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Abstract

Full Text

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SYNTHESIS OF SOME FLUORINE-CONTAINING SILYLFERROCENES

Various investigators (1–5) have already synthesized, from dilithioferrocene and various trialkyl-(aryl)-chlorosilanes, a series of bis-[trialkyl-(aryl)-silyl]ferrocenes according to the scheme

$$\text{Li-ferrocene-Li} + 2R_3\text{SiCl} \longrightarrow (\text{R}_3\text{Si})\text{-ferrocene-}(\text{SiR}_3)$$

The starting trialkyl-(aryl)-chlorosilanes were usually obtained according to the scheme:

$$\text{Mg} + \text{RCl} \rightarrow \text{RMgCl}, \qquad 3\text{RMgCl} + \text{SiCl}_4 \rightarrow \text{R}_3\text{SiCl} + 3\text{MgCl}_2$$

However, among the bis-[trialkyl-(aryl)-silyl]ferrocenes obtained, fluorinated derivatives of this series are still lacking.

In order to fill this gap, the present investigation was undertaken.

Since, upon metalation of ferrocene with lithium, di- and monosubstituted ferrocene derivatives are obtained, we expected that from tris-($\gamma\gamma\gamma$-trifluoropropyl)-chlorosilane and ferrocenyl lithium we would obtain both compound I and compound II.

$$\text{Li-ferrocene-Li} + \text{ClSi}(\text{CH}_2\text{CH}_2\text{CF}_3)_3 \longrightarrow \underset{\text{(I)}}{(\text{CF}_3\text{CH}_2\text{CH}_2)_3\text{Si-ferrocene-Si}(\text{CH}_2\text{CH}_2\text{CF}_3)_3}$$

$$+ \underset{\text{(II)}}{\text{ferrocene-Si}(\text{CH}_2\text{CH}_2\text{CF}_3)_3}$$

Indeed, by fractionation and recrystallization, compound I with m.p. 155° and compound II with m.p. 105° were obtained. However, as a small impurity it was also possible to isolate compound III, with m.p. 141–142°, which did not contain iron and, according to analytical data, corresponded rather closely to hexa-($\gamma\gamma\gamma$-trifluoropropyl)-disiloxane, described earlier (6). Apparently this compound was formed according to the scheme:

$$2(CF_3CH_2CH_2)_3SiCl + H_2O \rightarrow 2HCl + (CF_3CH_2CH_2)_3SiOSi(CH_2CH_2CF_3)_3 \tag{III}$$

We synthesized for the first time bis-(tripropylsilyl)-ferrocene (VI), analogous to compound

$$(CH_2CH_2CH_3)_3Si\text{-ferrocene-}Si(CH_2CH_2CH_3)_3 \tag{VI}$$

which proved to be a liquid with b.p. 227–233° at 1 mm.

From dimethyl-*m*-benzotrifluoridechlorosilane* and ferrocenyl lithium also

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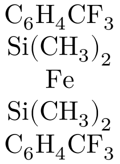
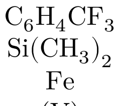
* Here and below, benzotrifluoride denotes the *m*-trifluoromethylphenyl residue.

Compounds IV with m.p. 71° and V with m.p. 50° were obtained.



$$\begin{array}{c} C_6H_4CF_3 \\ Si(CH_3)_2 \\ Fe \\ Si(CH_3)_2 \\ C_6H_4CF_3 \end{array}$$

(IV)



$$\begin{array}{c} C_6H_4CF_3 \\ Si(CH_3)_2 \\ Fe \end{array}$$

(V)

Dimethylphenylsilylferrocene, described in the literature and not containing a CF_3 group (7), has m.p. 83–84.5°.

Experimental Section

1. Dimethyl-*m*-benzotrifluoridechlorosilane. Into a three-necked flask equipped with a stirrer with a mercury seal, a dropping funnel, and a reflux condenser were charged 24 g (1 mole) of magnesium in 100 ml of absolute ether, and an ethereal solution of 225 g (1 mole) of *m*-bromobenzotrifluoride (8) and 142 g (1.1 mole) of dimethyldichlorosilane was added gradually. The reaction mixture was boiled for 6 hours, then filtered, and the filtrate was distilled. Forty-three grams of product distilling at 90–100°/15 mm, with chlorine content 13.4%, was isolated and used in subsequent syntheses.

II. Tris-($\gamma\gamma\gamma$-trifluoropropyl)-chlorosilane was obtained from 133 g (1 mole) of $\gamma\gamma\gamma$-trifluorochloropropane, 24 g (1 mole) of magnesium, and 55 g (0.32 mole) of silicon tetrachloride, as described above. Fifty-eight grams of product with b.p. 80–120°/20 mm and chlorine content 12.9%* was isolated.

There is a report on the preparation of this compound in the patent literature (9), but no constants are given.

III. [Tris-($\gamma\gamma\gamma$)-trifluoropropyl)-silyl]-ferrocene. Into an apparatus equipped as before were placed 18 g (0.1 mole) of ferrocene; to it was added an ethereal solution of 0.21 *M* *n*-butyllithium, and the mixture was stirred in a stream of dry oxygen-free nitrogen at room temperature for 3 days, with a break overnight.

Then 58 g (0.16 *M*) of tris-($\gamma\gamma\gamma$-trifluoropropyl)-chlorosilane in 100 ml of absolute ether was added to the reaction mixture, and the mixture was stirred at room temperature for another 3 days. After this the reaction mass was treated with ice water; the organic layer was separated and dried over sodium sulfate.

By evaporating the excess ether, 3 g of unreacted ferrocene was isolated. Repeated crystallization of the residue from a benzene—petroleum ether—carbon disulfide mixture (2 : 2 : 1) gave 0.7 g of III with m.p. 141—142°, which showed no depression with the product obtained by other authors (^{6}).

Found, %:	C 31.6; H 3.9; Si 8.6; F 50.0
$C_6H_8OSiF_6$. Calculated, %:	C 33.0; H 3.6; Si 8.5; F 52.2.

The residue after crystallization was distilled in a stream of nitrogen. At 180—205°/12 mm, 7.5 g of crystals with m.p. 93—95° distilled over; after recrystallization from a benzene—petroleum ether (1 : 1) mixture and methanol, they had m.p. 105° (II).

Found, %:	C 45.5; H 4.4; Si 6.2; Fe 11.8; F 30.5
$C_{19}H_{21}F_9SiFe$. Calculated, %:	C 45.2; H 4.17; Si 5.5; Fe 11.1; F 33.9.

IV. Bis-[tris-($\gamma\gamma\gamma$-trifluoropropyl)-silyl]-ferrocene. The product was obtained by repeated crystallization of the residue after distil—

* N. L. Kopnova, V. S. Chugunov, A. L. Klebanskii (in press).

II from a benzene-petroleum ether and benzene-methanol mixture; yellow crystals with m.p. 155° were isolated.

Found, %: C 41.5; H 4.1; Si 7.6; F 38.2; Fe 6.9

$C_{28}H_{32}Si_2F_{18}Fe$. Calculated, %: C 40.9; H 3.9; Si 6.8; F 41.6; Fe 6.8

V. Dimethyl-*m*-benzotrifluoride-silylferrocene. To 16 g (0.85 mole) of ferrocene was added 0.2 *M* ethereal solution of *n*-butyllithium. The reaction mixture was stirred for 4 days at room temperature. Then 71 g (0.29 mole) of dimethyl-*m*-benzotrifluoride-chlorosilane was added to the mixture in several portions until the alkaline reaction to phenolphthalein disappeared, and the mixture was stirred at room temperature for another 3 days. The reaction mass was decomposed with water and separated; the ether was evaporated in air, unreacted ferrocene was removed by steam distillation, and the residue was dried with sodium sulfate and distilled.

There were isolated 8 g of a dark oil with b.p. 205-232° at 17 mm, n_D^{20} 1.5350, and about 5 g of a crystallizing product distilling at 232-235° at 17-5 mm with decomposition.

By chromatography of the oil on alumina and repeated crystallization from petroleum ether, V was isolated with m.p. 50°.

Found, %: C 59.4; H 5.3; Si 7.8; Fe 15.1; F 12.15
$C_{19}H_{19}SiFeF_3$. Calculated, %: C 58.8; H 4.9; Si 7.2; Fe 14.4; F 14.7

Bis-(dimethyl-*m*-benzotrifluoride-silyl)-ferrocene. From the fraction with b.p. 232-235° at 17-5 mm, by repeated crystallization from petroleum ether, IV was isolated with m.p. 70-71°. An additional amount of product with m.p. 71° was isolated from the mother liquor by chromatography on alumina.

Found, %: C 57.7; H 5.1; Si 9.6; Fe 17.5; F 10.7
$C_{28}H_{28}Si_2FeF_6$. Calculated, %: C 56.9; H 4.7; Si 9.5; Fe 19.3; F 10.5

VI. Bis-(tripropylsilyl)-ferrocene. To 13 g (0.07 mole) of ferrocene were added 0.14 mole of an ethereal solution of *n*-butyllithium and 60 g of THF. The mixture was stirred for 48 hours in a stream of dry nitrogen. Then 35 g of tripropylbromosilane was added (and after 10 hours another 16 g), after which the mixture was stirred for another 40 hours at room temperature and boiled for 3 hours. Decomposition was carried out with ice water; the ether layer was dried over Na_2SO_4. Fifteen grams of bis-(tripropylsilyl)-ferrocene was obtained, b.p. 227-233° at 1 mm, n_D^{20} 1.5203, d_4^{20} 1.0214.

Found, %: C 67.2; H 10.9; Si 11.9; Fe 12.2
$C_{28}H_{50}Si_2Fe$. Calculated, %: C 67.3; H 10.04; Si 11.2; Fe 11.2

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Note: Figure translations are in progress. See original paper for figures.

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