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Structure and Properties of the Macrocyclic Tridentate Ferrocenylphosphine Ligand $(-PhPC_5H_4FeC_5H_4-)_3$

Tsutomu Mizuta,* Tomoyuki Aotani, Yuki Imamura, Kazuyuki Kubo, and Katsuhiko Miyoshi

Department of Chemistry, Graduate School of Science, Hiroshima University, Kagamiyama 1-3-1, Higashi-hiroshima 739-8526, Japan

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Isolation and characterization were carried out for a novel tridentate ferrocenylphosphine macrocycle, $(-PhPC_5H_4FeC_5H_4-)_3$, as follows. A photolytic ring-opening reaction of PPh-bridged [1]ferrocenophane in ether gave a mixture of its oligomers. After their sulfurization, GPC separation of low-molecular-weight species afforded two isomers of a macrocyclic trimer, 1,1″:1′,1⁗:1‴,1′′′′′-tris(phenylthiophosphinidene)tris(ferrocene), in which three 1,1′-ferrocenediyl units and three P(S)Ph groups were alternately linked to form a macrocyclic ring. Although yields of both isomers were low (17% in total), they were successfully desulfurized in good yields without configurational inversion at their phosphorus centers by treatment with $MeOTf/P(NMe_2)_3$ ($OTf = CF_3SO_3$), to give the respective tridentate macrocyclic phosphine ligands. The molecular structure of one isomer (C_3 isomer) with C_3 symmetry was determined by X-ray analysis, while the other was identified as the C_s isomer on the basis of ^1H, ^{13}C, and ^{31}P NMR data. When the C_3 isomer was heated in toluene at around 80 °C, it isomerized gradually but almost completely to the C_s isomer with the activation energy $\Delta G_{350}^{\ddagger} = 26.2 \pm 0.6$ kcal mol^{-1}. The reaction of AgOTf with the C_3 isomer in CH_2Cl_2 gave a mononuclear silver complex in which the C_3 isomer encircled the Ag^+ ion as a tridentate ligand. To our surprise, a similar reaction using the C_s isomer gave the same silver complex as above, indicating that a facile conversion of the C_s isomer to the C_3 isomer took place upon coordination to the Ag^+ ion at room temperature.

Ferrocenylphosphines constitute an important subset of phosphorus ligands serving as a very useful and powerful auxiliary ligand in metal-complex catalysts for organic reactions.[1] For example, bis(diphenylphosphino)ferrocene (dppf) is widely used as an excellent ligand for homogeneous catalyses,[2] and 1,2-disubstituted ferrocenylphosphines have been extensively applied as planar-chirality ligands for asymmetric catalyses.[3–6]

Phosphorus-bridged [1]ferrocenophanes such as **1** are not only structurally attractive ferrocenylphosphine ligands bearing a distorted ferrocene unit[7–19] but also useful precursors for the preparation of a variety of their derivatives, since they readily open their ring structure to release a substantial steric strain built into a distorted [1]ferrocenophane framework, as demonstrated by some groups.[20–28] Our group also carried out a photoinduced ring-opening oligomerization of **1**.[29,30] From a mixture of the oligomers obtained, two types of dimers were

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* To whom correspondence should be addressed. Fax: +81-82-424-0729. E-mail: mizuta@sci.hiroshima-u.ac.jp.

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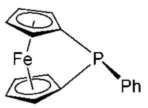
isolated and characterized to be bidentate ferrocenylphosphine macrocycles **2** bearing syn- and anti-PPh-bridged [1.1]ferrocenophane frameworks.[30]



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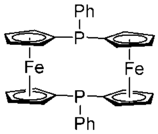

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A vast number of aza and oxa macrocyclic ligands have been investigated so far.[31,32] In contrast, studies on phospha macrocycles, especially on those with a medium ring size, are relatively limited in number.[33,34] Since the early works by Horner et al. and Kyba et al., who synthesized [11]ane P_3 macrocycles 30 years ago,[35,36] several groups have reported the synthesis of medium-ring-size phospha macrocycles.[37–47] In particular, Edwards et al. recently established a metal-template hydrophosphination method, in which a ring structure was constructed on a metal center by a self-coupling reaction among primary or secondary alkenylphosphines.[48] By use of the ingenious template method above, a dozen P_3 macrocycles are known to date, but those having a functional group on their chelate rings have not been reported so far.

In our oligomerization reaction of **1** mentioned above, cyclic oligomers with a ring size larger than that of **2** must have been formed. Actually, we briefly mentioned the formation of the trimer **3**.[29] The P_3 macrocycle **3** is unprecedented in that chelate backbones are composed only of ferrocene units known to function as a redox-active bulky group. Since such a P_3 macrocycle serves potentially as a unique tridentate ligand to a transition metal, we report herein the characterization and structural properties of **3** in detail. In addition, **3** is found to readily undergo pyramidal inversion at the phosphorus center upon coordination to an Ag^+ ion at room temperature, in marked contrast to our consensus that usual trialkyl- and triarylphosphines invert their configurations only if they are heated to 100 °C.[49,50] The mechanism for the unexpectedly facile inversion is also discussed.

Results and Discussion

Separation and Characterization of Isomeric Trimers. The photolysis of **1** in ether gave the cyclic dimers **2** in a total yield of ca. 30% together with a mixture of several oligomers, as

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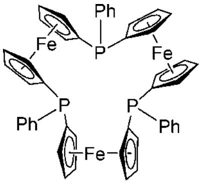

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described earlier.[51] After the insoluble anti dimer, sparingly soluble syn dimer, and polymeric precipitates were removed by filtration, the remaining oligomeric mixture was sulfurized with elemental sulfur. Subsequent separation was performed with a preparative-scale recycling-GPC equipment. MALDI-TOF mass spectra of each band revealed that the only last three bands contained low-molecular-weight oligomers of interest to us: a mixture of trimeric and tetrameric sulfides in band 1, another trimeric sulfide in band 2, and a small amount of a dimeric syn sulfide in band 3, which were eluted in this order. Band 2, containing the trimeric sulfide **4b** only, was completely separated from the other two bands after 6 recycles, while the other trimeric sulfide in band 1, **4a**, was found at this stage to be still contaminated with the tetrameric sulfide. Complete separation of **4a** was marginally achieved after overnight (25 times) recycles. Trace amounts of higher oligomers up to a hexamer were detected in some bands eluted earlier.

A $^{31}P\{^{1}H\}$ NMR spectrum of **4a** showed a sharp singlet at 39.2 ppm, implying that **4a** has a C_3-symmetric cyclic structure. The structure of **4a** was determined by X-ray analysis, as shown in Figure 1, where three ferrocene units and three P(S)Ph groups are alternately linked to form a macrocyclic framework. The molecule has C_3 symmetry with the P=S and P−Ph bonds on each phosphorus atom directed outside the ring. On the other hand, the other trimeric sulfide isolated from band 2, **4b**, gave a complicated $^{31}P\{^{1}H\}$ NMR spectrum consisting of five peaks: a broad peak at 42.7 ppm and a sharp peak at 44.3 ppm with a 2:1 intensity ratio and three minor signals with equal intensity at 40.4, 40.5, and 40.7 ppm. The complexity is probably due to the presence of conformational isomers. In fact, when **4b** was heated above 50 °C, considerable peak broadening was observed for the three minor signals, while the first two signals became sharper, suggesting that the frequency of the conformational interconversion became comparable to or greater than the NMR time scale. In accordance with the complicated $^{31}P\{^{1}H\}$ NMR spectrum, ^{1}H and $^{13}C\{^{1}H\}$ NMR signals of **4b** were too complicated to assign. Final structural assignment of **4b** was accomplished after it was desulfurized (vide infra).

The macrocyclic trimeric sulfides **4a**,**b** were both successfully desulfurized by treatment with MeOTf (OTf = CF_3SO_3) and $P(NMe_2)_3$ with their symmetries retained (eq 1).[30,52] The desulfurized product **3a** obtained from **4a** showed a single $^{31}P\{^{1}H\}$ NMR peak at −35.5 ppm. In ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra, only four ferrocene proton signals and five C_5H_4 carbon signals were observed. These NMR data were consistent with **3a** having C_3 symmetry, which was unequivocally confirmed by the crystal structure, shown in Figure 2. The ligand **3a** provides the second example in which the molecular structure of the free P_3 macrocycle has been determined by X-ray analysis.[53] Figure 2 shows that three bulky ferrocene units and three phenyl groups are all located outward to avoid steric congestion. As a result, the three lone pairs of **3a** are all directed toward the center of the macrocycle, and so **3a** is expected to encircle a metal ion as a tridentate ligand (vide infra). When **3a** is compared in structure with the sulfurized derivative **4a** shown in Figure 1, some notable conformational differences are found. The three P=S bonds in **4a**, corresponding to the three lone pairs in **3a**, are directed outside the ring to avoid a steric repulsion that would emerge if the three P=S bonds were all directed toward the center of the macrocycle, like the three lone pairs in **3a**. This leads to the three ferrocene units becoming closer in **4a** than in **3a**. As a result, **4a** is subjected to a limited conformational flexibility, and therefore, **4a** has a $^{13}C\{^{1}H\}$ NMR spectrum in which the 10 carbon atoms in one ferrocene unit

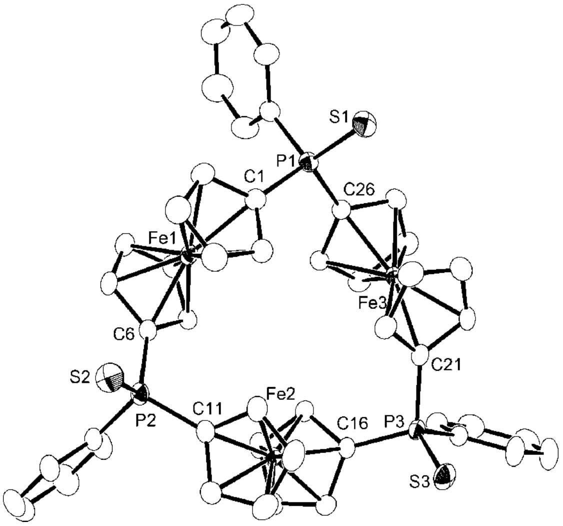

Figure 1. Molecular structure of **4a** with thermal ellipsoids given at the 50% probability level. Three independent molecules were found in the asymmetric unit, but only one of the three similar structures is shown. Selected bond distances (Å) and angles (deg): P1−S1 = 1.9586(7), P2−S2 = 1.9585(8), P3−S3 = 1.9582(7), P1−C1 = 1.796(2), P1−C26 = 1.7915(19), P2−C6 = 1.790(2), P2−C11 = 1.797(2), P3−C16 = 1.793(2), P3−C21 = 1.793(2); C1−P1−C26 = 109.80(9), C6−P2−C11 = 109.66(9), C16−P3−C21 = 109.72(9).

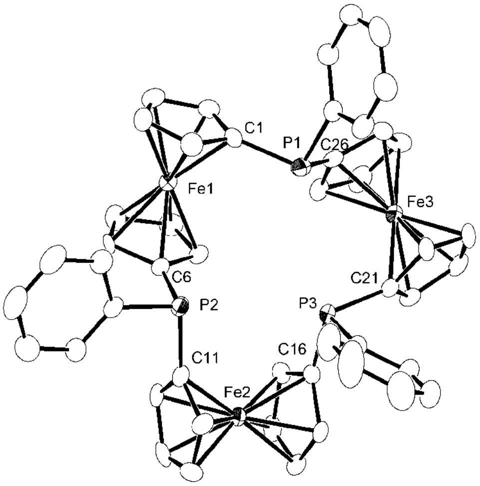

Figure 2. Molecular structure of **3a** with thermal ellipsoids given at the 50% probability level. Selected bond distances (Å) and angles (deg): P1−C1 = 1.818(5), P1−C26 = 1.829(6), P2−C6 = 1.825(6), P2−C11 = 1.824(6), P3−C16 = 1.822(5), P3−C21 = 1.832(5); C1−P1−C26 = 103.4(3), C6−P2−C11 = 99.5(2), C16−P3−C21 = 102.0(2).

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(51) The reaction in THF gave higher polymers as major products.[28,29] Mixed solvent systems, for example, THF−ether mixtures, were also examined but resulted in rather lower yields of the trimer **3**.

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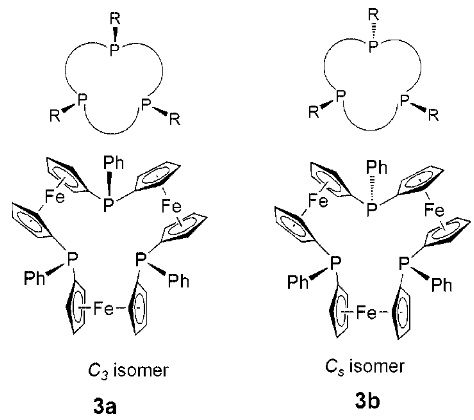
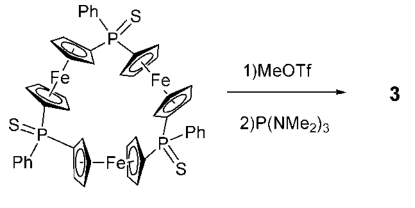
Chart 1



C_3 isomer
3a

C_s isomer
3b

are all observed as inequivalent, while **3a**, having a more flexible macrocyclic framework, has only five ^{13}C signals for the ferrocene units.



4 (1)

After similar desulfurization of the other isomer, **4b**, a ^{31}P{^{1}H} NMR spectrum of the resulting product, **3b**, showed only two sharp signals at −21.7 and −22.8 ppm with a 1:2 intensity ratio, implying that **3b** adopts C_s symmetry and is gifted with a considerable conformational flexibility like **3a**. In principle, only two configurational isomers are possible for a P_3 macrocycle, as shown in Chart 1. Since **3a** has been unambiguously identified as the C_3 isomer by X-ray analysis, **3b** must be the other isomer having C_s symmetry with one of the three phosphorus centers inverted in configuration. The C_s structure of **3b** was also deduced by an ^{1}H−^{1}H COSY spectrum, which was consistent with the presence of three inequivalent C_5H_4 rings.

Reaction with Ag^{+} Ion. The C_3 isomer **3a** was allowed to react with AgOTf in CH_2Cl_2 to give the expected tricoordinate silver complex [Ag(**3a**)]OTf (**5**), which showed one set of ^{31}P{^{1}H} NMR signals centered at −17.3 ppm coupled with ^{107}Ag ($^{1}J_{^{31}\mathrm{P}-^{107}\mathrm{Ag}}$ = 325 Hz) and ^{109}Ag ($^{1}J_{^{31}\mathrm{P}-^{109}\mathrm{Ag}}$ = 375 Hz) and only four ^{1}H and five ^{13}C{^{1}H} NMR signals due to the three equivalent ferrocene units. The X-ray crystal structure of **5** is shown in Figure 3, where the three phosphorus donors encircle the Ag^{+} center with Ag−P bond distances of 2.4600(17), 2.4586(17), and 2.4663(17) Å. They are comparable to those found in, for example, tricoordinate [Ag(PPh$_3$)$_3$]BF$_4$ and [Ag$_2$(μ-dppf)(dppf)$_2$](PF$_6$)$_2$.[54,55] In addition to the three phosphorus donors, an OTf^{-} anion in **5** coordinates weakly to the [Ag(**3a**)]$^{+}$ cation at a much greater Ag−O distance of 2.772(7) Å, in comparison to the three Ag−P distances. The geometry around the Ag^{+} center is thus pseudotetrahedral if the OTf^{-} anion is included, with three neighboring P−Ag−P angles of 110.73(6), 110.95(6), and 111.30(6)°. It is not known at present whether the OTf^{-} ion remains in the coordination sphere of the Ag^{+} ion in solution.

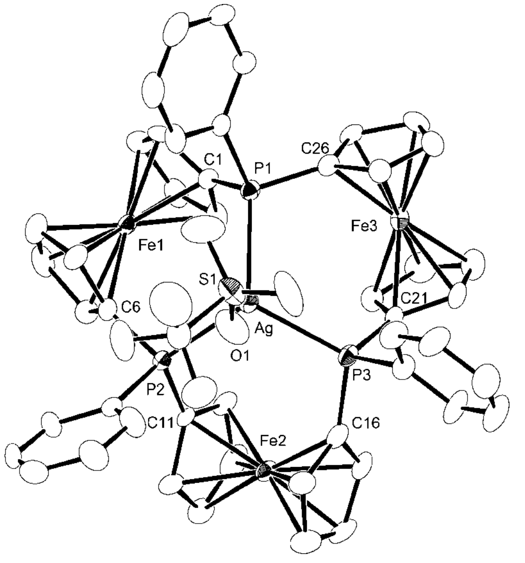


Figure 3. Molecular structure of [Ag(**3a**)]OTf (**5**) with thermal ellipsoids given at the 50% probability level. Selected bond distances (Å) and angles (deg): Ag−P1 = 2.4600(17), Ag−P2 = 2.4586(17), Ag−P3 = 2.4663(17), P1−C1 = 1.827(6), P1−C26 = 1.803(7), P2−C6 = 1.809(7), P2−C11 = 1.808(7), P3−C16 = 1.808(7), P3−C21 = 1.808(7); P1−Ag−P2 = 110.73(6), P2−Ag−P3 = 110.95(6), P1−Ag−P3 = 111.30(6), C1−P1−C26 = 103.5(3), C6−P2−C11 = 103.6(3), C16−P3−C21 = 104.0(3).

A similar reaction of the C_s isomer **3b** with AgOTf in CH_2Cl_2 was also carried out at room temperature. To our surprise, the product had the same ^{31}P{^{1}H} signal as that of **5**, indicating that the C_s isomer **3b** has been converted to the C_3 isomer **3a** upon coordination to the Ag^{+} ion. This conversion requires pyramidal inversion at the phosphorus center which differs in configuration from the remaining two phosphorus centers (see Chart 1). In general, pyramidal inversion of tertiary phosphines requires heating over 100 °C, owing to their high energy barriers ranging from 30 to 38 kcal mol^{-1}.[49,50] Actually, the free ligands **3a**,**b** started to interconvert only on heating, and **3a** isomerized gradually but almost completely to the thermodynamically more stable **3b**. When this isomerization process was monitored with ^{31}P NMR, the activation barrier was estimated to be $\Delta G_{350}^{\ddagger}$ = 26.2 ± 0.6 kcal mol^{-1}. Since the macrocycle frameworks of **3a**,**b** are both considered to be sufficiently flexible, like the related macrocycles (−$CH_2C_5H_4FeC_5H_4$−)$_n$ (n = 2, 3),[56–59] it is the inversion barrier of the phosphorus center itself that is mainly responsible for the present barrier of ca. 26 kcal mol^{-1}; the flexible but bulky ferrocene backbones seem to make no practical steric contribution to the isomerization barrier. Although the barrier is slightly lower than those expected for triarylphosphines,[49] in part because of the entropic term RT ln 3, it is still sufficiently high to prevent the room-temperature isomerization; no inversion was in fact observed for **3a**,**b** at room temperature.

The observed facile inversion induced by the Ag^{+} ion is rationally understood, assuming the reaction intermediate shown

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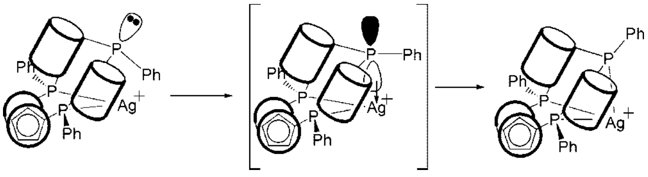

Figure 4. Mechanism for the pyramidal inversion of the third phosphorus center induced by the backside attack of an Ag$^+$ ion. Each cylindrical shape represents a ferrocene unit.

in Figure 4. First, the Ag$^+$ ion is considered to be bound to **3b** in a manner shown at the left side of Figure 4, where the two phosphorus centers donating their lone pairs are those bearing the same configuration in the free C_s isomer shown in Chart 1. The Ag$^+$ ion then attacks the third phosphorus center. It is generally accepted that a phosphorus center in the transition state of the pyramidal inversion adopts a trigonal-planar geometry in which the lone pair resides in the p orbital. If a metal ion interacts with this lone pair, considerable stabilization of the planar phosphorus center will be attained, resulting in a reduction in the inversion barrier. In the center structure of Figure 4, the two phosphorus centers of **3b** bind to the Ag$^+$ ion as a bidentate chelate so as to locate the Ag$^+$ ion at a position suitable for interaction with the lone pair on the third phosphorus center. Finally, the inversion is accomplished to form [Ag(**3a**)]$^+$, in which the starting **3b** has been converted to **3a** and the Ag$^+$ ion has attained a full interaction with the third phosphorus atom. Fryzuk et al. also reported a similar reduction in the inversion barrier for the reaction of a P_2N_2 macrocycle with MCl_3 (M = Al, Ga), in which the pyramidal inversion at 80 °C was accelerated by 20−70 times compared with that of the free ligand.[60] It is interesting to note that, when the solvent for the present reaction of **3b** with AgOTf was changed from CH_2Cl_2 to THF, the $^{31}P\{^1H\}$ NMR spectrum of the resulting silver complex showed complicated coupling patterns at −9.1 and −18.0 ppm with a 2:1 intensity ratio. These signals could be analyzed as an A_2MX spin system in which only two of the three phosphorus centers were firmly bound to the $^{107}Ag^+$ or $^{109}Ag^+$ ion. The results suggest that **3b** coordinates to the Ag$^+$ ion with its C_s configuration retained upon the reaction in THF, which is in marked contrast to the facile C_s-to-C_3 isomerization observed for the reaction in CH_2Cl_2. When it is taken into consideration that the donating ability of THF is stronger than that of CH_2Cl_2, coordination of THF to the Ag$^+$ ion probably interrupts the subsequent interaction of the third phosphorus center with the Ag$^+$ ion shown in Figure 4.

In conclusion, both of the possible C_3 and C_s isomers were isolated for the P_3 macrocycle bearing ferrocene units as chelate backbones. Not only the C_3 but also the C_s isomers are found to coordinate smoothly to the Ag$^+$ ion in CH_2Cl_2 at room temperature to give the identical C_3-isomer complex. Since the free C_3 isomer can be converted almost completely to the free C_s isomer upon heating, the direction of the isomerization can be intentionally controlled by choosing either the heat- or silver-assisted reaction. The facile C_s-to-C_3 isomerization phenomenon observed in this study affords a new method for the configurational regulation of medium-sized phospha macrocycles.

Experimental Section

General Remarks. All reactions were carried out under an atmosphere of dry nitrogen using Schlenk tube techniques. All solvents were dried and distilled from sodium (for hexane), sodium/benzophenone (for ether and THF), or P_2O_5 (for CH_2Cl_2). These purified solvents were stored under an N_2 atmosphere. The PPh-bridged [1]ferrocenophane **1** was prepared according to a previously described method.[25c] Other reagents were used as received.

NMR spectra were recorded on JEOL LA-300 and LA-500 spectrometers. ^1H and ^{13}C NMR chemical shifts were reported relative to Me_4Si and were determined by reference to the residual solvent peaks. ^{31}P NMR chemical shifts were reported relative to H_3PO_4 (85%) used as an external reference. Elemental analyses were performed with a Perkin-Elmer 2400CHN elemental analyzer. MALDI-TOF mass spectra were recorded on a Shimadzu/Kratos Axima CFR+ mass spectrometer.

Photolysis was carried out with Pyrex-glass-filtered emission from a 400 W mercury arc lamp (Riko-Kagaku Sangyo UVL-400P). The emission lines used (in nm) and their relative intensities (given in parentheses) were as follows: 577.0 (69), 546.1 (82), 435.8 (69), 404.7 (42), 365.0 (100), 334.1 (7), 312.6 (38), and 302.2 (9). Preparative-scale GPC was performed with a recycling HPLC system (Japan Analytical Industry Model LC-908) with JAIGEL-1H (20 mm i.d. × 600 mm; exclusion limit 1.0×10^3) and JAIGEL-2H (20 mm i.d. × 600 mm; exclusion limit 5.0×10^3) columns.

Isolation of Trimeric Sulfides. The PPh-bridged [1]ferrocenophane **1** (2040 mg, 6.98 mmol) was dissolved in ether (230 mL). Half portions of the solution were separately put into two Pyrex Schlenk tubes and irradiated with a 400 W mercury arc lamp at 0 °C for 2.5 h. Each supernatant solution was collected by decantation, and the residue in each tube was extracted with ether (50 mL). All solutions were combined, and ether was removed in vacuo. The residue was redissolved in CH_2Cl_2 and allowed to react with an excess amount of sulfur for 3 h, and this mixture was then loaded on an Al_2O_3 column and eluted with THF. An orange band was collected, and the solvent was removed. The residue dissolved in $CHCl_3$ was separated with recycling GPC equipment. Only the last three bands were found to contain low-molecular-weight oligomers: a mixture of trimeric and tetrameric sulfides in band 1, another trimeric sulfide in band 2, and a small amount of a syn dimeric sulfide in band 3, which were eluted in that order. Band 3 and the bands containing oligomers with higher molecular weights were removed after two times of recycling, and the remaining bands 1 and 2 were further recycled four times to lead to complete separation. Each band was collected separately, and band 1 was loaded again. After overnight recycling (25 times), **4a** was separated from the tetramer. After workup, the amounts of **4a**,**b** obtained were 121 mg (5.3%) and 274 mg (12.1%), respectively, both of which were recrystallized from CH_2Cl_2. **4a**: ^1H NMR (300.5 MHz, $CDCl_3$) δ 3.97 (br, 3H, C_5H_4), 4.39 (br, 3H, C_5H_4), 4.7 (br, 3H, C_5H_4), 4.85 (br, 6H, C_5H_4), 5.35 (br, 3H, C_5H_4), 5.53 (br, 3H, C_5H_4), 5.74 (br, 3H, C_5H_4), 7.49 (m, 9H, Ph), 7.86 (dd, J_{PH} = 13.7 Hz, J_{HH} = 6.9 Hz, 6H, Ph); $^{13}C\{^1H\}$ NMR (75.6 MHz, $CDCl_3$) δ 71.4 (d, J_{PC} = 14 Hz, C_5H_4), 72.6 (d, J_{PC} = 13 Hz, C_5H_4), 72.6 (d, J_{PC} = 9 Hz, C_5H_4), 73.0 (d, J_{PC} = 9 Hz, C_5H_4), 73.5 (d, J_{PC} = 7 Hz, C_5H_4), 73.7 (d, J_{PC} = 13 Hz, C_5H_4), 74.9 (d, J_{PC} = 9 Hz, C_5H_4), 76.9 (d, J_{PC} = 9 Hz, C_5H_4), 77.9 (d, J_{PC} = 100 Hz, C_5H_4), 82.3 (d, J_{PC} = 96 Hz, C_5H_4), 128.2 (d, J_{PC} = 12 Hz, Ph), 130.9 (d, J_{PC} = 11 Hz, Ph), 131.6 (d, J_{PC} = 2 Hz, Ph), 133.3 (d, J_{PC} = 89 Hz, Ph); $^{31}P\{^1H\}$ NMR (121.7 MHz, $CDCl_3$) δ 39.2 (s). Anal. Calcd for $C_{48}H_{39}Fe_3P_3S_3 \cdot {}^1/_3 CH_2Cl_2$: C, 58.01; H, 4.00. Found: C, 58.07; H, 3.78. **4b**: ^1H NMR (499.2 MHz, $CDCl_3$) δ 3.90−6.00 (br, 24H, C_5H_4, major peaks 4.14, 4.50, 4.55, 4.62, 4.89, 5.14, 5.23, 5.90), 7.37 (br, 9H, Ph), 7.69 (br, 2H, Ph), 7.78 (br, 4H, Ph); $^{13}C\{^1H\}$ NMR (125.5 MHz, $CDCl_3$) δ 72.7 (br, C_5H_4), 73.3 (br, C_5H_4), 73.8 (br, C_5H_4), 74.3 (br, C_5H_4), 76.5 (br, C_5H_4), 78.1 (br, C_5H_4), 80.9 (br d, J_{PC} = 98 Hz, C_5H_4), 82.5 (br d, J_{PC} = 98 Hz, C_5H_4), 83.3 (br d, J_{PC} = 98 Hz, C_5H_4), 127.9 (d, J_{PC} = 11 Hz, Ph), 127.9 (d, J_{PC} = 11 Hz, Ph), 130.9 (br, Ph), 131.1 (d, J_{PC} = 11 Hz, Ph), 131.3 (d, J_{PC} = 10 Hz, Ph), 136.0 (d, J_{PC} = 93 Hz, Ph); $^{31}P\{^1H\}$ NMR (202.1 MHz,

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Table 1. Crystallographic Data

	3a	**4a**	**5**
formula	$C_{48}H_{39}Fe_3P_3.CHCl_3$	$C_{48}H_{39}Fe_3P_3S_3\cdot 2C_4H_8O$	$C_{49}H_{39}AgF_3Fe_3O_3P_3S\cdot C_6H_4Cl_2$
cryst color, habit	orange, plate	orange, stick	orange, plate
cryst syst	triclinic	trigonal	monoclinic
space group	$P\bar{1}$ (No. 2)	$R\bar{3}$ (No. 148)	$P2_1/n$ (No. 14)
a/Å	12.6200(4)	49.6210(2)	13.3090(2)
b/Å	13.0130(5)	49.6210	24.3990(4)
c/Å	14.9790(6)	25.4250(1)	16.3170(3)
α/deg	94.816(2)	90.0	90.0
β/deg	95.710(2)	90.0	106.752(1)
γ/deg	118.712(1)	120.0	90.0
V/Å^3	2122.14(1)	54 215.4(3)	5073.69(15)
Z	2	42	4
temp/K	200	200	200
μ(Mo Kα)/mm^{-1}	1.350	1.088	1.518
diffractometer		MacScience DIP2030 imaging plate	
no. of rflns			
measd	9073	28 659	11 030
obsd ($I > 2.00\sigma(I)$, $2\theta < 55°$)	6405	26 606	8014
R1 ($I > 2\sigma(I)$)	0.064	0.042	0.070
wR2[a]	0.150	0.114	0.181
GOF	1.089	1.053	1.071
a/b[a]	0.0527/11.86	0.0589/166.15	0.0505/58.46

[a] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$.

$CDCl_3$) δ 40.4 (s), 40.5 (s), 40.7 (s), 42.7 (br), 44.3 (s). Anal. Calcd for $C_{48}H_{39}Fe_3P_3S_3\cdot{}^2/_3CH_2Cl_2$: C, 56.80; H, 3.95. Found: C, 56.77; H, 3.85.

Desulfurization of 4a. To **4a** (100 mg, 0.10 mmol) dissolved in CH_2Cl_2 (10 mL) was added MeOTf (40 μL, 0.35 mmol). The mixture was stirred for 3 h at room temperature. The volatiles were removed in vacuo, and $P(NMe_2)_3$ (65 μL, 0.36 mmol) was then added to the residue dissolved in CH_2Cl_2 (10 mL) at room temperature. After the solution was left for 3 h at room temperature, the volatiles were removed in vacuo. The residue was extracted with benzene (10 mL), and the solvent was removed. The product was recrystallized from CH_2Cl_2 (1 mL)/ether (3 mL) and dried in vacuo to give **3a** (70 mg, 78%). ^1H NMR (499.2 MHz, C_6D_6): δ 4.02 (dt, J_{PH} = 1.3 Hz, J_{HH} = 2.4 Hz, 6H, C_5H_4), 4.05 (br, 6H, C_5H_4), 4.24 (dt, J_{PH} = 1.3 Hz, J_{HH} = 2.4 Hz, 6H, C_5H_4), 4.95 (m, 6H, C_5H_4), 7.17 (m, 9H, Ph), 7.92 (m, 6H, Ph). $^{13}C\{^1H\}$ NMR (125.5 MHz, C_6D_6): δ 69.9 (s, C_5H_4), 70.1 (s, C_5H_4), 73.0 (m, C_5H_4), 82.1 (m, C_5H_4), 74.1 (m, C_5H_4), 82.1 (m, C_5H_4), 128.9 (s, Ph), 135.4 (m, Ph), 140.5 (m, Ph). $^{31}P\{^1H\}$ NMR (202.1 MHz, C_6D_6): δ −35.5 (s). The elemental analysis of **3a** did not give satisfactory and reproducible results, but that of the Ag^+ complex with **3a** did, as given below.

Desulfurization of 4b. The desulfurization was carried out similarly to that for **4a** using **4b** (100 mg, 0.10 mmol), MeOTf (40 μL, 0.35 mmol), and $P(NMe_2)_3$ (65 μL, 0.36 mmol). The residue was dissolved in CH_2Cl_2, loaded on an Al_2O_3 column, and eluted with CH_2Cl_2. The first orange band was collected and dried in vacuo to give **3b** (85 mg, 94%). ^1H NMR (499.2 MHz, $CDCl_3$): δ 4.08 (br, 6H, C_5H_4), 4.32 (br, 6H, C_5H_4), 4.49 (br, 6H, C_5H_4), 4.62 (br, 6H, C_5H_4), 7.42 (m, 9H, Ph), 7.74 (m, 6H, Ph). $^{13}C\{^1H\}$ NMR (125.5 MHz, $CDCl_3$): δ 71.0 (m, C_5H_4), 71.2 (m, C_5H_4), 73.1 (m, C_5H_4), 74.2 (m, C_5H_4), 78.9 (m, C_5H_4), 128.8 (m, Ph), 130.7 (s, Ph), 134.8 (m, Ph). $^{31}P\{^1H\}$ NMR (202.1 MHz, $CDCl_3$): δ −21.7 (s, 1P), −22.8 (s, 2P). Anal. Calcd for $C_{48}H_{39}Fe_3P_3$: C, 65.79; H, 4.49. Found: C, 66.14; H, 4.71.

[Ag(3a)]OTf (5). AgOTf (35 mg, 0.14 mmol) was added to **3a** or **3b** (120 mg, 0.14 mmol) dissolved in CH_2Cl_2 (28 mL). After 30 min, the solvent was removed in vacuo. The residue was washed with ether and hexane and dried to give a yellow powder (136 mg, 88%). ^1H NMR (499.2 MHz, $CDCl_3$): δ 4.08 (br, 6H, C_5H_4), 4.32 (br, 6H, C_5H_4), 4.49 (br, 6H, C_5H_4), 4.62 (br, 6H, C_5H_4), 7.42 (m, 9H, Ph), 7.74 (m, 6H, Ph). $^{13}C\{^1H\}$ NMR (125.5 MHz, $CDCl_3$): δ 71.0 (m, C_5H_4), 71.2 (m, C_5H_4), 73.1 (m, C_5H_4), 74.2 (m, C_5H_4), 78.9 (m, C_5H_4), 128.8 (m, Ph), 130.7 (s, Ph), 134.8 (m, Ph). $^{31}P\{^1H\}$ NMR (202.1 MHz, $CDCl_3$): δ −17.3 (d-d, $^1J_{^{31}P-^{107}Ag}$ = 325 Hz, $^1J_{^{31}P-^{109}Ag}$ = 375 Hz). Anal. Calcd for $C_{49}H_{39}AgF_3Fe_3O_3P_3S$: C, 51.93; H, 3.47. Found: C, 51.67; H, 3.34.

Isomerization of the C_3 Trimer to the C_s Trimer. A toluene solution of the C_3 isomer **3a** was put into five 5 mm NMR tubes under an atmosphere of nitrogen. The tubes were transferred to an NMR probe maintained at 70, 75, 80, 85, and 90 °C, respectively, and resonances at −36.7 ppm for the isomer **3a** and those at −22.8 and −24.0 ppm for the C_s isomer **3b** were monitored periodically by ^{31}P NMR. The isomerization reactions followed reversible first-order kinetics approaching equilibrium and showed good fits to the usual plot of $-\ln\{1 - [C_s]/[C_s]_{eq}\}$ vs time. The equilibrium constant at each temperature was obtained when no further change in each spectrum was observed.

X-ray Crystallography. Slow diffusion of hexane into solutions of **3a**/$CHCl_3$, **4a**/THF, and **5**/$C_6H_4Cl_2$ gave crystals suitable for an X-ray diffraction study. They were mounted separately on glass fibers. All measurements were made on a Mac Science DIP2030 imaging plate area detector at 200 K. The data were collected to a maximum 2θ value of 55.8°. Cell parameters and intensities for the reflection were estimated using the program packages of HKL.[61] The structures were solved by direct methods and expanded using Fourier techniques. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located at ideal positions. All calculations were performed using the SHELXL-97 crystallographic software package.[62] In the crystals of **3a** and **4a**, considerably disordered solvent molecules were refined as molecules having rigid ideal structures. Three molecules of **4a** were found to be independent in the crystal, one of which lay on a crystallographic 3-fold axis. Details of data collection and refinement are given in Table 1, and bond distances and angles, atomic coordinates, and anisotropic thermal parameters are given as Supporting Information.

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Supporting Information Available: Figures giving kinetic data for the isomerization reaction from **3a** to **3b** and CIF files giving full crystallographic data for **3a**, **4a**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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