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Preliminary communication

Reaction of ferrocenylmethyl derivatives of silicon and germanium with methanol: Anomalous solvolysis of the metal–carbon bond

TADAO KONDO, KEIJI YAMAMOTO and MAKOTO KUMADA
Department of Synthetic Chemistry, Kyoto University, Kyoto (Japan)

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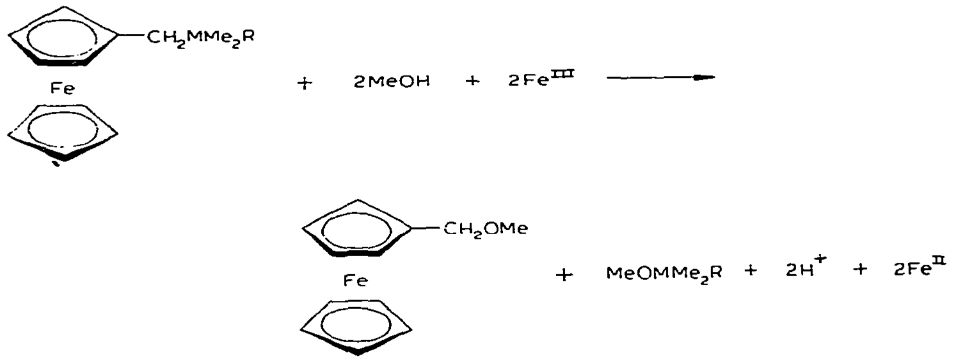
The chemistry of ferrocene and its derivatives, including ferricenium ion intermediates, has been a subject of much interest[1]. In connection with our continuing interest in reactions of ferrocene derivatives containing silicon or germanium as substituent[2], it became desirable to examine a reaction of ferrocenylmethyl–metal (Si or Ge) compounds.

We now report an anomalously facile cleavage of a metal–carbon bond of ferrocenylmethyl derivatives of silicon and germanium, which takes place when these compounds are treated with absolute methanol in the presence of ferric chloride[3]. Thus, to a solution of (ferrocenylmethyl)trimethylsilane (Ia) (0.37 mmole) dissolved in absolute methanol (10 ml) was added at room temperature ferric chloride (0.75 mmole) in methanol (10 ml) in a degassed sealed glass ampoule. The mixture immediately turned greenish blue in color, indicative of the formation of ferricenium ion, and then the color faded in about 40 min. The resulting yellow solution was distilled under reduced pressure, methoxytrimethylsilane being obtained from the distillate. The residue was chromatographed through an alumina column (1 X 15 cm) using ether as an eluent to give methoxymethylferrocene[4] in quantitative yield.

Two equivalents of ferric chloride for each molecule of the substrate were found to be essential for completion of the reaction when oxygen was rigorously removed from the solution prior to mixing.

Similarly, (ferrocenylmethyl)trimethylgermane (Ib) underwent the reaction but much faster than (Ia) (Eqn. (1)). Parallel relative rates were also observed with two ferrocenylmethyl–metal compounds (IIa) and (IIb), but their reactivities were markedly lower than those of (Ia) and (Ib), respectively. The relative rates of the reaction are: (Ia) 1.0, (Ib) 30, (IIa) 0.032, (IIb) 2.0, (III) 2.0, and (IV) 2.8.

This order of reactivity for each pair of the silicon and germanium compounds is not that expected for a usual base-catalyzed cleavage at the metal atom[5]. However, the facts that the relative reactivities of this reaction cannot be correlated to oxidation



(1)

Ia: R = Me, M = Si; Ib: R = Me, M = Ge; IIa: R = i-Pr, M = Si; IIb: R = i-Pr, M = Ge; III: R = OMe, M = Si; IV: R = Ph, M = Si.

potentials of the compounds concerned (half-wave potentials *vs.* S.C.E. in acetonitrile)★ and an electron-withdrawing substituent on silicon even slightly enhances the reactivity in the cases of (III) and (IV) seem to be consistent with a reaction mechanism involving rate-determining nucleophilic attack by oxygen of the solvent methanol on the metal.

Therefore, the present results may be best explained by Scheme 1. Step (a) may

$$\text{Fc--CH}_2\text{--MMe}_3 + \text{Fe}^{\text{III}} \overset{K}{\rightleftharpoons} \text{Fc}^+\text{--CH}_2\text{--MMe}_3 + \text{Fe}^{\text{II}} \qquad \text{(a)}$$

$$\text{Fc}^+\text{--CH}_2\text{--MMe}_3 + \text{MeOH} \xrightarrow{k} \text{Fc--}\dot{\text{C}}\text{H}_2 + \text{MeOMMe}_3 + \text{H}^+ \qquad \text{(b)}$$

$$\text{Fc--}\dot{\text{C}}\text{H}_2 + \text{Fe}^{\text{III}} \rightarrow [\text{Fc}^+\text{--}\dot{\text{C}}\text{H}_2] \rightarrow \text{Fc--CH}_2{}^+ \qquad \text{(c)}$$

$$\text{Fc--CH}_2{}^+ + \text{MeOH} \rightarrow \text{Fc--CH}_2\text{--OMe} + \text{H}^+ \qquad \text{(d)}$$

Scheme 1. (Fc = ferrocenyl group, M = Si or Ge).

reasonably be correlated to the oxidation potential, which reflects an electronic effect of a substituent on a fast electron-transfer process, and the pre-equilibrium constant of a silicon derivative may be little different from that of a germanium analog. Substituted ferricenium ions thus formed by ferric chloride now have a potentially good leaving group in the molecule with respect to the cleavage of the metal–carbon bond. In Step (b) the ferricenium ion gives a methoxymetal compound and a ferrocenylmethyl radical, the latter in turn having an interesting chemistry in its own right (Steps (c) and (d)).

Although the reasons for the reverse order of relative reactivity (Ge > Si) are not fully understood at the moment, dependence[5,7] of the rate constant for base-catalyzed cleavage of R–MMe_3 on the acidity of the corresponding hydrocarbon acid, R–H, is highly suggestive. If R is a good leaving group, then with a weak nucleophile the formation

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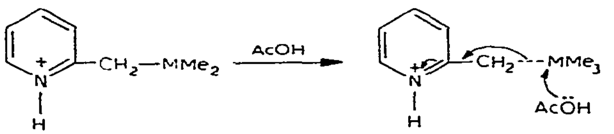
★ – $\Delta E_{1/2} = -464\sigma_p - 18$ (mV), ($r = 0.995$), where $\Delta E_{1/2}$ is a relative oxidation potential (*vs.* S.C.E.) to ferrocene itself, σ_p is a Hammett's *para*-substituent constant, and r is a correlation factor[6].

of a pentacoordinate intermediate [$RMMe_3$(nucleophile)] is the limiting step, followed by fast cleavage of the R–M bond. A germanium compound is more advantageous for making such a complex than is a silicon compound. On the other hand, if R–H is a weak acid, then with a strong nucleophile, a mechanism involving the rapid and reversible formation of the pentacoördinate complex followed by slow cleavage of the M–R bond will be suggested, and a silicon compound reacts by far faster than a germanium one, as was usually encountered in the cleavage of benzylmetal derivatives[5,7].

It is noteworthy that a comparable reactivity for α-picolyltrimethylmetal (Si and Ge) compounds[8] toward acetic acid was observed[9], which implies that there is formed a very good leaving group as shown in Eqn. (2). That is, an electron deficiency on the nitrogen atom caused by protonation, just like one-electron oxidation in ferrocene derivatives, is obviously responsible for facile cleavage of the metal–carbon bond.



(2)

REFERENCES

1 M. Rosenblum, *Chemistry of the Iron Group Metallocenes*, Wiley, New York, Part 1, 1965.
2 (a) M. Kumada, K. Mimura, M. Ishikawa and K. Shiina, *Tetrahedron Letters*, (1965) 83;
(b) M. Kumada, M. Ogura, H. Tsunemi and M. Ishikawa, *Chem. Commun.*, (1969) 207.
3 *Paper Pres. 24th Nat. Meeting Chem. Soc. Japan*, Osaka, April 1–5, 1971. See *Abstr., Part III*, p. 1229.
4 A.N. Nesmeyanov, E.G. Perevalova and Yu.A. Ustynyuk, *Doklady Akad. Nauk SSSR*, 133 (1960) 1105.
5 C. Eaborn and B.W. Bott, in A.G. MacDiarmid (Ed.), *Organometallic Compounds of the Group IV Elements*, Vol. 1, Part 1, Dekker, New York, 1968, p. 402.
6 T. Kondo, T. Omura, K. Yamamoto and M. Kumada, unpublished results.
7 I.P. Beletskaya, K.P. Butin and O.A. Reutov, *Organometal. Chem. Rev. A*, 7 (1971) 51.
8 (a) C. Eaborn and R.A. Shaw, *J. Chem. Soc.*, (1955) 3306; (b) W.K. Musker and R.L. Sholl, *J. Organometal. Chem.*, 27 (1971) 37.
9 T. Kondo, K. Yamamoto and M. Kumada, unpublished results.