Journal of Organometallic Chemistry, 370 (1989) C1–C4
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 9860PC

Preliminary communication

The stereochemistry at silicon of an iron to cyclopentadienyl ligand silyl group migration in $(\eta^5\text{-}C_5H_5)Fe(CO)_2SiR_3$

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(Received November 14th, 1988)

Abstract

The silyl group migration observed upon treating (R)-(+)-$(\eta^5\text{-}C_5H_5)Fe(CO)_2$-SiMePh(1-Np) with n-BuLi occurs with retention of configuration at silicon. The anion resulting from the migration, $(\eta^5\text{-}C_5H_4SiMePh(1\text{-}Np))Fe(CO)_2Li$, is alkylated with MeI to give (R)-(−)-$(\eta^5\text{-}C_5H_4SiMePh(1\text{-}Np))Fe(CO)_2Me$ (II). Compound II is independently prepared from $(\eta^5\text{-}C_5H_5)Fe(CO)_2Me$. A concerted mechanism for the migration involving frontside nucleophilic attack at silicon is suggested.

A number of reports of deprotonation of the cyclopentadienyl ligand in monocyclopentadienyl transition metal complexes with various σ-bonded ligands have recently appeared. Of particular interest are those reactions in which, subsequent to the deprotonation, the σ-bonded ligand migrates to the cyclopentadienyl ring producing a metal-centered anion. Ligands shown to undergo such an anionic rearrangement include silyl [1–4], polysilyl [5], germyl [6], acyl [7–9], and hydride [10].

Some of the mechanistic details of these rearrangements have been elucidated. First, the migration of the silyl group when $(\eta^5\text{-}C_5H_5)Fe(CO)_2SiMe_2R$ is treated with n-BuLi [2] and the migration of the acyl group when $(\eta^5\text{-}C_5H_5)Re(NO)$-$(PPh_3)(COR)$ is treated with lithium diisopropylamide (LDA) [9] are both intramolecular reactions. Second, the stereochemistry at the metal of acyl group migrations in iron and rhenium complexes has been investigated. Migration with retention at iron [8] and migrations with either retention or inversion at rhenium [7,9] occur. In addition, the migration of the alkoxycarbonyl group in $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)$-$(CO_2R)$ results in scrambling of stereochemistry at iron [8].

0022-328X/89/$03.50

This report concerns the stereochemistry at silicon of the migration of the silyl group in (η^5-C_5H_5)Fe(CO)$_2$SiR$_3$. The compound (*S*)-(−)-(η^5-C_5H_5)Fe(CO)$_2$SiMePh(1-Np) (1-Np = 1-naphthyl) has been synthesized and used to study the stereochemistry at silicon of various reactions which cleave the Fe–Si bond [11]. Thus, this system seemed to be an ideal one for investigating the stereochemistry of the migration.

Treatment of (*S*)-(−)-MePh(1-Np)SiCl ($[\alpha]_D$ −5.46°; 87% ee) with (η^5-C_5H_5)Fe(CO)$_2$Na gave (*R*)-(+)-(η^5-C_5H_5)Fe(CO)$_2$SiMePh(1-Np) (I) with $[\alpha]_D$ +29.35° (*c* 0.22; cyclohexane). This reaction has previously been assumed to occur with inversion of configuration at silicon on the basis of the known stereochemistry of nucleophilic displacements on chlorosilanes [11,12]. Addition of n-BuLi to a solution of I in THF at −78 °C followed by warming the mixture to 0 °C produced (η^5-C_5H_4SiMePh(1-Np))Fe(CO)$_2$Li which was characterized by IR spectroscopy. The spectrum in the CO stretching region (ν(CO) 1882. 1868, 1814, 1753 cm^{-1}) is virtually identical to that of (η^5-C_5H_5)Fe(CO)$_2$Li [14] and several of its ring-silylated derivatives [2]. Treatment of the anion with MeI gave (−)-(η^5-C_5H_4SiMePh(1-Np))Fe(CO)$_2$Me (II) in good yield with $[\alpha]_D$ −29.05° (*c* 0.16; cyclohexane) [15*].

In order to ascertain whether the migration occurs with retention or inversion at silicon it was necessary to prepare II using a reaction of known stereochemistry. It has previously been shown that the cyclopentadienyl ligand in complexes of the type (η^5-C_5H_5)Fe(CO)$_2$R, where R is a simple alkyl group, can be metalated with alkyllithium reagents or LDA. The alkyl group does not migrate in these reactions, and several ring-silylated compounds have been synthesized by reaction between ring-metalated intermediates and chlorosilanes [2,16]. Accordingly, the complex (η^5-C_5H_5)Fe(CO)$_2$Me was treated with LDA at −30 °C followed by (*S*)-(−)-MePh(1-Np)SiCl ($[\alpha]_D$ −5.62°; 89% ee). Compound II isolated from this reaction had $[\alpha]_D$ −20.83° (*c* 0.17; cyclohexane). Since it is well-established that simple alkyl- and aryl-lithium reagents react with chlorosilanes with predominant inversion of configuration [11,13] this reaction can be assumed to give II having (*R*) configuration at silicon. Compound II prepared by migration has the same sign of rotation so it is also (*R*)-(−)-(η^5-C_5H_4SiMePh(1-Np))Fe(CO)$_2$Me. Therefore, (*R*)-(+)-I was converted to (*R*)-(−)-II by an intramolecular migration of the silyl group with retention of configuration at silicon. These stereochemical results are outlined in Scheme 1.

It is interesting to note that II prepared by migration is of higher ee than II prepared by ring-metalation of (η^5-C_5H_5)Fe(CO)$_2$Me even though the chlorosilane used as a starting material in the latter reaction was of higher ee. This result implies that migration of the silyl group occurs with a high degree of stereospecifity. It was previously pointed out, based on the intramolecular nature of the reaction, that the silyl migration is an organometallic analogue of a Brook-type rearrangement [2]. The results presented here provide additional support for this kind of mechanism because retention of configuration at the silicon atom has also been determined to be the stereochemical outcome of the Brook rearrangement [17].

A species pentacoordinate at silicon, as shown below, was proposed for the migration based on the determination that the reaction is intramolecular [2]. A

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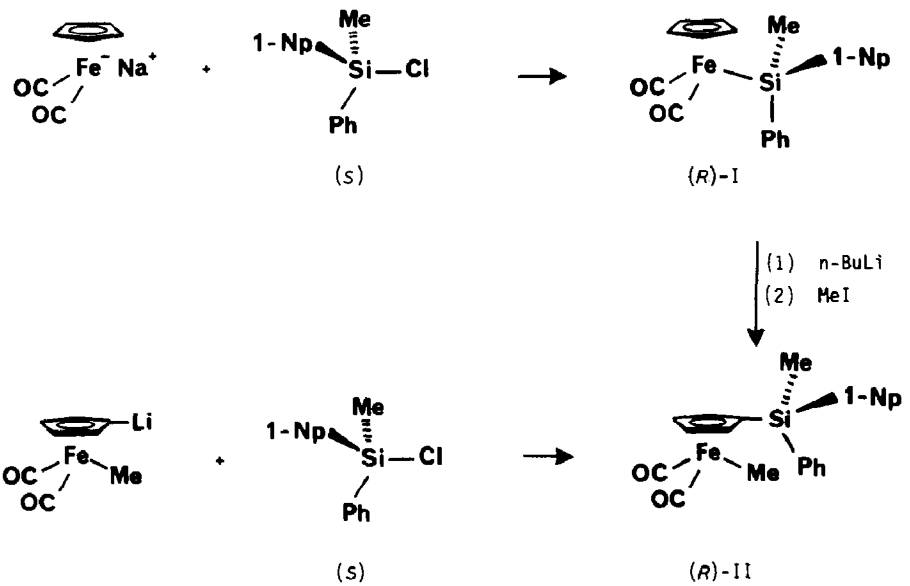
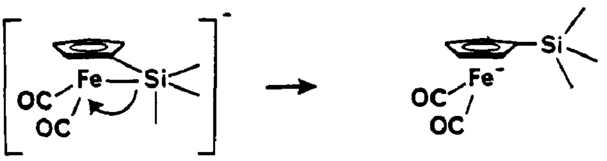
* Reference numbers with asterisks indicate notes in the list of references.



Scheme 1.

concerted frontside attack at an empty silicon *d*-orbital by the metalated cyclopentadienyl ligand would result in such a species and is consistent with the observed retention of configuration at silicon.



The number of recent reports of intramolecular, anionic rearrangements involving migrations of σ-bonded ligands from a metal to a deprotonated cyclopentadienyl ligand indicates the generality of this type of reaction. This study is the first to determine the stereochemical outcome at the migrating atom.

Experimental

Preparation of compound II by migration. A solution of 0.424 g (1 mmole) of I in 10 ml of THF at −78 °C was treated with 0.5 ml (1.25 mmoles) of a 2.5 M solution of n-BuLi in hexane. The mixture was allowed to warm to 0° over approximately 1.5 h, at which time an IR spectrum showed complete conversion to (η^5-C_5H_4SiMePh(1-Np))Fe$(CO)_2$Li. Methyl iodide (0.3 ml, 4.8 mmoles) was added, and the mixture was stirred at 0° for 1 h. Solvent was removed under reduced pressure, and the residue was extracted with a mixture of 90% hexane: 10% ether. The extract was filtered through filter-aid, and the filtrate was concentrated until slightly cloudy. After storage overnight in a freezer 0.36 g (82%) of (II) was collected as pale yellow crystals.

Preparation of compound II from (η^5-C_5H_5)Fe$(CO)_2$Me. A solution of 0.58 g (3 mmol) of (η^5-C_5H_5)Fe$(CO)_2$Me in 20 ml of THF at −30 °C was added by cannula to a −30 °C solution of 3.3 mmol of LDA in 10 ml of THF. After this mixture was stirred for 2 h at −30 °C, a solution of 0.85 g (3 mmol) of (*S*)-(−)-MePh(1-Np)SiCl in 3 ml of THF was added. The reaction mixture was stirred for 2 h while coming to ambient temperature, and the solvent was removed under reduced pressure. The residue was treated as described above to give 0.74 g (56%) of **II**.

Acknowledgement. This work was carried out during a sabbatical leave which S.R.B. spent in the laboratories of Professor Robert J.P. Corriu. The helpful advice and warm hospitality of Professor Christian Guérin and Dr. Bernard Henner are gratefully acknowledged.

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15 II: m.p. 114–116 °C; ^{1}H NMR (C_6D_6): δ 8.29 (d, J 8 Hz, 1H, Ar–H), 7.87 (m, 5H, Ar–H), 7.41 (m, 6H, Ar–H), 4.60 (m, 2H, Cp–H), 4.37 (m, 2H, Cp–H), 0.93 (s, 3H, Si–Me), 0.20 (s, 3H, Fe–Me); IR (hexane): 2007, 1956 cm^{-1}; MS m/e 410 ($M^+ - CO$), 382 ($M^+ - 2CO$), 367 ($M^+ - 2CO - Me$), 247 (100%, [SiMePh(1-Np)]$^+$); Anal. Found: C, 68.39; H, 5.04. $C_{25}H_{22}FeO_2Si$: C, 68.50; H, 5.06%.
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