BRIEF COMMUNICATIONS

NEW DIRECTIONS IN THE SYNTHESIS OF BIS(π-CYCLOPENTADIENYLDICARBONYLIRON)MERCURY

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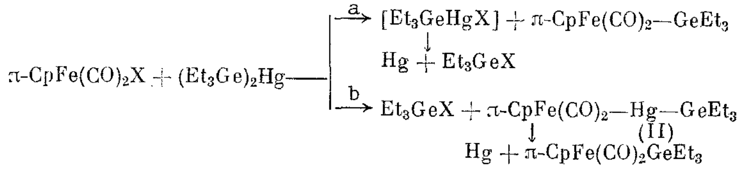
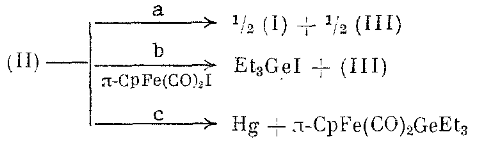
The synthesis of bisorganometallic compounds with the Fe—Ge group by the reaction of bis(triethylgermyl)mercury (I) with π-cyclopentadienyldicarbonyl iron complexes, π-CpFe$(CO)_2$X (X = Cl, Br) and [π-CpFe$(CO)_2]_2$ under optimal conditions (100°C, 2-6 h) is achieved with almost a quantitative yield of metallic mercury [1]. The mechanism for this reaction has not been elucidated.

For π-CpFe$(CO)_2$X and (I), two alternative pathways have been proposed leading to the same final products:



$$\pi\text{-CpFe(CO)}_2X + (Et_3Ge)_2Hg \begin{cases} \xrightarrow{a} [Et_3GeHgX] + \pi\text{-CpFe(CO)}_2\text{—GeEt}_3 \\ \qquad \downarrow \\ \qquad Hg + Et_3GeX \\ \xrightarrow{b} Et_3GeX + \pi\text{-CpFe(CO)}_2\text{—Hg—GeEt}_3 \ \text{(II)} \\ \qquad \downarrow \\ \qquad Hg + \pi\text{-CpFe(CO)}_2GeEt_3 \end{cases} \qquad (1)$$

In the present work, we have established that the reaction of (I) proceeds under milder conditions (∿20°C) and is not accompanied by the formation of mercury. Thus, the reaction of π-CpFe$(CO)_2$I with (I) in 2:1 mole ratio leads to the formation of triethylgermanium iodide and bis(π-cyclopentadienylirondicarbonyl)mercury (III) with 76 and 91% yields, respectively. The absence of mercury from the reaction products indicates that pathway a may be excluded. The subsequent transformation of intermediate (II) is accomplished by scheme (2) either by symmetrization (z) or reaction with a second π-CpFe$(CO)_2$I molecule (b). Under the conditions employed, the demercuration reaction (c) is realized only to a slight extent (the mercury yield is only 10%).

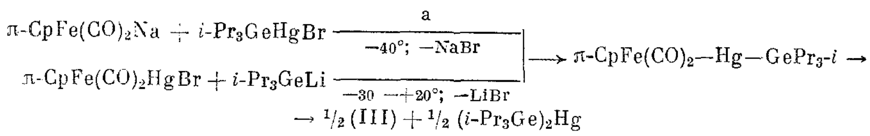


$$\text{(II)} \begin{cases} \xrightarrow{a} \tfrac{1}{2}\,\text{(I)} + \tfrac{1}{2}\,\text{(III)} \\ \xrightarrow[\pi\text{-CpFe(CO)}_2I]{b} Et_3GeI + \text{(III)} \\ \xrightarrow{c} Hg + \pi\text{-CpFe(CO)}_2GeEt_3 \end{cases} \qquad (2)$$

The substitution of (I) by $(Et_3Si)_2Hg$ and of π-CpFe$(CO)_2$I by π-CpFe$(CO)_2$Br probably does not markedly alter the reaction course since 8% mercury, 86% triethylbromosilane and 89% (III) were isolated under comparable conditions.

Special experiments showed that (III) and (I) react only upon heating to 100°C. The quantitative formation of mercury requires only heating for 3 h and the yield of triethyl(dicarbonyl-π-cyclopentadienyliron)germane is 89.5%.

Thus, it is quite likely that the equilibrium in reaction (2a) at about 20°C is shifted completely to the right and upon heating to 100°C to the left due to subsequent demercuration by reaction (2c). The reactions π-CpFe$(CO)_2$Na with triisopropylgermylmercuric bromide and of π-CpFe$(CO)_2$HgBr with triisopropylgermyllithium also proceed with the formation of an intermediate such as (II) which then symmetrizes.



$$\left.\begin{array}{l} \pi\text{-CpFe(CO)}_2Na + i\text{-}Pr_3GeHgBr \xrightarrow[-40^\circ;\ -NaBr]{a} \\ \pi\text{-CpFe(CO)}_2HgBr + i\text{-}Pr_3GeLi \xrightarrow[-30\ \to +20^\circ;\ -LiBr]{} \end{array}\right| \longrightarrow \pi\text{-CpFe(CO)}_2\text{—Hg—GePr}_3\text{-}i \rightarrow$$
$$\rightarrow \tfrac{1}{2}\,\text{(III)} + \tfrac{1}{2}\,(i\text{-}Pr_3Ge)_2Hg$$

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The yields of the final products in reaction (3a) are close to quantitative, while the formation of mercury is not observed. In the latter reaction, the yield of mercury is 19%, while the yields of (III) and $(i\text{-}Pr_3Ge)_2Hg$ are 56.5 and 68%, respectively.

EXPERIMENTAL

All the reactions were carried out in evacuated sealed ampuls with the careful exclusion of oxygen and moisture. The spectral and analytical data for the reaction products correspond to literature values.

Reaction of π-cyclopentadienylirondicarbonyl iodide with bis(triethylgermyl)mercury (I). A solution of 3.24 mmoles (I) in 15 ml toluene was added to a solution of 6.08 mmoles π-cyclopentadienylirondicarbonyl iodide in 30 ml toluene. Over 3-5 min, the color of the solution changed from green-brown to orange-red and 0.33 mg-atom (10%) mercury precipitated. The solution was decanted and the solvent and Et_3GeI (4.59 mmoles, 76%) were isolated in vacuum. A sample of 20 ml hexane was added to the residue to give a precipitate of 2.76 mmoles (91%) $[\pi\text{-}CpFe(CO)_2]_2Hg$.

Analogously, 4.48 mmoles π-cyclopentadienylirondicarbonyl bromide in 30 ml toluene and 2.24 mmoles $(Et_3Si)_2Hg$ in 15 ml toluene upon standing for 5 min at ∿20°C gave 0.18 mg-atom (8%) mercury, 3.86 mmoles (86%) Et_3SiBr and 2.00 mmoles (89%) $[\pi\text{-}CpFe(CO)_2]_2Hg$.

Reaction of π-cyclopentadienylirondicarbonylsodium with triisopropylgermylmercuric bromide. A solution of $\pi\text{-}CpFe(CO)_2Na$ (obtained from 0.52 g $[\pi\text{-}CpFe(CO)_2]_2$ and excess 3% sodium amalgam) in THF was added at −40°C to a suspension of $i\text{-}Pr_3GeHgBr$ in hexane prepared according to our previous procedure [2] (from 1.6 g $(i\text{-}Pr_3Ge)_2Hg$ and 0.42 g Br_2 in 20 ml hexane). The precipitate contained 1.87 mmole (71%) NaBr. The solvents in the mother liquor were replaced by hexane. An orange crystalline precipitate of $[\pi\text{-}CpFe(CO)_2]_2Hg$ was formed (0.67 g, 90%). Fractionation of the hexane solution in vacuum gave 1.23 mmole (93%) $(i\text{-}Pr_3Ge)_2Hg$.

Reaction of π-cyclopentadienylirondicarbonylmercuric bromide with triisopropylgermyllithium. A sample of 5.28 mmoles $i\text{-}Pr_3GeLi$ in 20 ml toluene at −30°C was added to 5.28 mmoles π-cyclopentadienylirondicarbonylmercuric bromide in 20 ml toluene. After 0.5 h the temperature was raised to about 20°C. The mercury formed (0.99 mg-atom, 19%) was separated and the solvent was removed in vacuum. A sample of 30 ml hexane was added to the residue. Washing of the precipitate with water gave 3.75 mmoles (71%) LiCl. The precipitate contained 1.21 mmole (56.5%) $[\pi\text{-}CpFe(CO)_2]_2Hg$.

CONCLUSIONS

1. Organosilicon and organogermanium derivatives of mercury and alkali metals may serve as starting reagents for the preparation of bis(π-cyclopentadienylirondicarbonyl)-mercury.

2. These reactions proceed through the formation of intermediates containing FeHgM groups (M = Si, Ge).

LITERATURE CITED

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