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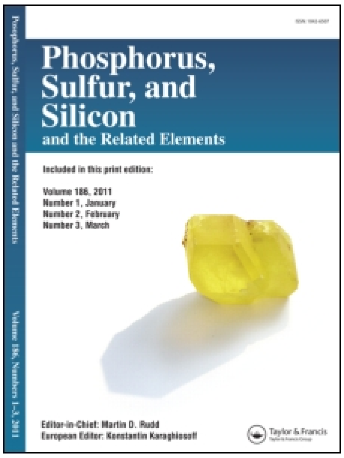

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Ferrocene and Silicon Containing Organotin (IV) Halides as Lewis Acidic Hosts for Anions

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Here we present the synthesis of the novel organotin (IV) compounds **1** – **15** containing silylmethylene-spacers and ferrocene moieties. Also reported are the reactions of the methylene-bridged ditin compound **15** and the ferrocenophanes **12** and **13** with halide ions.

Keywords: Lewis acids; silicon; tin; ferrocenophanes

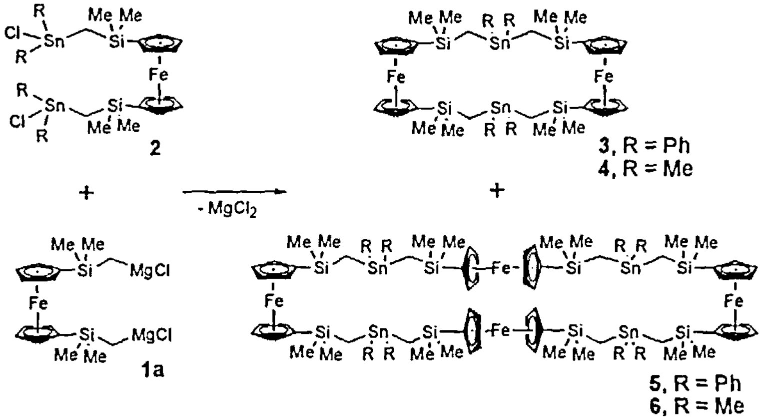
INTRODUCTION

The selective recognition of anions or neutral donor molecules by tailor-made host molecules has been intensively studied in the last two decades[1]. Multidentate Lewis acids containing elements such as boron[2a], indium[2b], silicon[2c], germanium[2d], tin[2e] and mercury[2f] as well as organometallic metallocene receptor systems[3] were shown to be efficient in coordinating anions and neutral Lewis bases. One conclusion from these investigations is that the selectivity strongly depends on the preorganization of the host molecule, i.e. the more rigid the host the better the expected selectivity.

The object of our research is to study the host-guest activity of spacer-bridged organotin(IV) halides. Here we present the synthesis and complexation behaviour of the first organotin compounds containing silicon atoms as well as ferrocenyl units.

RESULTS AND DISCUSSION

The reactions of the Grignard reagent **1a** of 1,1'-bis[(chloromethyl)-dimethylsilyl]ferrocene (**1**) with 1,1'-bis{[(chlorodiorganostannyl)-methyl]dimethylsilyl}ferrocene (**2**) gave the ferrocenophanes **3** - **6**, respectively (SCHEME 1).



SCHEME 1 Ferrocenophanes **3** - **6**.

The compounds were isolated by use of Size Exclusion Chromatography and their identity was confirmed unambiguously by crystal structure determination (3, 4)[4] as well as NMR spectroscopy, molecular weight determination, and Electrospray MS (5, 6). To the best of our knowledge these compounds are the first silicon and tin containing ferrocenophanes.

The reactions of the Grignard reagent of [(chloromethyl)-dimethylsilyl]ferrocene (7) with Ph_2SnCl_2, $(Ph_2FSn)_2CH_2$ or 1,1'-bis-{[(chlorodiphenylstannyl)methyl]dimethylsilyl}ferrocene (2), respectively, afforded the acyclic tin and silicon containing ferrocene derivatives **8** - **10** (CHART 1).

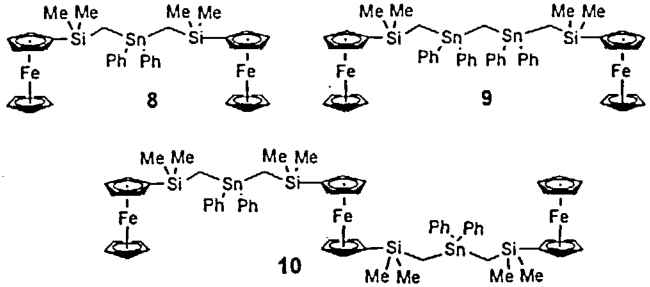
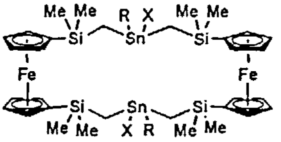


CHART 1

Reaction of the ferrocenophane **3** (SCHEME 1) with iodine afforded the iodo-substituted derivative **11** (CHART 2). Treatment of **11** with AgCl or aqueous KF provided the chloro and fluoro derivatives **12** and **13** respectively (CHART 2). The reaction of the methyl-substituted ferrocenophane **4** (SCHEME 1) with two mole equivalents of Me_2SnCl_2 provided **14** (CHART 2) and Me_3SnCl. Depending on the substituent pattern at tin the ferrocenophanes **3**, **4**, **11**, **12** and **14** show

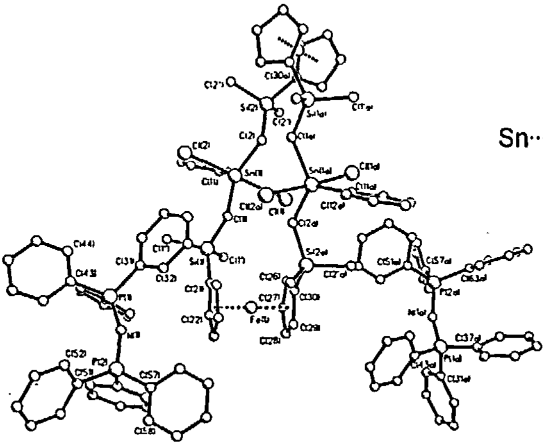
Sn(1)···Sn(2) distances ranging from 6.1975(9) Å to 9.4061(5), as established by x-ray crystallography (CHART 2).



3, X = R = Ph	Sn···Sn 9.4061(5) Å
4, X = R = Me	Sn···Sn 9.1202(2) Å
11, X = I; R = Ph	Sn···Sn 6.1975(9) Å
12, X = Cl, R = Ph	Sn···Sn 8.6718(6) Å
14, X = Cl, R = Me	Sn···Sn 8.829(3) Å

CHART 2

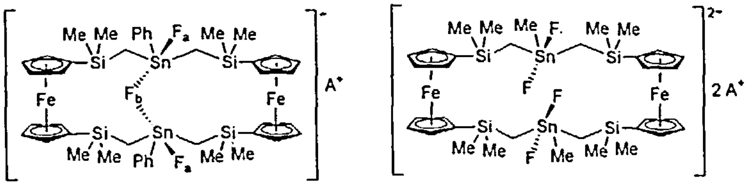
The reaction of the chloro species **12** with $(Ph_3P)_2NCl$ exclusively provided the 1:2 adduct **12a**. The Sn···Sn distance in **12a** (5.8233(7) Å) (FIGURE 1) is shorter than in **3**, **4**, **11**, **12** and **14** (CHART 2).



Sn···Sn 5.8233(7) Å

FIGURE 1 Crystal structure of the 1:2 complex **12a**.

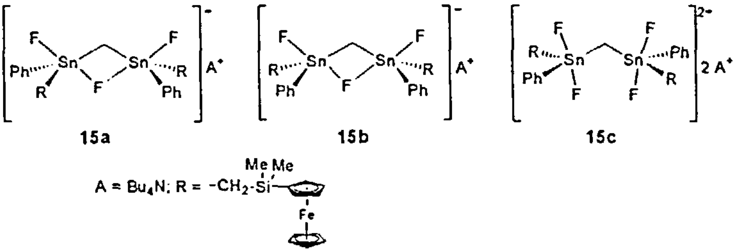
The addition of one mole equivalent of fluoride ions to a solution of the fluoro species **13** resulted in the *in situ* formation of the 1:1 complex **13a** (CHART 3). Addition of a second mole equivalent of fluoride ions gave the 1:2 adduct **13b**.



13a A = Bu_4N **13b**

CHART 3

Treatment of the methylene-bridged ditin compound **9** (CHART 1) with iodine in dichloromethane and reaction with aqueous KF afforded the fluoro species bis{[(ferrocenyldimethylsilyl)methyl]-phenylfluorostannyl}methane (**15**). The addition of one mole equivalent $Bu_4NF{\cdot}3H_2O$ to a solution of **15** in CH_2Cl_2 gave *in situ* both diastereomers **15a** and **15b** (ratio 4:1) of the 1:1 complex (CHART 4). These diastereomers are stable on the ^{119}Sn NMR time scale at -50°C. After addition of two mole equivalents of $Bu_4NF{\cdot}3H_2O$ to a solution of **15** both the 1:1 complex (diastereomers **15a** and **15b**) and the 1:2 complex **15c** (CHART 4) were observed (ratio **15a**:**15b**:**15c** = 8:2:7).



15a **15b** **15c**

CHART 4

Cyclovoltammetric studies on the compounds **2**, **11**, and **12** in CH_2Cl_2 (0.2 M Bu_4NPF_6 as supporting electrolyte) show a variation of the formal electrode potentials $E^{\circ\prime}$ (*vs.* SCE) for the oxidation of the ferrocene subunit(s) upon addition of anions. The addition of 5 mole equivalents of chloride or fluoride ions to solutions of **2**, **11**, or **12** results in changes of $\Delta E^{o\prime}$ in the range of 200 mV, whereas the addition of 5 mole equivalents of $[Bu_4N]^+[H_2PO_4]^-$ causes greater changes of the electrode potential with $\Delta E^{o\prime} = 560$ mV for **2**, 460 mV for **11** and 480 mV for **12**. To the best of our knowledge these $\Delta E^{o\prime}$ values are the greatest ones for ferrocene containing host molecules to which has been added $H_2PO_4^-$. This indicates that compounds **2**, **11**, and **12** hold potential for the selective recognition of $H_2PO_4^-$.

ACKNOWLEDGMENTS

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