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The substituent-dependent base-treatment chemistry of (η^5-C_5H_5)Fe(CO)$_2$SiR$_2$SiR$_2$Cl: formation of 1,2-disila-3-metallacyclobutanes, their ring-opened polymers, migrations and substitutions†

Hemant K. Sharma and Keith H. Pannell*
Department of Chemistry, University of Texas at El Paso, El Paso, TX, 79968-0513, USA.
E-mail: kpannell@utep.edu

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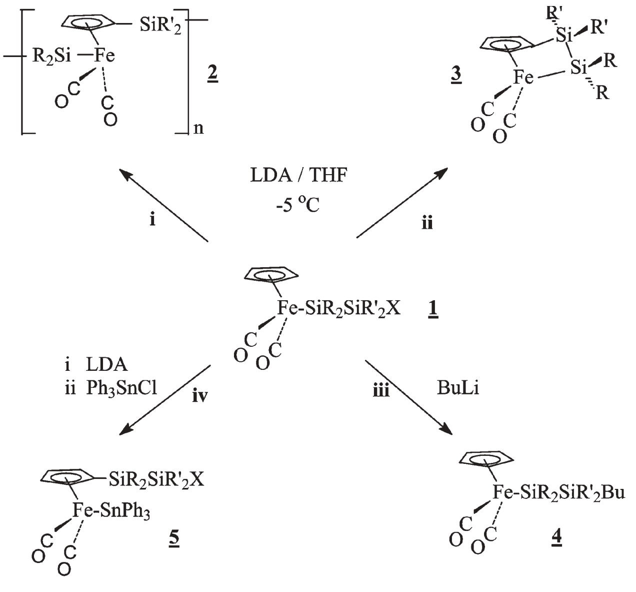
We report the formation of disilametallacycles, high molecular weight polymers or simple substitution products from the reactions of 1-(cyclopentadienyliron dicarbonyl)-2-chlorodisilanes with bases, LDA or *n*-BuLi.

Organometallic polymers in which the transition metals are part of the backbone offer useful chemical, electrochemical, optical and magnetic properties.[1,2] We recently reported that 1-sila-3-metallacyclobutanes of the type [(η^5-C_5H_4)Fe(CO)$_2$CH$_2$SiR$_2$] could be isolated, structurally characterized and ring-opened to the corresponding high MW polymers by base-treatment of (η^5-C_5H_5)Fe(CO)$_2$SiR$_2$CH$_2$Cl.[3] Since 1,2-disila polymers that also contain unsaturated or aromatic groups are photoactive and show conducting properties when the polymers are doped with oxidizing agents[4–6] we have investigated, and now report, the chemistry of the related disilyl systems, (η^5-C_5H_5)Fe(CO)$_2$SiR$_2$SiR$_2$Cl.

Base-treatment of FpSiMe$_2$SiMe$_2$Cl,[7] **1a**, [Fp = (η^5-C_5H_5)-Fe(CO)$_2$], with lithium diisopropylamide, LDA, in THF at −5 °C, resulted in clean and quantitative formation of the polymer **2**, Scheme 1(i), as a light brown material that precipitated directly from the THF solution. We observed no evidence for the formation of the supposed precursor 1,2-disila-3-ferracyclobutane, (η^5-C_5H_4)Fe(CO)$_2$SiMe$_2$SiMe$_2$. However, similar base-treatment of the 1,1,2,2-tetrabutyl and 1,1-dimethyl-2,2-dibutyl analogs, FpSiBu$_2$SiBu$_2$Cl, **1b**, and FpSiMe$_2$SiBu$_2$Cl, **1c**, resulted only in the isolation of the corresponding analytically pure 1,2-disila-3-ferracycle, **3b** and **3c**, Scheme 1(ii). We suppose that these complexes form *via* a base-mediated metal to cyclopentadienyl ring silatropic shift, and the subsequently formed ferrate species undergoes an intramolecular salt-elimination cyclization to form the disilametallacycles.[8] Gladysz *et al.* have reported the related rhenium complex, (η^5-C_5H_4)ReNO(PPh$_3$)SiMe$_2$SiMe$_2$ synthesized in an analogous reaction from (η^5-C_5H_5)ReNO(PPh$_3$)SiMe$_2$-SiMe$_2$Cl and butyllithium.[9] The ^{29}Si NMR spectra of the metallacycles **3b,c** exhibit two signals for the α-Si and β-Si with respect to the Fe atom at −39, −40 and −19, −15 ppm, respectively.

Upon changing the silicon-bonded substituents to 1,2-dimethyl-1,2-dibutyl groups, FpSiMeBuSiMeBuCl, **1d**, neither metallacycle nor polymer formation was observed upon treatment with LDA. However, treatment with *n*-BuLi resulted in the isolation in moderate yield of the direct nucleophilic substitution product, FpSiMeBuSiMeBu$_2$, **4**, Scheme 1(iii). NMR analysis of the crude reaction products provided no evidence for formation of the corresponding metallacycle. The nature of the substituents around the Si–Si bond dramatically affects the outcome of the base-mediated reactions.

Of interest is the change of chemistry when the terminal chloro group is replaced by a methoxy group. Treatment of FpSiMe$_2$-SiMe$_2$OMe[10] with LDA at low temperature in an attempt to synthesize the corresponding disilametallacyclobutane, resulted in the isolation of no materials; however, repeating the reaction and quenching with Ph$_3$SnCl resulted in clean migration of methoxydisilyl group from iron to the cyclopentadienyl ring, **5**, Scheme 1(iv).[8] Given the utility of alkoxysilanes in Grignard substitution reactions at silicon this is an unexpected result.



i: X = Cl, R = R' = Me. **ii:** X = Cl, R = R' = *n*-Bu; R = Me, R' = *n*-Bu.

iii: X = Cl, R$_2$ = R'$_2$ = Me(*n*-Bu). **iv:** X = OMe; R$_2$ = R'$_2$ = Me$_2$

Scheme 1

Polymer **2** is soluble in hot THF. Cross-polarization solid state ^{29}Si NMR of the polymer **2** exhibits two narrow resonances at 22.0 ppm (Fe–**Si**) and at −8.2 ppm (C$_5$H$_4$–**Si**) indicating the regular alternating arrangement of the building blocks in the polymer backbone and the structure is essentially retained in the solution as indicated by the solution NMR spectroscopy. Wide angle laser light scattering analysis of **2** revealed molecular weight M_w = 6400, M_n = 3200 with polydispersity of 2.0. Thin films can be cast from the THF solution of the polymer. The morphology of the polymer was investigated by WAXS; the scattering pattern indicated distinct peaks at 13.3° and 14.2° which confirms that the polymer was partially crystalline. Thermogravimetric analysis (TGA) of the polymer under N$_2$ atmosphere showed that the polymer underwent two successive weight losses, 6% between 50–75 °C and 16% weight loss between 200–300 °C, and about 50% residue remained at 500 °C.

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† Electronic supplementary information (ESI) available: experimental section. See http://www.rsc.org/suppdata/cc/b4/b410822a/

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Further studies on the properties of polymer **2** and synthesis and reactivity of related group 14 metallacycles and polymers are underway.

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