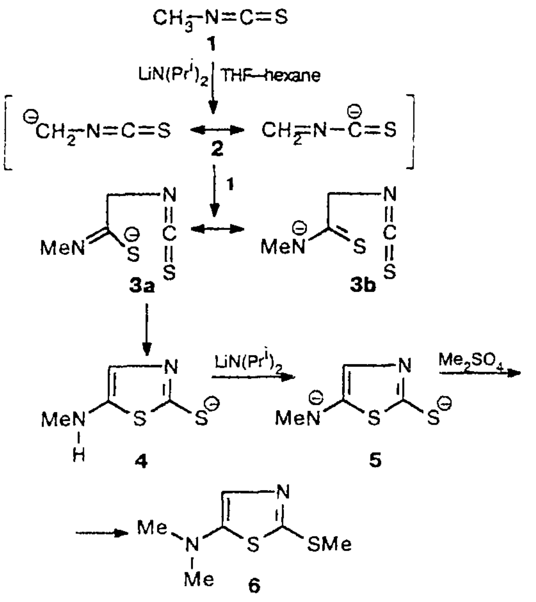
Scheme 1



CCl_4; Me_4Si as the internal standard). A GLC analysis was carried out on a Varian 3400 gas chromatograph (flame ionization detector; 15 m×0.53-mm capillary column; the thickness of the DB-5 stationary phase was 1.5 μm; nitrogen was the carrier gas).

All operations were carried out in an atmosphere of nitrogen. Tetrahydrofuran was purified with dispersed KOH (~50 g L^{-1}) and by distillation over $LiAlH_4$ in the presence of benzophenone in an atmosphere of nitrogen. Butyllithium (1.6 *M* solution in hexane) and the other reagents used in the work were commercial products.

Reaction of methyl isothiocyanate (1) with lithium diisopropylamide and dimethyl sulfate. A solution of methyl isothiocyanate (0.10 mol) in THF (10 mL) was added portionwise (within ~1 min) to a solution of lithium diisopropylamide (which was prepared from diisopropylamine (0.12 mol) and Bu^nLi (0.12 mol)) in a mixture of hexane (70 mL) and THF (70 mL) at temperatures from −100 to −50 °C. The temperature of the reaction mixture was decreased to −80 °C. Then dimethyl sulfate (0.13 mol) was added, the cooling bath was removed, and the reaction mixture was stirred until the temperature increased to 10 °C. The reaction mixture was treated with water (100 mL) with vigorous stirring. The organic layer was separated. The aqueous layer was extracted with pentane and ether. The combined extracts were dried with K_2CO_3. The solvents were evaporated under reduced pressure. The residue was distilled *in vacuo*. 5-Dimethylamino-2-methylthiothiazole (**6**) was obtained in a yield of 7.0 g (77.3%); the purity was 94.3% (GLC); b.p. ~110 °C (0.8 Torr). n^{20}_D 1.6110. Found (%): C, 42.06; H, 6.20; N, 15.41; S, 36.69. $C_6H_{10}N_2S_2$. Calculated (%): C, 41.38; H, 5.75; N, 16.09; S, 36.78.

IR, ν/cm^{-1}: 720, 740, 900, 950, 1000, 1040 sh, 1100, 1200, 1300, 1400, 1430 sh, 1500, 2770, 2850, 2900, 2930 sh, 2960 sh, 3070. ^1H NMR, δ: 2.55 (s, 3 H, SMe), 2.80 (s, 6 H, NMe_2), 6.55 (s, 1 H, CH=).

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Synthesis of (*m*-carboran-9-yl)ferrocene and (*m*-carboran-9-yl)cymantrene

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Cross-coupling reactions of 9-iodo-*m*-carborane with ferrocenylzinc chloride or cymantrenylzinc chloride catalyzed by $(Ph_3P)_2PdCl_2$ result in the formation of (*m*-carboran-9-yl)ferrocene and (*m*-carboran-9-yl)cymantrene, respectively.

Key words: cross-coupling reaction, 9-iodo-*m*-carborane, ferrocenylzinc chloride, cymantrenylzinc chloride.

Carboranylmetallocenes, in which the metallocenyl group is bonded to the boron atom of the carborane polyhedron by the C—B σ-bond, have been little studied. (*o*-Carboran-3-yl)ferrocene, the first and only metallocene derivative, in which the carbon atom is bonded to the carborane boron atom, was obtained in

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the reaction of 7,8-dicarbollide dianion with ferrocenylboron dichloride.[1] However, this procedure is rather complicated and has no practical importance.

Previously,[2] we reported that cross-coupling reactions of 9-iodo-*o*- and 9-iodo-*m*-carboranes with organozinc compounds catalyzed by palladium complexes can be used for synthesizing various 9-organyl-*o*- and -*m*-carboranes.

In this work, we used this cross-coupling reaction to synthesize carboranylmetallocenes containing the C—B σ-bond taking reactions between 9-iodo-*m*-carborane (**1**) and ferrocenylzinc chloride or cymantrenylzinc chloride catalyzed by palladium complexes as examples. Following this procedure, (*m*-carboran-9-yl)ferrocene (**2**) and (*m*-carboran-9-yl)cymantrene (**3**) are formed in high yields according to the following scheme:

$$(\pi\text{-}C_5H_5)_2Fe \xrightarrow[\text{THF}]{Bu^nLi} (\pi\text{-}C_5H_5)Fe(\pi\text{-}C_5H_4Li) \xrightarrow[\text{THF}]{ZnCl_2}$$

$$\longrightarrow (\pi\text{-}C_5H_5)Fe(\pi\text{-}C_5H_4ZnCl) + \underset{\mathbf{1}}{9\text{-}I\text{-}m\text{-}C_2B_{10}H_{11}} \xrightarrow{i}$$

$$\longrightarrow \underset{\mathbf{2}}{(\pi\text{-}C_5H_5)Fe(\pi\text{-}C_5H_4\text{-}9\text{-}m\text{-}C_2B_{10}H_{11})}$$

$$\pi\text{-}C_5H_5Mn(CO)_3 \xrightarrow[\text{THF, -40 °C}]{Bu^nLi} (\pi\text{-}C_5H_4Li)Mn(CO)_3 \xrightarrow[\text{20 °C}]{ZnCl_2}$$

$$\longrightarrow (\pi\text{-}C_5H_4ZnCl)Mn(CO)_3$$

$$(\pi\text{-}C_5H_4ZnCl)Mn(CO)_3 + \mathbf{1} \xrightarrow{i}$$

$$\longrightarrow \underset{\mathbf{3}}{(CO)_3Mn(\pi\text{-}C_5H_4\text{-}9\text{-}m\text{-}C_2B_{10}H_{11})}$$

i. $(Ph_3P)_2PdCl_2$, THF, Δ

Compounds **2** and **3** are air-stable orange and yellow crystalline substances, respectively. Their structure was confirmed by elemental analysis and IR spectroscopy.

Experimental

IR spectra were recorded on an UR-20 spectrophotometer. Ferrocenyllithium and cymantrenyllithium were obtained according to the procedures reported in Refs. 3 and 4, respectively.

(*m*-Carboran-9-yl)ferrocene (2). A 1 *M* benzene solution of Bu^nLi (15 mL, 16 mmol) was added to a solution of ferrocene (2 g, 10.75 mmol) in 15 mL of THF at 0 °C. The mixture was stirred for 4 h at 20 °C. Then $ZnCl_2$ (2.7 g, 16.1 mmol) in 15 mL of THF (15 mL) was added at 0 °C. The temperature was gradually raised to 20 °C over a period of 40 min with stirring. 9-Iodo-*m*-carborane (2 g, 7.4 mmol) and 0.1 g of $(Ph_3P)_2PdCl_2$ were added to the mixture obtained. The reaction mass was refluxed for 9 h, cooled, poured into water, and extracted with benzene, and the benzene solution was dried with Na_2SO_4. The solution was chromatographed on a column with silica gel (1.5×20 cm, with petroleum ether as eluent) to isolate (*m*-carboran-9-yl)ferrocene (1.5 g, 70%), m.p. 98—100 °C (hexane). IR (ν/cm^{-1}): 998, 1102 (deformation vibration of the C_5H_5 group), 2594 (BH), 3054 (carborane CH), 3100 (C_5H_5). Found (%): C, 40.60; H, 6.15. $C_{12}H_{20}B_{10}Fe$. Calculated (%): C, 39.47; H, 6.57.

(*m*-Carboran-9-yl)cymantrene (3). A benzene solution of Bu^nLi (13 mL, 13 mmol) was added to a solution of cymantrene (2.4 g, 12 mmol) in 15 mL of THF at −60 °C. The mixture was stirred for 30 min at −40 °C. At this temperature, a solution of $ZnCl_2$ (1.8 g, 13 mmol) in 20 mL of THF was added followed by raising the temperature to 20 °C. The mixture was stirred for 30 min and then 9-iodo-*m*-carborane (2.7 g, 10 mmol) and 0.1 g of $(Ph_3P)_2PdCl_2$ were added. The reaction mixture was heated for 16 h at 35—40 °C with stirring. The usual workup and chromatography on a column with SiO_2 (with petroleum ether as eluent) gave (*m*-carboran-9-yl)cymantrene (2 g, 58%), m.p. 55—57 °C (hexane). IR (ν/cm^{-1}): 3040 (carborane CH), 2609 (BH), 2022 and 1940 (CO), 1100, 1004, 811 (deformation vibration of the C_5H_5 group). Found (%): C, 34.58; H, 3.35; Mn, 16.13. $C_{10}H_{15}B_{10}MnO_3$. Calculated (%): C, 34.68; H, 4.34; Mn, 15.90.

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