

Ring-Opening Reaction of Phosphorus-Bridged [1]Ferrocenophane via Ring Slippage from η^5 - to η^1 -Cp

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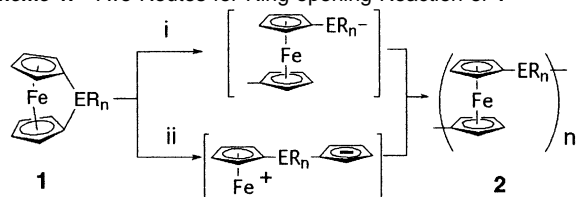
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Ferrocene has been generally recognized as a thermally stable molecule because of its large Fe–Cp dissociation energy of ca. 380 kJ/mol.¹ However, some ferrocene compounds such as acyl-substituted ferrocenes^{2,3} and boron-bridged [1]ferrocenophane,⁴ have been reported to undergo an Fe–Cp cleavage upon irradiation with light. Since ferrocene compounds are widely used in contemporary chemistry not only as a reagent in synthesis and catalysis but also as an advanced material,⁵ elucidation of a mechanism for such photolyses, especially isolation of intermediates during the Fe–Cp cleavage, is of general importance. On the basis of a ring-slippage chemistry of transition-metal Cp complexes,⁶ it is highly plausible that the photolytic Fe–Cp cleavage proceeds via a haptotropic shift of the Cp ligand. To the best of our knowledge, however, an intermediate of such a reaction has not been isolated regarding ferrocene compounds.

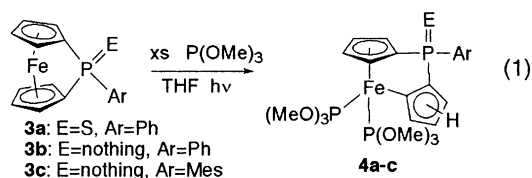
Recently, our group reported that phosphorus-bridged [1]ferrocenophanes polymerized on irradiation of UV–vis light.⁷ In analogy with the photolysis mentioned above, our photolytic polymerization may proceed also via the Fe–Cp cleavage (route ii in Scheme 1). On the other hand, thermal, living-anionic, and metal-catalyzed polymerizations of ER_n-bridged [1]ferrocenophanes (E = B, Si, Ge, Sn, and P) were investigated extensively,⁸ and it is reported that some of them proceed via the cleavage of a ferrocene–ER_n bond (route i).^{9–13} Here, we wish to report the unprecedented identification of the intermediates supporting the route ii mechanism for the photolytic polymerization of phosphorus-bridged [1]ferrocenophanes.

Scheme 1. Two Routes for Ring-opening Reaction of **1**



As previously reported, photoirradiation of PhP(S)-bridged [1]-ferrocenophane **3a** in THF gives polymeric products in an almost quantitative yield. The formation of the polymer can be readily confirmed by the appearance of ³¹P{¹H} NMR signals at 37.3 and 30.9 ppm with an intensity ratio of 94:6.^{10c} If this polymerization proceeds via the route ii, the dissociation of the Cp ring from the iron center should leave vacant coordination sites on the iron center, which are expected to be temporarily occupied by THF molecules before intermolecular recombination leading to polymerization. Therefore, if such a recombination can be suppressed by replacement of coordinating solvents with strongly coordinating ligands such as a phosphorus ligand, the reaction intermediate may be stable enough to be isolated and characterized. With this expectation in mind, we carried out the photolysis of **3** in the presence of P(OMe)₃ or PMe₃.

A THF solution of **3a** was irradiated in the presence of a large excess of P(OMe)₃ (eq 1). After 10 min irradiation, a ³¹P{¹H} NMR



spectrum of the resultant solution showed no signals attributable to polymeric products, but new signals were observed at 33.9, 186.1, and 194.4 ppm in addition to that at 141.0 ppm due to free P(OMe)₃. Since the signals at 186.1 and 194.4 ppm are mutually coupled with a large coupling constant (²J_{PP} = 151 Hz), they are assigned to the two P(OMe)₃ ligands coordinating to the iron center, and the remaining signal at 33.9 ppm is to the bridging phosphorus. Finally, a molecular structure of this product was determined by X-ray analysis as shown in Figure 1. One Cp ring coordinates to the iron center with a usual η^5 -mode, whereas the other has changed its coordination mode from η^5 to η^1 with itself connected to the η^5 -Cp ring through an S=PPh group. Although several reports described the ring slippage of ferrocene derivatives, to our best knowledge, this is the first example of the η^5 -to- η^1 haptotropic shift characterized by X-ray analysis. The geometry of the η^1 -Cp ring is interesting owing to its tautomerism. Summations of the bond angles around C6 and C7 are 359.7(9)° and 360.1(9)°, respectively, and bond lengths for C6–C7 and C9–C10 are 1.372(8) Å and 1.34(1) Å, respectively, which are significantly smaller than those for the other three bonds of the five-membered ring. These structural characteristics are consistent with a right-hand tautomeric structure shown in Figure 1.

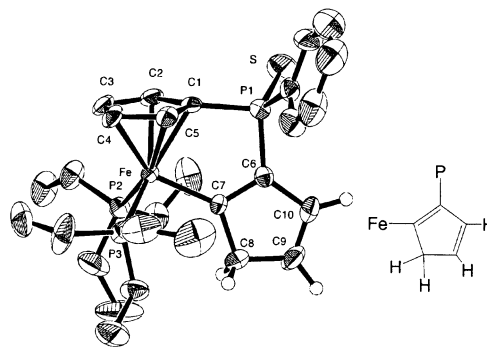


Figure 1. ORTEP drawing of **4a** at 50% probability. Hydrogen atoms are depicted only for an η^1 -Cp ring.

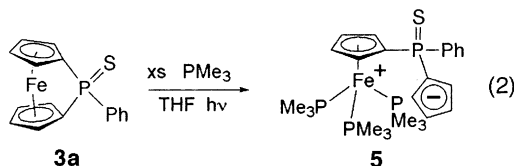
The two remaining coordination sites on the iron center are occupied by the two P(OMe)₃ ligands as expected. They were observed as an AB quartet in ³¹P{¹H} NMR, since these phosphite

ligands are at diastereotopic positions due to the presence of the asymmetric bridging phosphorus atom.

For PhP- and MesP-bridged [1]ferrocenophanes, **3b** and **3c**, respectively, a photolysis under similar conditions gave the products having AB quartets around 190 ppm in $^{31}\text{P}\{^1\text{H}\}$ NMR, indicating that the two $\text{P}(\text{OMe})_3$ ligands coordinate to the iron center after a ring-slippage similar to that observed for **4a**. In these cases, however, $^{31}\text{P}\{^1\text{H}\}$ NMR data of the reaction mixture given in the Supporting Information indicate the presence of two isomers, probably arising from the tautomerism of the $\eta^1\text{-Cp}$.

Here, to confirm that the isolated **4a** possesses structural characteristics requisite for the polymerization, a thermal polymerization of **4a** was carried out. After reflux of **4a** in THF for 24 h, a $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction mixture showed signals around 37 ppm as well as at 141.0 ppm due to free $\text{P}(\text{OMe})_3$. The former signals are identical to those of the polymer obtained by the photoreaction of **3a**. A yield of the product was 43% after treatment described in the Supporting Information. GPC analysis showed that the product obtained by the thermolysis is an oligomer having a molecular weight in a range of 300–10000 ($M_n = 730$ and $M_w/M_n = 2.23$ relative to polystyrene standards), which was considerably lower than that of the product formed by the direct photolysis of **3a** ($M_n = 2.9 \times 10^4$ and $M_w/M_n = 1.63$). It is probable that strongly coordinating $\text{P}(\text{OMe})_3$ ligands depress smooth propagation of a polymer chain.

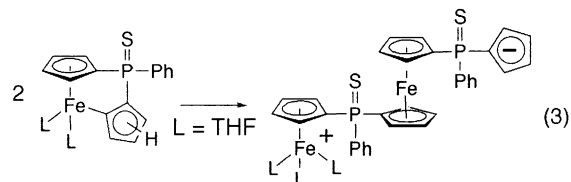
Finally, it is an important point whether the $\eta^1\text{-Cp}$ ring dissociates completely from the iron center, because such a step is indispensable for the polymerization reaction. To clarify this point, a similar photolysis of **3a** was carried out using more strongly coordinating PMe_3 in place of $\text{P}(\text{OMe})_3$. In a $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, the bridging phosphorus was observed at 26.0 ppm, and PMe_3 was observed at 23.4 ppm not as an AB quartet but a sharp siglet having a much higher intensity than that of the bridge. In ^1H NMR, PMe_3 was observed at 1.45 ppm with 27H of intensity. These NMR data regarding PMe_3 indicate that three PMe_3 ligands coordinate to the iron center to form a product **5** (eq 2). With respect to the



dissociated Cp^- , four protons on the ring were observed at 5.78 and 6.12 ppm, and five carbon atoms were at 114.6, 109.9, and 88.7 ppm, which are consistent with data reported for a Cp^- anion binding to a phosphorus fragment.¹⁴ The reaction of eq 2 indicates that a strongly coordinating ligand expels one of the two $\eta^5\text{-Cp}$ ligands from the iron center.

The results obtained in this study strongly support the view that the photolytic polymerization of **3a** proceeds via the route-ii type. An initiation step is probably an intermolecular combination between two ring-slipped products, in which the $\eta^1\text{-Cp}$ ring of one molecule attacks the iron center of the other to expel the Cp^- ring from the iron center (eq 3). The dimeric product has a $\text{CpFe}(\text{THF})_3$ head, a ferrocene- $\text{P}(\text{S})\text{Ph}$ body, and a dangling Cp^- tail. A successive intermolecular head-to-tail coupling is one of the

plausible mechanisms for the propagation step of the polymerization. Further study on this point is still under way.



Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research (No. 13640560) from the Ministry of Education, Science, Sports, and Culture, Japan.

Supporting Information Available: Experimental procedures for the syntheses of **4a**, **4b**, **4c**, and **5** and their NMR data (PDF) and crystallographic data for **4a** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA029297M