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Preliminary communication

REACTIVITY OF THE INORGANO-GRIGNARD $(\eta^5\text{-}C_5H_5)(Ph_2PCH_2CH_2PPh_2)$-FeMgBr TOWARDS HALOGENOGERMANES

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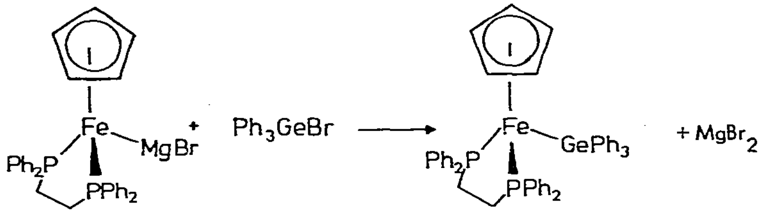
Summary

The inorgano-Grignard reagent $(\eta^5\text{-}C_5H_5)(Ph_2PCH_2CH_2PPh_2)FeMgBr$ reacts by a one-electron transfer process with Ph_3GeBr to give the complex $(\eta^5\text{-}C_5H_5)$-$(Ph_2PCH_2CH_2PPh_2)FeGePh_3$, which contains an Fe—Ge bond.

The synthesis, structure and properties of the inorgano-Grignard reagent CpFe(diphos)MgBr (1, Cp = $\eta^5\text{-}C_5H_5$; diphos = $Ph_2PCH_2CH_2PPh_2$) have been described by Felkin et al. [1]. Complex 1 is very basic and only weakly nucleophilic. 1 reacts with bromoalkanes by a one-electron transfer mechanism but is unreactive towards Group IV organometallic halides such as Me_3SiCl, Me_2SiHCl or Me_3SnCl [1]. We report here the reactivity of 1 towards polyaryl-(bromo)germanes in order to show that these reactions of 1 are not limited to organic bromides. Furthermore in connection with our study of the S_N-*Ge* reaction [2] it was of interest to know if the germanium derivatives used in stereochemical studies on optically active ($ArAr^IRGeX$ [3—5]) and geometric (1,2-dimethylgermacyclopentanes [2,6]) systems, which are very reactive towards classical nucleophiles ($LiAlH_4$, RLi, RMgX etc.), could also undergo substitution by one-electron transfer processes. Such a one-electron transfer mechanism appears to be unlikely in the case of the S_N2-*Si* reaction [7,8].

CpFe(diphos)Br [9] (500 mg, 0.8 mmol) in anhydrous tetrahydrofuran (40 ml) was added to activated magnesium powder [10] and the mixture stirred for 16 h at 20°C. Filtration gave a deep red solution of 1. The bromogermanes Ph_3GeBr, $Ph_2MeGeBr$ and $PhMe_2GeBr$ were prepared by brominolysis (without catalyst, 0°C) of the corresponding arylgermanes Ph_4Ge, Ph_3MeGe and Ph_2Me_2Ge respectively [11].

A solution of Ph_3GeBr (280 mg) in tetrahydrofuran (20 ml) was added to the solution of 1 under nitrogen. After 38 h at 20°C, water (0.1 ml) was added and the solvent evaporated. After extraction with Et_2O, CCl_4 (1 ml) was added to remove any CpFe(diphos)H by precipitation of the corresponding chloride. Chromatography (Al_2O_3, grade II—III, toluene) gave an orange solid after evaporation. Crystallisation from Et_2O gave orange needles of CpFe(diphos)$GePh_3$ (2) (Found: C, 71.22; H, 5.62; P, 7.47. $C_{49}H_{44}GeFeP_2$ calcd.: C, 71.49; H, 5.35; P, 7.54%); $m/e = 822$; τ (C_6D_6) 2.3—3.1 (35H, aryl-*H*), 5.6 (5H, Cp-*H*) and 7.9—8.3 (4H, CH_2).



1 2

Reaction of 1 with $Ph_2MeGeBr$ gave after hydrolysis, the bromide CpFe(diphos)Br. Treatment of 1 with $PhMe_2GeBr$ or Ph_3SiBr* gave after hydrolysis the hydride CpFe(diphos)H (the hydrolysis product of 1 [1]), indicating no reaction had taken place. The hydride CpFe(diphos)H slowly reacts with $Ph_2MeGeBr$ to give CpFe(diphos)Br.

These results suggest that the reactions of 1 with Ph_3GeBr and $Ph_2MeGeBr$ are one-electron transfer processes. This is in agreement with the conclusion for the reactions of 1 with organic halides. In the reaction of 1 with Ph_3GeBr, the initially formed $Ph_3Ge^{\bullet}$ appears to be sufficiently stable and electrophilic to accept a second electron-generating Ph_3Ge^- and $\mathrm{CpFe(diphos)}^+$, which combine to form 2 [12].

$$\begin{tikzcd}
1 + \mathrm{Ph_3GeBr} \arrow[r] & {[\mathrm{CpFe(diphos)}]^{\bullet} + \mathrm{Ph_3Ge}^{\bullet} + \mathrm{Br}^-} \arrow[d] \\
2 & {[\mathrm{CpFe(diphos)}]^+ + \mathrm{Ph_3Ge}^-} \arrow[l]
\end{tikzcd}$$

A similar Fe—Ge complex was not isolated from the reaction with $Ph_2MeGeBr$, presumably because the less electrophilic radical $Ph_2MeGe^{\bullet}$ does not accept a second electron.

$$\begin{tikzcd}
1 + \mathrm{Ph_2MeGeBr} \arrow[r] & {[\mathrm{CpFe(diphos)}]^{\bullet} + \mathrm{Ph_2MeGe}^{\bullet} + \mathrm{Br}^-} \arrow[d, "\mathrm{Ph_2MeGeBr}"] \\
\mathrm{CpFe(diphos)Br} & {[\mathrm{CpFe(diphos)}]^+ + \mathrm{Br}^- + \mathrm{Ph_2MeGe}^{\bullet}} \arrow[l]
\end{tikzcd}$$

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Presumably neither $PhMe_2GeBr$ nor Ph_3SiBr react with 1 because they are not sufficiently electrophilic to accept an electron from 1 [13].

In conclusion, while the halogenosilanes, even Ph_3SiBr, do not take part in one-electron transfer reactions, at least with 1, polyaryl(halo)germanes, which are better electrophiles than the analogous halosilanes, readily undergo this reaction, which may therefore be involved in substitution reactions at germanium. The reaction of inorgano-Grignard reagents such as 1 with halogermanes provides a method for synthesis of transition metal—germanium bonds.

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