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HEPTAMETHYLCYCLOHEXADIENYLIRON TRICARBONYL CATION

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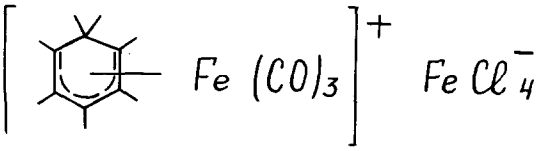
Iron carbonyl complexes having formally a carbonium ion as one of ligands are well known /1/. The usual methods for producing these compounds consist in the initial preparation of precursors - complexes of olefines - with subsequent protonation or hydride-ion abstraction.

We have succeeded in obtaining heptamethylcyclohexadienyliron tricarbonyl cation as its tetrachloroferrate (I) by direct interaction of heptamethylbenzenonium tetrachloroaluminate (II) /2/ and $Fe(CO)_5$.



I

The mixture of 2.3g (0.0066 mole) of II and 5.6g (0.0286 mole) of $Fe(CO)_5$ was kept at 150°C for 8 hours in a sealed tube. The resulting solid was collected and washed with benzene. Extraction of the residue

by C_6H_5Cl gave 0.2g of the solid which was recrystallized from C_6H_5Cl to yield I. The main part of the residue was a salt of bis(hexamethylbenzene)-iron (Fe^{+2}), identified as its ditetraphenylborate (2.36g) by comparison with an authentic sample, synthesized according to E.O. Fischer et al. /3/.

Salt I was the yellow fine needles, soluble in water. (Calc. for $C_{16}H_{21}O_3Cl_4Fe_2$: C, 37.2; H, 4.08; Cl, 27.6; Fe, 21.7. Found: C, 37.6; H, 4.06; Cl, 27.3; Fe, 21.8.) Infrared spectrum: ν_{CO}^{KBr} 2028, 2041 and 2083cm^{-1}. Boiling of the solution of I in hydrochloric acid gave hexamethylbenzene (90%). Heptamethylcyclohexadienyliron tricarbonyl tetraphenylborate was prepared by an exchange reaction of I with $NaB(C_6H_5)_4$. (Calc. for $C_{40}H_{41}O_3BFe$: C, 75.5; H, 6.45. Found: C, 75.5; H, 6.48.)

In order to obtain the high-resolution n.m.r. spectrum the paramagnetic ions were removed from the solution of I in 20% hydrochloric acid by extraction with $(C_2H_5)_2O$. N.m.r. spectrum (chemical shifts in τ-scale, internal standard $N(CH_3)_4Br$): 7.34(1), 7.76(2), 8.22(2), 8.52(1) and 9.39(1).

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