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Perfluorozinc aromatics by direct insertion of zinc into C–F or C–Cl bonds

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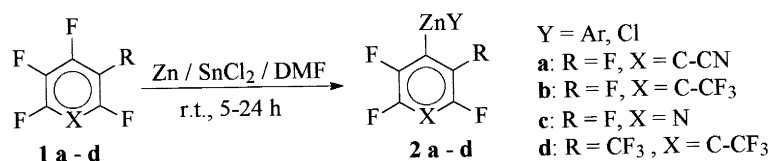
Abstract

For the first time perfluoroaromatic organozinc compounds were obtained by direct action of zinc on C–F bonds in the presence of metal salts (SnCl₂, CuCl₂, ZnBr₂). The reactions are accelerated by ultrasound. The scope of the method can be extended to polyfluoroaromatics which contain other halogen atoms (Cl) in the aromatic ring. © 2000 Elsevier Science Ltd. All rights reserved.

Organozinc compounds are well known organometallics¹ but their use in synthetic organic chemistry except for the Reformatsky reaction is limited as they were replaced by the more active organolithium and organomagnesium compounds. Recently, the relative stable organozinc compounds are used as precursors in order to prepare more reactive organometallics by transmetalation procedures.² Therefore, simple methods for the synthesis of organozinc compounds from accessible precursors are desired. Perfluorinated zinc aromatics are directly formed from iodo- and bromoarenes and zinc or dimethylzinc.³ Activated arenes with C–Cl bonds can also be used.^{4,5} In contrast, there are no reports in the literature on the direct formation of a C–Zn bond from a C–F bond in a perfluoroarene. There are few examples concerning the direct insertion of other metals into a C_{arom.}–F bond but the yields are poor.^{6,7}

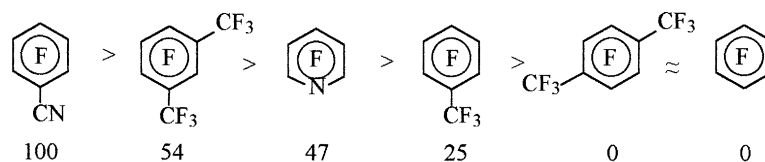
We have found that aryl zinc compounds **2a–d** are formed at room temperature from perfluoroarenes **1a–d** by reaction with zinc in DMF in the presence of SnCl₂ (Scheme 1).⁸ The corresponding organozinc compounds were characterized by ¹⁹F NMR spectra.⁹ All signals can be assigned as signals from fluorine located in the aromatic part of the molecule or from the corresponding CF₃ groups. The signals of the *ortho*-fluorine in perfluorozinc arenes are characteristically shifted compared to the perfluorinated precursor as reported in the literature for other perfluorometallic aromatics.¹⁰ Fluoride signals of Zn–F were not observed in our spectra. Thus, the insertion of zinc into the C–F bond is accompanied by an F–Cl exchange resulting in the formation of ArZnCl species.

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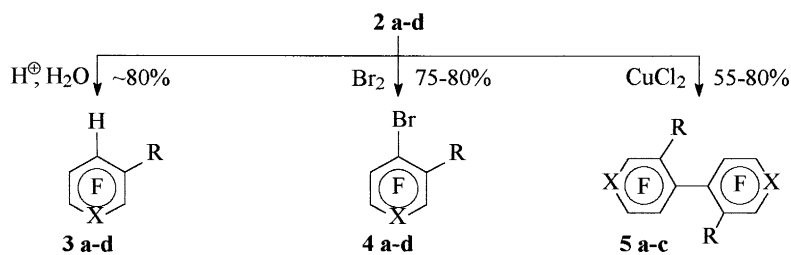
Scheme 1.

In analogy to reports in the literature¹¹ we observe an equilibrium between Ar₂Zn and Ar-Zn-Hal species in solution, but the content of the Ar-Zn-Hal species directly depends on the amount of the catalyst SnCl₂. The addition of ZnBr₂ to the reaction solution shifted the equilibrium nearly completely to the Ar-Zn-Hal species whereas KF does not influence the products ratio at all. Other solvents and salts can also be used for the reaction. However, the reaction rate decreased in THF or if ZnBr₂ or CuCl₂ was used. Furthermore, perfluorodiaryls were especially found as by-products if the reaction was promoted by CuCl₂. The reaction failed without addition of salts. It is possible to use ultrasound or heating to accelerate the formation of the organozinc compounds. As far as the perfluorinated arene precursor is concerned, we found the following range of substrate reactivity (Scheme 2):

Scheme 2. Percentage conversion of perfluoroarenes with Zn/SnCl₂ in DMF (sonication, 20°C, 10 h)

Scheme 2 represents the conversion of the starting compounds into perfluorozincarenes under similar conditions.¹² Without the application of ultrasound the conversion of octafluorotoluene is reduced from 25% to less than 10%. No reaction was found for hexafluorobenzene and perfluoro-*p*-xylene at room temperature even after 24 h. Pentafluoropyridine always gives, irrespective of the salt used, an amount of perfluorobipyridyl. If water is added to the reagents mixture, hydrodefluorination takes place.

To confirm the formation of organozinc compounds **2** the reaction mixture was treated with water, bromine and copper (II) chloride, respectively. The reaction products **3–5** (Scheme 3) are obtained in good yield.¹³ The reaction of 4-tetrafluoropyridylzinc **2c** with copper(I) chloride gives the corresponding copperarene.¹⁴



Scheme 3.

It was also interesting to evaluate the reaction of chloropolyfluoroarenes under the conditions applied for the formation compounds **2a–d**. Thus, chloropentafluorobenzene reacts with zinc in the presence of SnCl₂ at room temperature to give pentafluorophenyl zinc chloride after 40 h in 60% yield. After five days starting material was not detectable by ¹⁹F NMR spectroscopy. The ratio of C₆F₅ZnCl:(C₆F₅)₂Zn (11.5:1) determined in DMF:CDCl₃ (1:1) at room temperature was similar to literature data.¹¹

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8. Formation of organozinc compounds. A mixture of the perfluoroarene (6 mmol), Zn (30 mmol), and SnCl₂ (1 mmol) in dry DMF (8 ml) was treated in a closed flask with ultrasound¹² or stirring. After the necessary time (5–24 h) 150–200 mg of the solution were diluted with CDCl₃ (~1:1) and ¹⁹F NMR spectra were recorded.
9. ¹⁹F NMR (C₆F₆, DMF–CDCl₃): Compound **2a** (Y=Cl): 47.1 (2-F, 6-F), 26.9–27.1 (3-F, 5-F); *J*_{2,3}=30.0 Hz, *J*_{2,5}=18.0 Hz, *J*_{2,6} and *J*_{3,5}=7.7 Hz and 3.3 Hz. Compound **2b** (Y=Cl): 105.8 (CF₃, *J*=21.6 Hz), 45.9 (2-F, 6-F), 19.4 (3-F, 5-F); *J*_{2,3}=30.5 Hz, *J*_{2,5}=17.8 Hz, *J*_{2,6} and *J*_{3,5}=7.3 Hz and 3.8 Hz. Compound **2c** (Y=Cl): 64.6 (2-F, 6-F), 40.0 (3-F, 5-F); *J*_{2,3}=34.2 Hz, *J*_{2,5}=26.7 Hz, *J*_{2,6}=11.7 Hz, *J*_{3,5}≈0 Hz. Compound **2d** (Y=Cl): 105.9 (dd, *J*_{3F}=*J*_{5F}=22.4 Hz, 4-CF₃), 103.1 (dd, *J*_{3F}=19.2 Hz, *J*_{5F}=1.3 Hz, 2-CF₃) 47.8 (6-F) 43.6 (3-F), 30.6 (5-F), *J*_{3,6}=20.5 Hz, *J*_{5,6}=30.9 Hz. 4-Tetrafluoropyridylcopper: 63.5 (m, 2-F, 6-F), 45.7 (m, 3-F, 5-F).¹⁴ C₆F₅ZnCl: 45.9 (2-F, 6-F); 4.0 (4-F), –0.3 (3-F, 5-F); *J*_{2,3}=31.8 Hz, *J*_{2,4}=0 Hz, *J*_{2,5}=13.9 Hz, *J*_{3,4}=19.3 Hz, *J*_{2,6} and *J*_{3,5}=7.7 Hz and 3.1 Hz.
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12. Ultrasonic bath Sonorex RK 102 H (Bandelin), 35 kHz, 2×120 W_{elec}, power input: 0.1 W_{cal}/cm³.
13. Reactions of organozinc compounds. The solution of **2a–d**⁸ was diluted with aq. HCl or separated from the excess of zinc and then added dropwise under stirring into a solution of Br₂ (1.5 equiv.) and CuCl₂ (1.2 equiv.) in 8 and 15 ml DMF, respectively. The mixture was stirred for 1 h and diluted with water. The products **4a–d** and **5b–c**, respectively, were separated by steam distillation. Then, liquids were separated and solid products extracted with CH₂Cl₂. The work-up of nitrile **5a** was made by addition of a fourfold amount of 2% aq. HCl followed by extraction with equal amounts of diethyl ether. After drying (Na₂SO₄), evaporating of the solvent and recrystallisation from heptane:CCl₄ (1:1) pure **5a** was isolated (mp 131–133°C; Ref. ¹⁵ 129.5–131°C). The excess of bromine in case of **4a–d** was removed by treatment with aqueous Na₂SO₃ solution. Compound **4a**: mp 77–78°C (heptane); Ref. ¹⁵ 76–76.5°C. Identification of the compounds was made by ¹⁹F NMR spectroscopy.
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