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Preliminary communication

COORDINATION CHEMISTRY OF SILOLES: A NEW ASPECT OF THE STEREOCHEMICAL BEHAVIOUR OF (η^4-*exo*- AND -*endo*-1-CHLORO-2,5-DIPHENYLSILACYCLOPENTADIENE)TRICARBONYLIRON COMPLEXES

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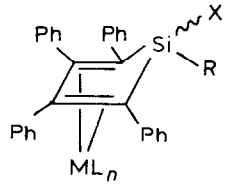
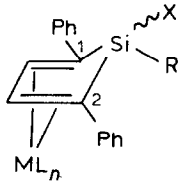
Summary

It has been shown that (η^4-1-chloro-2,5-diphenylsilacyclopentadiene)tricarbonyliron complexes undergo nucleophilic displacements at silicon with complete retention of configuration at both *exo* and *endo* positions. The substitution is faster at the *exo* than at the *endo* position. The observations are discussed in terms of electronic factors.

(η^4-2,3,4,5-Tetraphenyl-) and (η^4-2,5-diphenyl-)silacyclopentadiene)-transition metal complexes, **1** and **2** respectively, are good stereomodels for nucleophilic displacements at silicon [1]. The position of the groups attached at silicon, i.e., *endo*



(1)



(2)

(X = leaving group)

or *exo* with respect to ML_n, can be unequivocally assigned by ^1H NMR spectroscopy [2] and, thus, the stereochemistry of the reactions can be easily studied. Moreover, these compounds are interesting from a mechanistic point of view since the stereochemistry of nucleophilic displacements at silicon can be controlled by two very different factors, viz.

(i) The difference in the steric hindrance at the *endo* and *exo* positions at silicon, which favours attack of the nucleophile on the side away from the metal, i.e., giving retention for the *exo* and inversion for the *endo* isomer.

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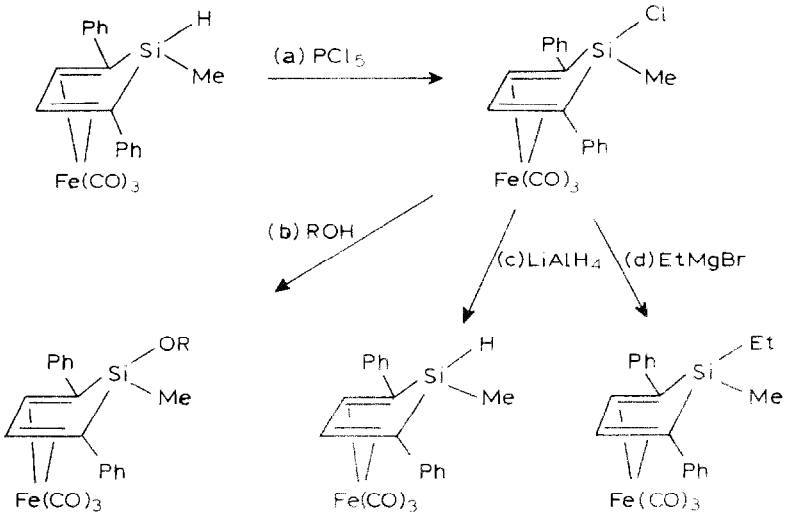


SCHEME 1. Synthesis and stereochemical behavior of (η^4-*exo*-1-chloro-2,5-diphenylsilacyclopentadiene)tricarbonyliron. Stereochemical assignments were made by ^{1}H NMR spectroscopy [2]. a, PCl_5, Et_2O, −20°C, 1 h (90%); b, ROH, r.t., 1 h, ROH = MeOH (90%), ROH = H_2O (90%); c, $LiAlH_4$, Et_2O, 0.5 h (80%); d, EtMgBr, Et_2O, r.t., 3 h (70%).

(ii) The angular strain (C(1)–Si–C(2) 90° [3]) at silicon, which implies a change of hybridization [4]; on the arguments of Minot and Anh [4], this change should favor retention at silicon for both *exo* and *endo* isomers.

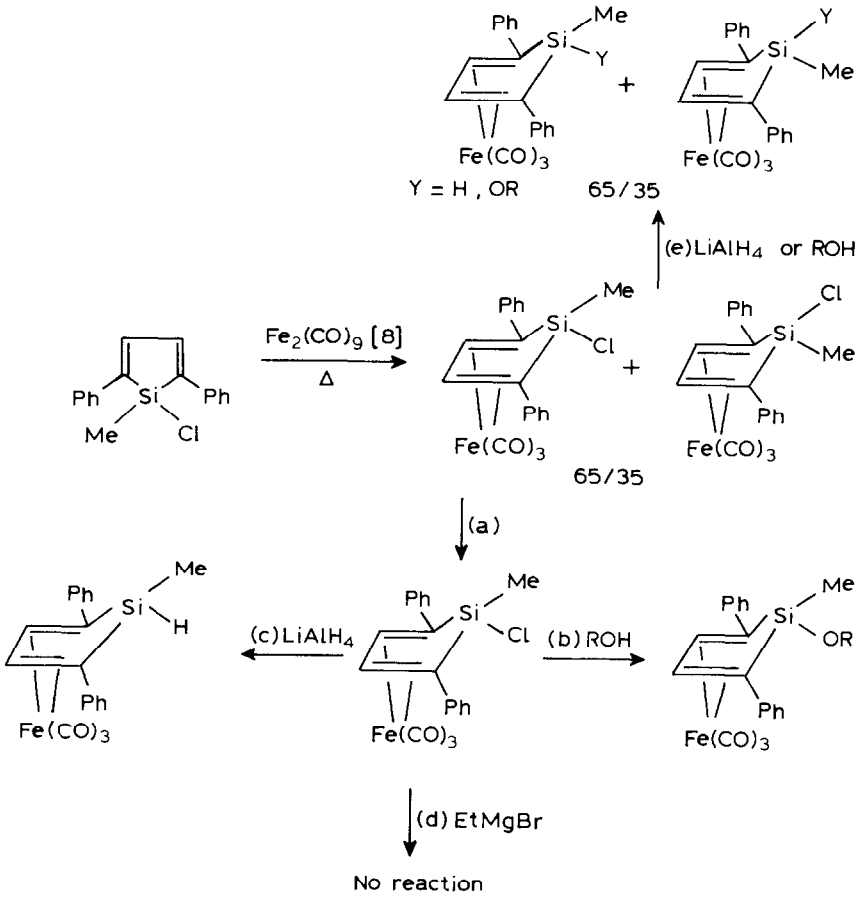
Sakurai et al. [5] and Jutzi et al. [6] have previously noted the lability of the *exo* substituent and its selective replacement with retention of configuration (*exo* from *exo*). However, the experiments were restricted to a few *exo* isomers of (η^4-2,3,4,5-tetraphenylsilacyclopentadiene)-transition metal complexes; and to our knowledge, no results have previously been reported for the *endo* isomers. We thus decided to compare the reactions at silicon for the *exo*- and *endo*-chloro(η^4-2,5-diphenylsilacyclopentadiene)tricarbonyliron complexes and results are summarized in Schemes 1 and 2.

The features of the results are as follows:

(i) The (η^4-*exo*-1-chloro-2,5-diphenylsilacyclopentadiene)tricarbonyliron shows similar behavior to that of the (η^4-2,3,4,5-tetraphenylsilole) analogue. Reactions occurred with complete retention of configuration whatever the nucleophile (Scheme 1), whereas the same reactions carried out with optically active acyclic chlorosilanes proceed selectively with inversion [9]. A similar situation, i.e., retention of configuration, was previously observed for the highly strained silacyclobutanes [9].

(ii) Much more interesting is the stereochemistry observed for the *endo*-chloro isomer. All the reactions also took place selectively with retention (*endo* from *endo*) (Scheme 2), instead of inversion as would be expected on the basis of steric considerations invoked by earlier workers [5].

(iii) When a 65/35 mixture of *endo*- and *exo*-chloro isomers was used in the reaction with H_2O, MeOH or $LiAlH_4$, the products in each case showed the same isomeric ratio after complete reaction. This clearly rules out any isomerisation, and so thermodynamic control of the sterochemistry in these reactions.



SCHEME 2. Synthesis and stereochemical behavior of (η^4-*endo*-1-chloro-2,5-diphenylsilacyclopentadiene)tricarbonyliron. Stereochemical assignments were made by ^{1}H NMR spectroscopy [2]. a, fractional recrystallisation (40%); b, ROH, r.t., 3 h, ROH = MeOH (90%), ROH = H_2O (90%); c, $LiAlH_4$, Et_2O, 1 h (80%); d, EtMgBr, Et_2O, r.t., 30 h; e, ROH[b], AlH_4Li[c].

(iv) The *exo*-chloro compound is, 30–50 times more reactive than its isomer in the methanolysis reaction at −20°C. The reactivity difference is very large in the reaction with EtMgBr, in which the *exo*-chloro group was cleanly displaced whereas no reaction was detected with the *endo*-chloro derivative.

The behavior of the *exo*-chloro group would be consistent with operation of steric factors, since front-side attack on the side away from the bulky $Fe(CO)_3$ is favoured and this leads to retention. However, the *endo*-chloro group, with the same effect would lead to inversion, contrary to observation.

In contrast, the results are clearly consistent with control of the stereochemistry by electronic factors. As pointed out above, angle strain at silicon (C(1)–Si–C(2) ≃ 90° [3]) implies a change of the hybridization of the Si–X bond (X = leaving group) when the C(1)–Si–C(2) angle becomes smaller than the tetrahedral value [4]; the σ^*(Si–X) MO has a large amount of *s* character at silicon. Front-side attack is thus favoured, and retention is the expected stereochemical outcome for either an *exo* or

endo leaving group. Steric factors account for the enhanced reactivity of the *exo*-Si–X bond, but do not control the sterochemical outcome at silicon.

Stereochemical and kinetic studies are in progress involving change in the nature of the leaving group (H, OR) and the metal.

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