Journal of Organometallic Chemistry, 73 (1974) 85—92

THE CHEMISTRY OF THE TRANSITION METAL—CARBON σ-BOND. INSERTION REACTIONS BETWEEN STANNOUS CHLORIDE AND h^1-ALLYL AND h^1-PROPARGYL COMPLEXES OF h^5-CYCLOPENTADIENYLDICARBONYLIRON

CHARLES V. MAGATTI and WARREN P. GIERING

Department of Chemistry, Boston University, Boston, Massachusetts 02215 (U.S.A.)

(Received December 6th, 1973)

Summary

The reactions between h^5-CpFe(CO)$_2$R (R = CH$_2$CH=CH$_2$; CH$_2$CMe=CH$_2$; CH$_2$CH=CHMe; CH$_2$CH=CMe$_2$) and stannous chloride in tetrahydrofuran afford the insertion products h^5-CpFe(CO)$_2$SnCl$_2$R. When treated with stannous chloride in methanol or with excess stannous chloride in tetrahydrofuran, h^5-CpFe(CO)$_2$CH$_2$CMe=CH$_2$ affords primarily h^5-CpFe(CO)$_2$SnCl$_3$. The allenyl, 2-butynyl or cationic isobutylene complexes (R = CH=C=CH$_2$; CH$_2$C≡CMe; CH$_2$CMe$_2^+$) yield only h^5-CpFe(CO)$_2$SnCl$_3$. Stannous iodide reacts with h^5-CpFe(CO)$_2$CH$_2$CH=CH$_2$ in benzene to form h^5-CpFe(CO)$_2$I. Plumbous chloride in methanol fails to react with the above complexes.

Introduction

The complexes h^5-CpFe(CO)$_2$R (R = alkyl, h^1-allyl, h^1-propargyl, allenyl, cyclopropyl and cyclopropylmethyl) are known to enter into insertion and cycloaddition reactions with a number of inorganic and organic electrophiles notably sulfur dioxide and trioxide, organic isocyanates, electrophilic olefins and germanium dihalides. Continuing our investigations into the reactivity of the transition metal—carbon σ-bond we turned our attention toward stannous chloride* which is known to insert into transition metal—metal [2], and —halogen [3] bonds. Reported herein are the results of our investigation of the reactions between stannous chloride and the allyl and related complexes of the type h^5-CpFe(CO)$_2$R.

---

*Stannous chloride has been reported to cleave the W—CH$_3$ bond of h^5-CpW(CO)$_3$CH$_3$ [3] and more recently, to insert into the Fe—CH$_3$ bond of h^5-CpFe(CO)$_2$CH$_3$ [1n].

Experimental

General procedures

In general all reactions were carried out under a nitrogen atmosphere. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York.

Physical measurements

Infrared spectra were recorded on a Perkin—Elmer Model 180 Spectrophoto meter. PMR spectra were obtained on a Jeol C-60 High Resolution Spectrometer using tetramethylsilane as an internal standard. Melting points are uncorrected.

Materials

Anhydrous stannous chloride and iodide were used as purchased from Alfa—Ventron. Iron pentacarbonyl was purchased from General Aniline and Film. The benzene sulfonate of 2-butynol (Farchan Research Laboratories) was prepared according to standard procedures. Tetrahydrofuran was routinely vacuum distilled from lithium aluminum hydride and used immediately. Nitromethane-d_3 and dimethyl sulfoxide-d_6 were used as purchased from Aldrich Chemical Company and Stohler Isotopes, Inc.

Preparation of h^5-$CpFe(CO)_2R$

The following general procedure was used for the preparation of these complexes. An appropriate organic chloride or benzene sulfonate was added to a freshly prepared tetrahydrofuran solution of a 10% molar excess of Na-h^5-CpFe-$(CO)_2$. Each of the reaction mixtures was stirred for 1 h at room temperature. After the addition of an equal volume of petroleum ether, the reaction mixture was filtered through a bed of celite. Removal of the solvent from the filtrate on a rotary evaporator afforded a deep red oil which was again taken up in petroleum ether and filtered. Removal of the solvent afforded a deep orange oil. Due to its instability toward high vacuum (10^{-6} mm) distillation, the 1,1-dimethylpropenyl complex 1d was used as obtained at this point. The remainder of the complexes were further purified by short path high vacuum distillation. The identity and purity of these complexes were determined by NMR spectroscopy.

Reaction between h^5-$CpFe(CO)_2CH_2CH{=}CH_2$ and stannous chloride

Anhydrous stannous chloride, 2.32 g (12 mmol), and 40 ml of tetrahydrofuran were added to a 100 ml 3-necked round-bottom flask equipped with a magnetic stirrer. The solution was gently heated until the stannous chloride dissolved. After cooling, h^5-$CpFe(CO)_2CH_2CH{=}CH_2$, 1.20 g (5.5 mmol), was added via a syringe to the flask. The reaction was followed by NMR spectroscopy and reached completion in approximately 3 h as evidenced by the appearance of a single new C_5H_5 resonance at approximately τ 4.72. After removal of the tetrahydrofuran on a rotary evaporator, the residue was taken up in methylene chloride, filtered and the solvent again removed to yield a deep orange solid. The crude product was purified by crystallization from hot cyclohexane and finally sublimed under high vacuum to yield 1.5 g (54.5%) h^5-$CpFe(CO)_2SnCl_2$-$CH_2CH{=}CH_2$, IIa: m.p. 63—65°; IR (KBr) 2025, 1955 cm^{-1} ($C{\equiv}O$); NMR

(CD_3NO_2) τ 3.88 (m, 1, CH); 4.72 (s, 5, C_5H_5); 4.91 (m, 2, CH_2); 7.18 (d, 2, J 9 Hz, CH_2). (Found: C, 29.15; H, 2.59. Calcd. C, 29.80; H, 2.40%.)

Reaction between excess h^5-$CpFe(CO)_2CH_2CMe{=}CH_2$ and stannous chloride

h^5-$CpFe(CO)_2CH_2CMe{=}CH_2$, 5.16 g (24 mmol) was added to a solution of stannous chloride, 2.32 g (12 mmol) in 50 ml of tetrahydrofuran prepared as previously described. After stirring for 24 h at room temperature the NMR spectrum of the final reaction mixture showed the presence of the insertion product and a small amount of h^5-$CpFe(CO)_2SnCl_3$ (10%). After removal of the tetrahydrofuran, the residue was washed several times with petroleum ether and the insoluble residue sublimed to yield 3.34 g (66%) h^5-$CpFe(CO)_2SnCl_2CH_2CMe{=}CH_2$, IIb: m.p. 66—68°, IR (KBr) 2025, 1962 cm^{-1} (C≡O), NMR (DMSO-d_6) τ 4.72 (s, 5, C_5H_5), 5.22 (m, 2 CH_2), 7.16 (s, 2, CH_2), 8.19 (s, 3, CH_3). (Found C, 31.00; H, 3.02. Calcd. C, 31.38; H, 2.86%.)

Reaction between h^5-$CpFe(CO)_2CH_2CMe{=}CH_2$ and excess stannous chloride

h^5-$CpFe(CO)_2CH_2CMe{=}CH_2$, 1.08 g (5 mmol), was added to a solution of stannous chloride 2.32 g (12 mmol) in 50 ml of tetrahydrofuran. After 24 h at room temperature the NMR spectrum of the final reaction mixture showed that 80% of parent complex was transformed into h^5-$CpFe(CO)_2SnCl_3$ while the remainder was present as h^5-$CpFe(CO)_2SnCl_2CH_2CMe{=}CH_2$. After removal of the solvent, the residue was recrystallized from hot cyclohexane to afford h^5-$CpFe(CO)_2SnCl_3$ 1.63 g (79%) as orange crystals: m.p. 163—166° (lit. [4] 167—168); IR (KBr) 2042, 2007 cm^{-1} (C≡O); NMR (CD_3NO_2) τ 4.64 (s, C_5H_5).

Reaction between h^5-$CpFe(CO)_2CH_2CH{=}CHMe$ and stannous chloride

A mixture of the *cis* and *trans* isomers of h^5-$CpFe(CO)_2CH_2CH{=}CHMe$, 1.16 g (5.5 mmol), was added to a solution of stannous chloride, 0.47 g (2.5 mmol) in 50 ml of tetrahydrofuran. After 24 h at room temperature the final NMR spectrum of the reaction mixture showed that the products were a 3/1 mixture of h^5-$CpFe(CO)_2SnCl_2CH_2CH{=}CHMe$, and h^5-$CpFe(CO)_2SnCl_3$. After removal of the solvent the gummy residue was placed in a Soxhlet extractor and extracted with cyclohexane. Removal of the solvent under high vacuum afforded h^5-$CpFe(CO)_2SnCl_2CH_2CH{=}CHMe$, IIc, 0.41 g (38%) as an orange oil: IR (neat) 2030, 1962 cm^{-1} (C≡O): NMR (CD_3NO_2) τ 4.31 (m, 2, CH=CH), 4.72 (s, 5, C_5H_5), 7.22 (m, 2, CH_2), 8.30 (m, 3, CH_3). (Found: C, 30.79, H, 2.73. Calcd.: C, 31.38; H, 2.86%.)

Reaction between h^5-$CpFe(CO)_2CH_2CH{=}CMe_2$ and stannous chloride

h^5-$CpFe(CO)_2CH_2CH{=}CMe_2$, 0.61 g (2.5 mmol), was added to a solution of stannous chloride, 1.04 g (5.5 mmol) in 50 ml of tetrahydrofuran. After 24 h the solvent was removed and the residue recrystallized from hot cyclohexane to afford h^5-$CpFe(CO)_2SnCl_2CH_2CH{=}CMe_2$, IId, 1.1 g (86%), as orange crystals: m.p. 86—89°, IR (KBr) 2030, 1962 cm^{-1} (C≡O): NMR ($CDCl_3$) τ 4.50 (m, 1, CH); 7.24 (d, 2, CH_2, J 9Hz, CH_3) (s, 5, C_5H_5), 8.30 (s, 6, Me). (Found: C, 32.82; H, 3.80. Calcd.: C, 32.92; H, 3.65%.)

Reaction between h^5-CpFe(CO)$_2$CH=C=CH$_2$ and stannous chloride

h^5-CpFe(CO)$_2$CH=C=CH$_2$, 1.19 g (5.5 mmol) was added to a solution of stannous chloride, 1.09 g (5.5 mmol) in 50 ml of tetrahydrofuran. After 24 h the NMR spectrum of the reaction mixture showed only the presence of h^5-CpFe(CO)$_2$SnCl$_3$. Removal of the solvent and recrystallization from hot cyclohexane afforded h^5-CpFe(CO)$_2$SnCl$_3$, 1.86 g (83%).

Reaction between h^5-CpFe(CO)$_2$CH$_2$C≡CCH$_3$ and stannous chloride

h^5-CpFe(CO)$_2$CH$_2$C≡CCH$_3$, 0.62 g (2.5 mmol), was added to a solution of stannous chloride 1.09 g (5.5 mmol) in 50 ml of tetrahydrofuran. After 24 h the NMR spectrum of the reaction mixture showed only the presence of h^5-CpFe(CO)$_2$SnCl$_3$. Removal of the solvent and recrystallization from hot cyclohexane afforded h^5-CpFe(CO)$_2$SnCl$_3$, 1.86 g (83%).

Reaction between h^5-CpFe(CO)$_2$ (CH$_2$=CMe$_2$)$^+$BF$_4^-$ and stannous chloride

A heterogeneous mixture of h^5-CpFe(CO)$_2$(CH$_2$=CMe$_2$)$^+$BF$_4^-$ [5], 1.50 g (5.0 mmol), and stannous chloride, 0.94 g (5.0 mmol), in 50 ml of tetrahydrofuran was refluxed for 24 h. After removal of the solvent the residue was recrystallized from hot cyclohexane to afford h^5-CpFe(CO)$_2$SnCl$_3$, 1.73 g (86%).

Results

Treatment of the h^1-allyl—iron complexes, h^5-CpFe(CO)$_2$R (FpR); (Ia—Id) with a tetrahydrofuran solution of anhydrous stannous chloride affords the insertion products, IIa—IId, as orange crystalline solids with the exception of IIc which remained as an orange oil even after repeated attempts to effect crystallization. All of the insertion products IIa—IId are oxidatively and thermally stable when pure; however, each is slowly oxidized in solution if not protected from atmosphere oxygen.

$$\underset{\text{(I)}}{\mathrm{FpCH_2CR^1{=}CR^2R^3}} \xrightarrow[\text{THF}]{\mathrm{SnCl_2}} \underset{\text{(II)}}{\mathrm{FpSnCl_2CH_2CR^1{=}CR^2R^3}}$$

a: $R^1 = R^2 = R^3 = H$
b: $R^1 = Me$, $R^2 = R^3 = H$
c: $R^1 = R^2 = H$, $R^3 = Me$
d: $R^1 = H$, $R^2 = R^3 = Me$

Fp = h^5-CpFe(CO)$_2$

Insertion of the SnCl$_2$ moiety into the Fe—C bond is clearly evidenced by the shift of the carbonyl stretching frequencies to higher frequencies in the product as compared to the parent h^1-allyl complexes. Analogously the presence of the relatively electronegative SnCl$_2$ moiety effects a downfield shift of the C$_5$H$_5$ resonance to ~ τ 4.7 as compared to ~ τ 5.3 in the h^1-allyl complexes. The NMR spectra of the insertion products also show that the original h^1-allyl ligands in Ic and Id do not undergo allylic rearrangement upon transformation to the insertion products IIc and IId. Thus, the NMR spectrum of both IIc and

IId exhibit 1-proton multiplets in the olefinic region between τ 4.0 and 4.6. In addition, the 2-proton methylene resonance (τ 7.22) and the 3-proton methyl resonance (τ 8.30) of IIc are comprised of pairs of doublets attributable to the *cis* and *trans* isomers of IIc. The NMR spectrum of IId also exhibits a 2-proton doublet methylene resonance (τ 7.24) and a pair of very closely spaced methyl resonances (~ τ 8.30) which appear as a broadened singlet.

The insertion product IIa is the exclusive product formed regardless of the relative stoichiometry of stannous chloride and Ia used whereas both IIc and IId are formed along with minor amounts of $FpSnCl_3$. The nature of the products formed in the reaction between Ib and stannous chloride is strongly dependent on the relative stoichiometry of reactants and the solvent. Thus when a two-fold excess of Ib is used a 66% yield of the insertion product IIb is obtained. However, when a two-fold excess of stannous chloride is used an 80% yield of $FpSnCl_3$ is obtained. Substitution of methanol for tetrahydrofuran results in the exclusive formation of $FpSnCl_3$ even though a two-fold excess of Ib is used. Similar results were obtained for Ib whether the reaction was run in the light or dark.

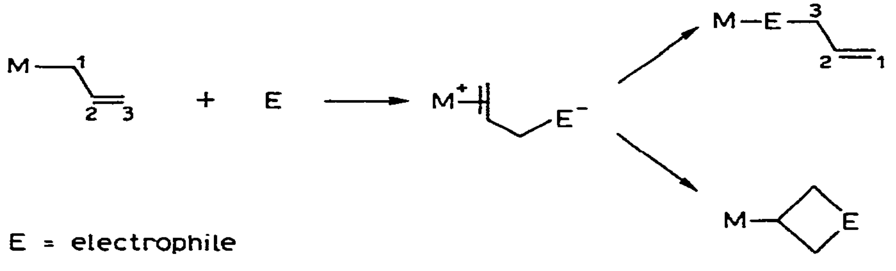
Treatment of the allynyl, III, 2-butynyl, IV, or cationic isobutylene, V, complexes with a tetrahydrofuran solution of stannous chloride affords only high yields of $FpSnCl_3$. The expected insertion products from III and IV were not observed at any time by NMR spectroscopy in the reaction mixture.

$$\left.\begin{array}{lcl} \mathrm{FpCH{=}C{=}CH_2} & + & \mathrm{SnCl_2} \\ \quad\mathrm{(III)} & & \\ \mathrm{FpCH_2\,C{\equiv}CMe} & + & \mathrm{SnCl_2} \\ \quad\mathrm{(IV)} & & \\ \mathrm{Fp(CH_2{=}CMe_2)^+} & + & \mathrm{SnCl_2} \\ \quad\mathrm{(V)} & & \end{array}\right] \rightarrow \quad \mathrm{FpSnCl_3}$$

Treatment of Ic with stannous iodide in benzene gave only FpI. Plumbous chloride in methanol did not react with any of the aforementioned complexes.

Discussion

The cycloaddition or insertion reactions (which proceed with migration of the metal) of the h^1-allyl, Ia, b, allenyl, III, and butynyl, IV, complexes are thought to occur by initial electrophilic attack at C(3) [1a] of the ligand to generate a zwitterionic complex [1d, h, e]. Subsequent addition of the anionic terminus to the coordinated double bond results in cycloaddition whereas displacement of the olefin results in insertion. The conversion of the zwitterionic



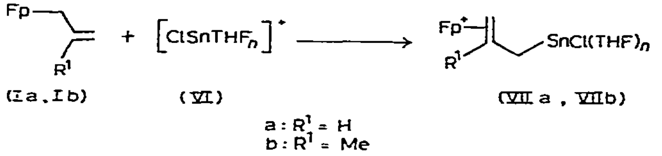
E = electrophile

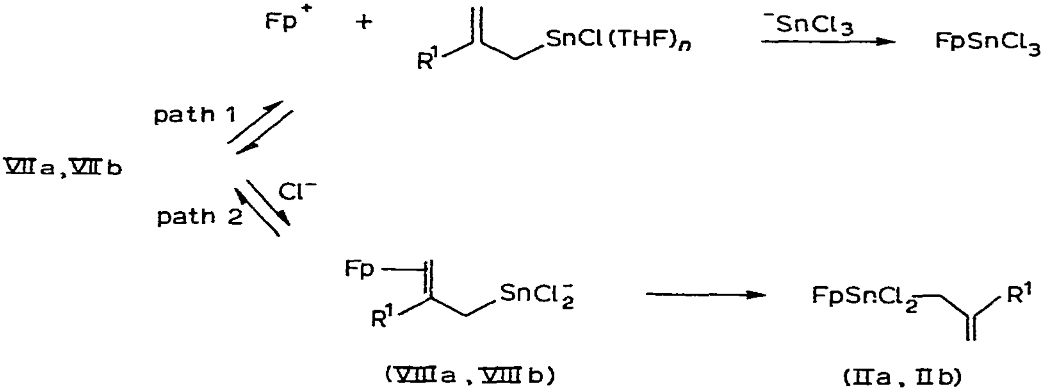
intermediate to the insertion product may occur by a concerted intramolecular rearrangement or by dissociation of the metal—olefin linkage followed by addition of the anionic terminus to the coordinatively unsaturated cationic metal. In either case, the anionic terminus, because of its proximity to the metal, will be the most effective nucleophilic species for attacking the cationic metal.

In contrast to the aforementioned complexes the more highly substituted ligands in Ic and Id are also susceptible to electrophilic attack at either C(1) or at the methyl hydrogens [1a, 6]. Thus the formation of IIc and IId, which possess unrearranged R groups, has precedent and may be attributed to steric inhibition of electrophilic attack at C(3).

A mechanistic rationalization of the reactions between Ia, Ib, III or IV and stannous chloride involving initial electrophilic addition at C(3) best accounts for the observed products, IIa, IIb and $FpSnCl_3$. However, the mechanism involving stannous chloride as the primary reacting electrophile does not satisfactorily explain the formation of $FpSnCl_3$; the dependence of the product ratio in the reaction between Ib and stannous chloride on the relative stoichiometry of the reactants and the solvent; the exclusive convertion of III and IV to $FpSnCl_3$; or the exclusive conversion of Ia to the insertion product IIa.

At the heart of the problem is the nature of the reactive electrophile in a tetrahydrofuran solution of stannous chloride. The nature of stannous chloride in organic solvents is not well studied. It has been proposed that stannous chloride exists as $ClSnL^+SnCl_3^-$ in heterocyclic amine solvents (L) [7]. We believe that a similar ionic species $ClSnTHF_n^+SnCl_3^-$ best accounts for the observed reactions in tetrahydrofuran or methanol. Thus addition of $ClSnTHF_n^+$, VI, to I generates a cationic olefin complex, VII, which, in contrast to the previously described zwitterions, possesses a non-nucleophilic neutral tin moiety. Decomposition of VII may occur by a reversible dissociation to the olefin and Fp^+ (path 1) followed by formation of $FpSnCl_3$ by addition of $SnCl_3^-$ to Fp^+. Alternatively, the formation of a zwitterionic complex VIII (path 2) may compete with dissociation of VII if the iron—olefin bond in VII is relatively non-labile. In a dissociative or concerted manner, VIII may be transformed into the insertion products II.

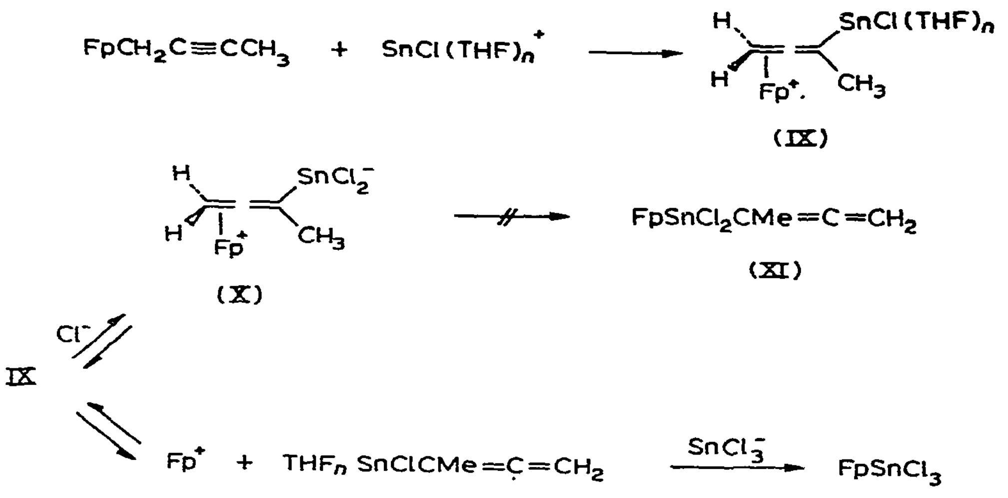




Path 1 will be most important when the ratio $SnCl_2$/complex is large and when the iron—olefin bond is labile. Thus the lability of the iron—olefin bond of the Fp(isobutylene)$^+$ and Fp(alkyne)$^+$ complexes [11, 5] partially accounts for the facile conversion of Ib and III to $FpSnCl_3$. Also in path 1, both the olefin and $SnCl_3^-$ are competing for Fp^+. Thus, as observed, an increase in the concentration of $SnCl_2$ (and thereby the concentration of $SnCl_3^-$) will shift the product toward $FpSnCl_3$.

When the iron—olefin bond is relatively non-labile path 2 will effectively compete with path 1. The allyl complex, Ia, will form a substituted propene complex, VIIa, which will be considerably less labile than the isobutylene or alkyne complexes formed by Ib or III [8]. Therefore the rate of conversion of these less labile olefin complexes to the zwitterionic complexes VIII may be considerably faster than the dissociation of VII. In support of this latter hypothesis, Ia, which should form the least labile cationic olefin complex, is exclusively converted to the insertion product IIa.

A comparison of the reactions between the butynyl complex IV or Ia and stannous chloride in tetrahydrofuran lends strong support to a concerted rearrangement of VIII to IIa. The addition of $(SnClTHF_n)^+$ to IV would generate the cationic allene complex IX in which the large iron and tin groups are held in a *trans*-periplanar orientation [11]. Like the Fp(propene)$^+$ complexes, Fp(allene)$^+$ complexes have been demonstrated to be remarkably nonlabile [9]. Therefore an equilibrium, analogous to that between VIIa and VIIIa, will be established between IX and X. The *trans*-periplanar orientation of the iron and tin group in X precludes a concerted conversion of X to the insertion product XI. The conversion of X to XI could be effected in a dissociative manner. However, the complete absence of XI in the reaction mixture indicates that this is not a viable pathway. Since the allene ligand in IX or X should be of comparable lability the absence of the insertion product IV suggests that IX is strongly favored in the equilibrium between IX and X. Thus IX decomposes via a slow dissociation to Fp^+ and the substituted allene followed by formation of $FpSnCl_3$ by addition of $SnCl_3^-$ to Fp^+.



In contrast to IV, Ia is exclusively converted to the insertion product IIa. The intermediate substituted propene complexes VIIa and VIIIa may be expected to be relatively non-labile. Based on the arguments developed to explain the conversion of IV to $FpSnCl_3$, it may also be expected that VIIa will be favored in the equilibrium between VIIa and VIIIa. This seems reasonable since the equilibria VIIa ⇌ VIIIa and IX ⇌ X are only dependent upon the solvent and the tin group. A dissociative conversion to VIIIa to IIa can be ruled out since the lability of the Fp—olefin$^+$ bond in both VIIa and VIIIa should be similar. If a dissociative process were involved substantial amounts of $FpSnCl_3$ (unobserved) would be expected to be formed by VIIa. Therefore IIa must be rapidly formed from VIIIa by a process which is not accessible to the intermediate zwitterionic complex X. This process can only be a concerted intramolecular rearrangement of VIIIa to IIa.

Acknowledgment

We gratefully acknowledge the support of the Graduate School of Boston University.

References

1 A. Wojcicki, Accounts Chem. Res., 4 (1972) 344;
(b) S.E. Jacobson, P. Reich-Rohwig and A. Wojcicki, Inorg. Chem., 12 (1973) 717;
(c) S.E. Jacobson, P. Reich-Rohwig and A. Wojcicki, J. Chem. Soc. D. (1971) 1526;
(d) W.P. Giering, S. Raghu, M. Rosenblum, A. Cutler, D. Ehntholt and R.W. Fish, J. Amer. Chem. Soc., 94 (1972) 8251;
(e) S. Su and A. Wojcicki, J. Organometal. Chem., 31 (1971) C34;
(f) J.L. Roustan, J.Y. Merour, J. Benaim and C. Charrier, C.R. Acad. Sci., Ser. C, 274 (1972) 537;
(g) W.P. Giering and M. Rosenblum, J. Amer. Chem. Soc., 93 (1971) 5299;
(h) D.W. Lichtenberg and A. Wojcicki, J. Organometal. Chem., 33 (1971) C77;
(i) M.R. Churchill, J. Wormald, D.A. Ross, J.E. Thomasson and A. Wojcicki, J. Amer. Chem. Soc., 92 (1970) 1795;
(j) S. Raghu and M. Rosenblum, J. Amer. Chem. Soc., 95 (1973) 3060;
(k) A. Rosen, M. Rosenblum and J. Tancrede, J. Amer. Chem. Soc., 95 (1973) 3062;
(l) S.E. Jacobson and A. Wojcicki, J. Amer. Chem. Soc., 95 (1973) 6962;
(m) Y. Yamamoto and A. Wojcicki, Inorg. Chem., 12 (1973) 1779;
(n) B.J. Cole, J.D. Cotton and D. McWilliam, J. Organometal. Chem., 64 (1974) 223;
(o) A.N. Nesmeyanov, K.N. Anisimov, N.E. Kolobova and F.S. Denisov, Dokl. Akad. Nauk SSSR, Ser. Khim., (1968) 1419;
(p) A.N. Nesmeyanov, N.E. Kolobova, K.S. Anisimov and F.S. Denisov, Dokl. Akad. Nauk SSSR, 192 (1970) 813.
2 For example see P. Hackett and A.R. Manning, J. Chem. Soc. Dalton, (1972) 2434 and ref. therein.
3 F. Bonati and G. Wilkinson, J. Chem. Soc., (1964) 179.
4 P. Hackett and A.R. Manning, J. Chem. Soc., (A), (1972) 1487.
5 W.P. Giering and M. Rosenblum, Chem. Commun., (1971) 441.
6 L. Cohen, W.P. Giering, D. Kenedy, C.V. Magatti and A. Sanders, J. Organometal. Chem., 65 (1974) C57.
7 T.N. Sumarokova and D.E. Surpina, Izv. Akad. Nauk Kaz. SSR Sci. Khim., (1969) 16; Chem. Abstr., 72 (1969) 279263.
8 C. Magatti and W.P. Giering, unpublished results.
9 S. Raghu and M. Rosenblum, personal commmunication.