Preparation and Crystal Structure of π-Cyclopentadienyl-1,2-bis-(diphenylphosphino)ethaneironmagnesium Bromide Tris(tetrahydrofuran), a Transition–Metal Grignard Reagent

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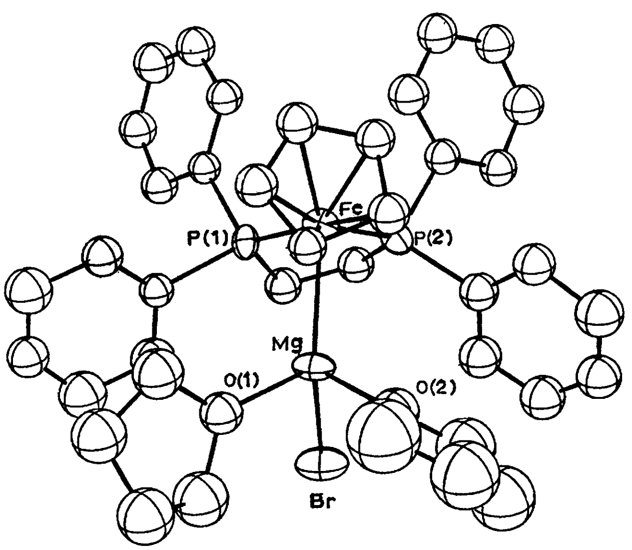
Summary π-Cyclopentadienyl-1,2-bis(diphenylphosphino)-ethane iron bromide and magnesium in tetrahydrofuran (THF) afford the novel crystalline inorganic magnesium reagent $(\pi\text{-}C_5H_5)$(diphos)FeMgBr,3THF, containing a covalent iron-magnesium bond (Fe–Mg 2·59 Å).

NO crystal structures of compounds containing transition-metal–magnesium bonds have yet been reported, and indeed only very few systems thought to contain such transition-metal Grignard reagents have been described.[1] We now report the preparation and crystal structure of π-cyclopentadienyl-1,2-bis(diphenylphosphino)ethaneiron-magnesium bromide tris(tetrahydrofuran) (I), the first example of a crystalline compound which has been shown to contain a covalent transition-metal–magnesium bond.

Reaction of $(\pi\text{-}C_5H_5)$(diphos)FeBr†[2] (6 mmol), CH_2BrCH_2Br (0·6 mmol), and excess of magnesium in dry THF (35 ml) under N_2 at room temperature consumed 6·6 mmol of Mg and afforded a red solution which after 6—60 h, deposited red crystals of $(\pi\text{-}C_5H_5)$(diphos)FeMgBr,3(THF) (I) (*ca.* 3·3 mmol). Elemental analyses were satisfactory for metals but consistently low for C and H.[3] The n.m.r. spectrum (in C_6D_6) showed δ (Me_4Si) 7·15 (Ph), 4·23 (s, C_5H_5), 3·42 (CH_2O of THF), and 1·3 (CH_2 of diphos THF), with relative intensities 20 : 5 : 12 : 15 [calc. for (I) 20 : 5 : 12 : 16]. One of the three tetrahydrofuran molecules was easily displaced, *e.g.*, by recrystallisation from benzene, which afforded red crystals containing (n.m.r.) two tetrahydrofuran and one benzene molecule. The chemical behaviour of this iron Grignard reagent is reminiscent of that of the analogous nickel reagents, $(\pi\text{-}C_5H_5)(PR_3)$NiMgBr (obtained only in solution[2]) and will be reported later.

Crystal data: Crystals of (I) are monoclinic, space group $P2_1/c$, $a = 12.258(4)$, $b = 13{\cdot}027(4)$, $c = 26{\cdot}577(11)$ Å, $\beta = 102{\cdot}48(2)°$, $Z = 4$. 1505 independent reflections, collected with monochromated Mo-K_α radiation on a Picker automatic diffractometer, were used to solve the structure by standard Patterson, Fourier, and least-squares methods. The present R value is 0·08. The crystal structure of (I) consists of $(\pi\text{-}C_5H_5)$(diphos)FeMgBr,2(THF) molecules (Figure) and one THF molecule of crystallisation.



FIGURE

The $(\pi\text{-}C_5H_5)$(diphos)Fe fragment is directly linked to the MgBr,2(THF) fragment. The Fe–Mg bond distance of 2·593(7) Å indicates a bond with a strong covalent character. The magnesium atom has a distorted tetrahedral environment similar to that in many organic Grignard reagents,[4] ∠ Fe–Mg–Br 129·2(2)°, Fe–Mg–O(1) 119·0(5)°, Fe–Mg–O(2) 115·8(6)°, and O(1)–Mg–O(2) 91·7(9)°. The Mg–Br and Mg–O bond distances are respectively 2·522(7), and 2·075-(15) and 2·098(15) Å, not significantly different from the average values found in EtMgBr,$2Et_2O$, PhMgBr,2THF, and MeMgBr,3THF,[4] which are 2·47(3) Å for Mg–Br and 2·06(3) Å for Mg–O. The molecular geometry of the $(\pi\text{-}C_5H_5)$(diphos)Fe unit is normal.

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† diphos = 1,2-bis(diphenylphosphino)ethane.

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