ligands by decarboxylation is a convenient synthetic approach to these compounds [1]. In cadmium chemistry this method is limited to $\text{Cd}(\text{C}_6\text{F}_5)_2$ [2]. Alternative routes for the synthesis of fluorine-containing organocadmium derivatives are ligand exchange reactions of dialkylcadmium and organoiodine derivatives [3–7] or mercury compounds [8].

Herein we describe the synthesis of $\text{Cd}(2,6\text{-F}_2\text{C}_6\text{H}_3)_2$ via decarboxylation of the corresponding benzoate.

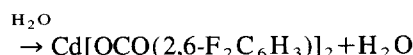
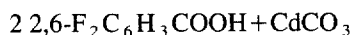
2. Results

$\text{Cd}[\text{OCO}(2,6\text{-F}_2\text{C}_6\text{H}_3)]_2$ was synthesized by analogy with literature procedures for $\text{Cd}[\text{OCOC}_6\text{F}_5]_2$ [9].

Method A

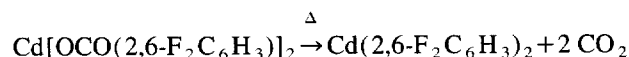


Method B



The yields were 75% (Method A) and 85% (Method B). $\text{Cd}[\text{OCO}(2,6\text{-F}_2\text{C}_6\text{H}_3)]_2$ was obtained as a colourless solid.

Decarboxylation was carried out in a round-bottom flask equipped with a water-cooled sublimation finger. At an oil bath temperature of ca. 230°C $\text{Cd}(2,6\text{-F}_2\text{C}_6\text{H}_3)_2$ is deposited on the sublimation finger as a pale yellow solid in 17% yield based on $\text{Cd}[\text{OCO}(2,6\text{-F}_2\text{C}_6\text{H}_3)]_2$.



The compound is extremely moisture sensitive and reacts with water within a few seconds to give 1,3-difluorobenzene as the only fluorine-containing product. In a sealed ampoule $\text{Cd}(2,6\text{-F}_2\text{C}_6\text{H}_3)_2$ melts at 205–208°C.

The reaction of $\text{Cd}(\text{CH}_3)_2$ and 1-I-2,6-F₂C₆H₃ in CH₃CN gave no spectroscopic evidence for the formation of $\text{Cd}(2,6\text{-F}_2\text{C}_6\text{H}_3)_2$ after stirring the mixture for 24 h at ambient temperature.

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3. Experimental

All manipulations except those in water were carried out in carefully dried vessels in a dry nitrogen atmosphere.

2,6-F₂C₆H₃COOH was purchased from ABCR, CdCO₃ from Riedel-de Haën. CdCl₂·H₂O was purchased from Riedel-de Haën and used after careful dehydration in vacuo.

NMR spectra were recorded on the Bruker spectrometer AMX 300 operating at 300.1 MHz (¹H), 282.4 MHz (¹⁹F), 75.5 MHz (¹³C) and 66.5 MHz (¹¹³Cd). Si(CH₃)₄ (¹H, ¹³C), CCl₃F (¹⁹F) and Cd(CH₃)₂ [50% in CDCl₃] (¹¹³Cd) were used as external standards.

The mass spectrum was measured with a modified Varian MAT CH5 spectrometer.

3.1. Synthesis of Cd[OCO(2,6-F₂C₆H₃)]₂

3.1.1. Method A

A total of 3.16 g (20 mmol) 2,6-F₂C₆H₃COOH were suspended in 80 ml water and neutralized with 0.80 g (20 mmol) NaOH giving a colourless solution. 3.40 g (20 mmol) AgNO₃ dissolved in 20 ml water were added. Immediately after combining both solutions, precipitation of Ag[OCO(2,6-F₂C₆H₃)] began. Precipitation was complete after storing the reaction mixture for 3 h at 0°C. The solid was filtered and dried in vacuo.

Ag[OCO(2,6-F₂C₆H₃)] and CdCl₂ were suspended in 50 ml THF and refluxed for 2 days. After distillation of THF a grey solid remained that was washed with concentrated ammonia to remove AgCl. After drying in vacuo 3.39 g (75%) Cd[OCO(2,6-F₂C₆H₃)]₂ were obtained as a colourless solid.

3.1.2. Method B

A total of 7.00 g (44.3 mmol) 2,6-F₂C₆H₃COOH were dissolved in 100 ml boiling water giving a pale yellow solution. 2.80 g (22.1 mmol) CdCO₃ were added in small portions until the pH became 7. The evolution of CO₂ was indicated by strong foaming. Reduction of the volume to 30 ml effected the precipitation of crystals at room temperature and below (0°C). After filtration and drying in vacuo, 8.49 g (85%) Cd[OCO(2,6-F₂C₆H₃)]₂ were isolated. Decomposition begins at ca. 60°C and is complete at 260°C leaving a brown solid.

Elemental analysis for C₁₄H₆CdF₄O₄ [found (calculated)]: Cd 26.2% (26.3%); F 17.7% (17.8%).

MS (15 eV, 200°C): 340 (97%, [Cd(C₆H₃F₂)₂]⁺), 227 (95%, [Cd(C₆H₃F₂)]⁺), 141 (98%, [(C₆H₃F₂)CO]⁺); 114 (100%, [C₆H₄F₂]⁺); 44 (71%, [CO₂]⁺).

NMR data of Cd[OCO(2,6-F₂C₆H₃)]₂ in CD₃CN: ¹⁹F{¹H}: δ -112.5 ppm, s. ¹H: δ(H-4) 7.34 ppm, m, 1H; δ(H-3,5) 6.94 ppm, m, 2H. ¹¹³Cd{¹H}: δ -792 ppm, broad. ¹³C: δ(CO₂) 168.8 ppm, s; δ(C-2,6) 159.8 ppm, dm, ¹J(¹⁹F-¹³C) = 233 Hz; δ(C-4) 131.2 ppm, dm, ¹J(¹³C-¹H) = 160 Hz, δ(C-1) 116.0 ppm, tm, ²J(¹⁹F-¹³C) = 21 Hz; δ(C-3,5) 112.0 ppm, dm, ¹J(¹³C-¹H) = 167 Hz.

3.2. Synthesis of Cd(2,6-F₂C₆H₃)₂

In a 250-ml round-bottom flask equipped with a water-cooled sublimation finger 8.0 g (18.7 mmol) Cd[OCO(2,6-F₂C₆H₃)]₂ were heated in an oil bath at ca. 230°C for 6 h. CO₂ was continually pumped off. Cd(2,6-F₂C₆H₃)₂ condensed at the sublimation finger as small pale yellow crystals, while 1.07 g (17%) Cd(2,6-F₂C₆H₃)₂ were isolated; melting point: 205–208°C.

Elemental analysis for C₁₂H₆CdF₄ [found (calculated)]: Cd 33.8% (33.2%); F 20.1% (22.4%).

MS (15 eV, 80°C): 340 (95%, [Cd(C₆H₃F₂)₂]⁺), 227 (15%, [Cd(C₆H₃F₂)]⁺), 114 (100%, [C₆H₄F₂]⁺).

NMR data of Cd(2,6-F₂C₆H₃)₂ in CDCl₃: ¹⁹F{¹H}: δ -84.9 ppm, s, ³J(^{111/113}Cd-¹⁹F) ≈ 71 Hz. ¹H: δ(H-4) 7.27 ppm, m, 1H; δ(H-3,5) 6.88 ppm, m, 2H. ¹¹³Cd{¹H}: δ -240 ppm, broad; δ -225 ppm, broad in CH₃CN. ¹³C: δ(C-2,6) 167.5 ppm, dm, ¹J(¹⁹F-¹³C) = 224 Hz; δ(C-4) 131.8 ppm, dm, ¹J(¹³C-¹H) = 164 Hz, δ(C-1) 122.8 ppm, m; δ(C-3,5) 110.3 ppm, ddm, ¹J(¹³C-¹H) = 170 Hz, ²J(¹⁹F-¹³C) = 29 Hz.

Acknowledgements

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