Synthesis of Optically Active Silicon–Iron Compounds. Stereochemistry of Silicon–Iron Bond Breaking

By Geneviève Cerveau, Ernesto Colomer, Robert Corriu*, and William E. Douglas

(*Laboratoire de Chimie des Organométalliques, Laboratoire associé au C.N.R.S., N° 82, Université des Sciences et Techniques du Languedoc,* 34060 *Montpellier Cédex, France*)

Summary U.v. irradiation of the optically active compound (+)-[(π-Cp)Fe(CO)$_2$SiMePh(1-Np)] (I) in the presence of PPh$_3$ gives the diastereoisomers (—)- and (+)-[(π-Cp)Fe(CO)(PPh$_3$)SiMePh(1-Np)] (II); cleavage by chlorine of the Si–Fe bond occurs with predominant retention at silicon in the case of (I) and (II), and with predominant inversion for the diastereoisomers (II) in the presence of PPh$_3$.

Compounds containing an optically active silicon atom bound to a transition metal are not very common. Sommer *et al.*[1] have obtained a compound with an Si–Co bond, Eaborn *et al.*[2] compounds with Si–Pt and Ge–Pt bonds, and recently we reported[3] the preparation of the optically active (—)-[(π-Cp)Fe(CO)$_2$SiMePh(1-Np)] (I).

The two enantiomeric complexes (I) ($[\alpha]_D^{95}$ — 25·5° or + 26°) were formed from the chlorosilanes ($[\alpha]_D^{25}$ + 6·3° or — 6·4° respectively) with an average stereoselectivity of 80%. Successive crystallisations of (—)-(I) ($[\alpha]_D^{25}$ — 25·5°) led to the 98% optically pure complex $[\alpha]_D^{25}$ — 41·5° (*c* 0·49 in cyclohexane), m.p. 117 °C.[4] Since acyclic chlorosilanes react with organometallic reagents with inversion,[5] it is probable that the reaction occurs with inversion at silicon. We have carried out further work with samples of the (+)-enantiomer (I) of different optical purities (O.P.).

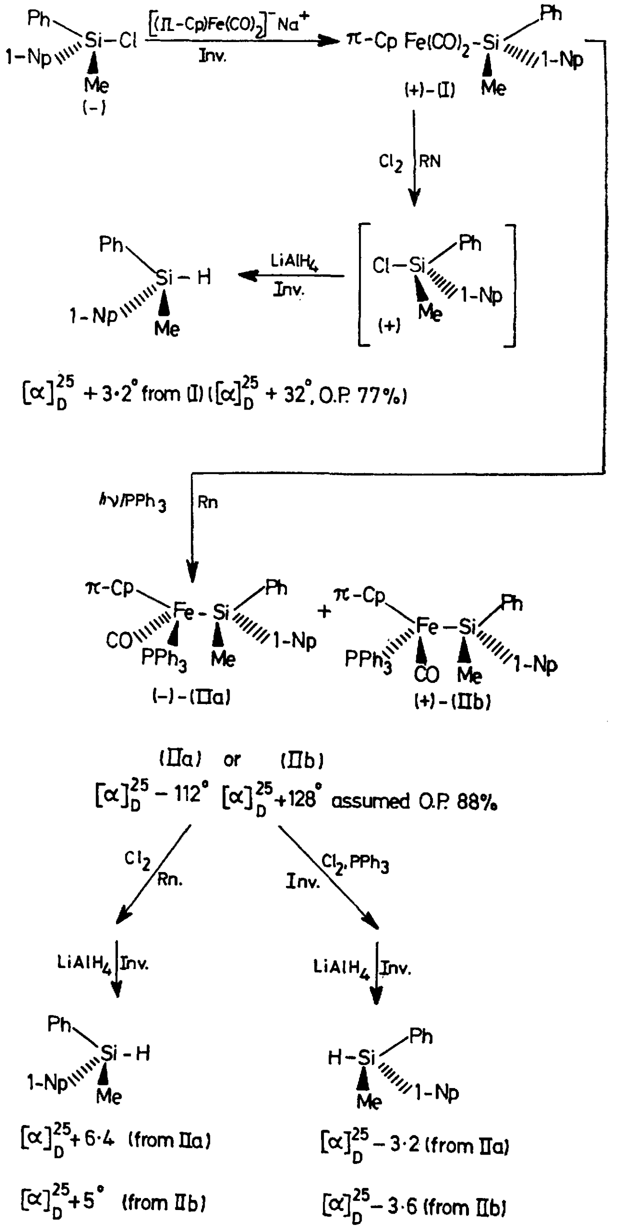
Table[a]

Compound	Reagent	Yield of silane/%[d]	Stereo-selectivity/%[e]
(I)	Cl$_2$	72	56 Rn.
(I)	Cl$_2$+PPh$_3$[b]	No reaction	
(IIa)	Cl$_2$	90	63 Rn.
(IIa)	Cl$_2$+PPh$_3$[c]	73	Racemisation
(IIa)	Cl$_2$+PPh$_3$[b]	67	57 Inv.
(IIb)	Cl$_2$	90	61 Rn.
(IIb)	Cl$_2$+PPh$_3$[b]	77	58 Inv.

[a] Reactions were carried out in CCl$_4$ with 1 mol of Cl$_2$ per mol of organometallic compound. [b] 2·5 mol or [c] 0·3 mol of PPh$_3$ added per mol of organometallic compound. [d] From LiAlH$_4$ reduction of the chlorosilane. Rotations were measured on the crude silane after chromatography. As a first approximation, stereoselectivities of the cleavages of (IIa) and (IIb) are based on the O.P. of compound (I) used in their preparation. [e] Calculated from $[\alpha]_D$ of the recovered silane. The $[\alpha]_D^{25}$ of MePh(1-Np)SiH pure is +36°. (L. H. Sommer, 'Stereochemistry, Mechanism, and Silicon,' McGraw-Hill, New York, 1965).

U.v. irradiation of a dilute solution of (I) ($[\alpha]_D^{25}$ + 36·5°, O.P. 88%) in n-hexane in the presence of PPh$_3$ gave the diastereoisomers (IIa) and (IIb) in high yield, with an asymmetric synthesis of *ca.* 10%. The amount of each diastereoisomer was determined by comparing the intensities of the two (π-C$_5$H$_5$) ^{1}H n.m.r. resonances for the crude product before separation by successive crystallisations.

The diastereoisomer (IIa), $[\alpha]_D^{25}$ — 139° (*c* 0·22 in cyclohexane) was obtained chemically pure by recrystallisation but (IIb), $[\alpha]_D^{25}$ + 162·7° (*c* 0·44 in cyclohexane) contained 8% of (IIa) because of its high solubility in hexane. We have studied the cleavage reactions of (IIa) (91% pure, $[\alpha]_D^{25}$ — 112°) and (IIb) (83% pure, $[\alpha]_D^{25}$ + 128°); the assumed O.P at silicon is 88% since the substitution of CO by PPh$_3$ affects only the iron centre. Cleavage by chlorine of the Si–Fe bond in (I), (IIa), and (IIb) occurs with retention at silicon (see Scheme). (Reduction of chlorosilanes[6] is known to take place stereospecifically with



Scheme. Rn = retention; Inv. = inversion. π-Cp = π-cyclopentadienyl; 1-Np = α-naphthyl.

inversion at silicon). Racemisation of the chlorosilane under similar conditions was not observed. [(π-Cp)Fe-$(CO)_2Cl$][7] was isolated from the cleavage of (I). From (IIa) and (IIb), a green solid, presumably [(π-Cp)Fe(CO)-$(PPh_3)Cl$] was obtained. This compound is known to decompose on attempted purification.[8]

In the presence of an excess of PPh_3, compound (I) is not cleaved by chlorine, but under the same conditions (IIa) and (IIb) are slowly cleaved with predominant inversion at silicon instead of the retention observed in the reaction without PPh_3. There is some further racemisation of the chlorosilane in CCl_4 in the presence of Cl_2 and PPh_3. The results of the various cleavages are reported in the Table.

The stereochemistry of the cleavage depends on the reagents; thus (IIa) and (IIb) are cleaved with retention by Cl_2 and with inversion by the almost completely ionic compound obtained in the reaction of Cl_2 with PPh_3.[9] However the change in the steric course is also related to the nature of the Fe–Si bond; thus (I), having two π-acceptor ligands on iron, is not cleaved by Cl_2–PPh_3 while (IIa) and (IIb), with only one, undergo cleavage with a change of stereochemistry. Racemisation, starting with (IIa), with small amounts of PPh_3 takes place *via* two competitive reactions.

We thank Dr. J. Jacques and Madame Leclerc for determining the optical purities of mixtures of (I).

(*Received, 7th March* 1974; *Com.* 265.)

---

[1] L. H. Sommer, J. E. Lyons, and H. Fujimoto, *J. Amer. Chem. Soc.*, 1969, **91**, 7051.

[2] C. Eaborn, P. N. Kapoor, D. J. Tune, C. L. Turpin, and D. R. M. Walton, *J. Organometallic Chem.*, 1972, **34**, 153; C. Eaborn, D. J. Tune, and D. R. M. Walton, *J.C.S. Chem. Comm.*, 1972, 1223.

[3] R. J. P. Corriu and W. E. Douglas, *J. Organometallic Chem.*, 1973, **51**, C3.

[4] C. Fouquey and J. Jacques, *Tetrahedron*, 1967, **23**, 4009.

[5] R. Corriu and G. Royo, *Tetrahedron*, 1971, **27**, 4289.

[6] L. H. Sommer, C. L. Frye, G. A. Parker, and K. W. Michael, *J. Amer. Chem. Soc.*, 1964, **86**, 3271.

[7] T. S. Piper, F. A. Cotton, and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1955, **1**, 165.

[8] P. M. Treichel, R. L. Shubkin, K. W. Barnett, and D. Reichard, *Inorg. Chem.*, 1966, **5**, 1177.

[9] K. Issleib and W. Seidel, *Z. anorg. Chem.* 1956, **288**, 201 and references therein.