

Phosphorus-Bridged [1.1]Ferrocenophane with *syn* and *anti* Conformations

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Photolysis of PPh-bridged [1]ferrocenophane (**1**) in THF gave PPh-bridged [1.1]ferrocenophane (**2**) as a minor dimer along with major polymeric products. After subsequent sulfuration of the reaction mixture with elemental sulfur, both *syn* and *anti* isomers of P(S)Ph-bridged [1.1]ferrocenophane (**3**) were successfully isolated and characterized by X-ray analysis. *syn*-**3** thus obtained was desulfurized stereoretentively to *syn*-**2** with Si₂Cl₆ in refluxing benzene, while *anti*-**3** primarily gave the isomerized product, *syn*-**2**. Stereoretentive desulfuration of *anti*-**3** to *anti*-**2** was achieved with CF₃SO₃Me/P(NMe₂)₃ at room temperature. *anti*-**2** thus obtained could be converted almost completely to *syn*-**2** upon simple heating in toluene, indicative of the thermal instability of the *anti* isomer over the *syn* isomer. The yield of *syn*-**2** was improved from 9% to 32% when THF used in the photolysis was replaced with ether and the reaction mixture was heated so as to isomerize *anti*-**2**, which had been formed concomitantly. A potential utility of *syn*-**2** as a ligand was demonstrated by the formation of [CoCl₂(*syn*-**2**)] (**5**) through a reaction of *syn*-**2** with CoCl₂.

Introduction

[1.1]Ferrocenophanes, in which two ferrocenes are linked together via two ER_n groups (Figure 1), have been a subject of intensive study since the 1960s.^{1,2} Much attention has been paid to their peculiar molecular structures ever since the first X-ray structure was reported for 1,12-dimethyl[1.1]ferrocenophane by Watts et al.³ Many types of [1.1]ferrocenophanes bearing a variety of ER_n bridging groups have been synthesized and characterized by X-ray analysis, as listed in Table 1.⁴ Among them, heteroatom bridges such as group 13 (B, Ga),^{5,6} group 14 (Si, Sn),^{7,8} and group 15 (P)⁹ have

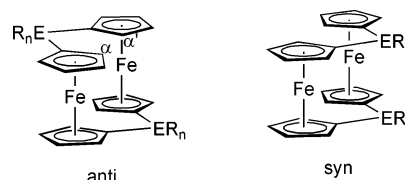


Figure 1. Two conformations of ER_n-bridged [1.1]ferrocenophane.

recently attracted interest. These ferrocenophanes take either a *syn*- or *anti*-conformation, as shown in Figure 1.

It is known that whether a [1.1]ferrocenophane adopts a *syn*- or *anti*-conformation depends on the balance of the two types of intramolecular steric repulsions in it.² One is that between the two hydrogen atoms at α - and α' -positions. Molecular models demonstrate that the

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(1) (a) Watts, W. E. *J. Am. Chem. Soc.* **1966**, *88*, 855–856. (b) Watts, W. E. *J. Organomet. Chem.* **1967**, *10*, 191–192.

(2) Mueller-Westerhoff, U. T. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 702–717.

(3) McKechnie, J. S.; Bersted, B. H.; Paul, I. C.; Watts, W. E. *J. Organomet. Chem.* **1967**, *8*, P29–P31.

(4) (a) Watanabe, M.; Sato, M.; Nagasawa, A.; Motoyama, I.; Takayama, T. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 2127–2136. (b) Ahlberg, P.; Davidsson, Ö.; Löwendahl, M.; Hilmersson, G.; Karlsson, A.; Håkansson, M. *J. Am. Chem. Soc.* **1997**, *119*, 1745–1750. (c) Löwendahl, J.-M.; Håkansson, M. *Organometallics* **1995**, *14*, 4736–4741. (d) Ahlberg, P.; Davidsson, Ö.; Hilmersson, G.; Löwendahl, M.; Håkansson, M. *J. Chem. Soc., Chem. Commun.* **1994**, 1573–1574. (e) Löwendahl, M.; Davidsson, Ö.; Ahlberg, P.; Håkansson, M. *Organometallics* **1993**, *12*, 2417–2419. (f) Håkansson, M.; Löwendahl, M.; Davidsson, Ö.; Ahlberg, P. *Organometallics* **1993**, *12*, 2841–2844. (g) Rheingold, A. L.; Mueller-Westerhoff, U. T.; Swiegers, G. F.; Haas, T. *J. Organometallics* **1992**, *11*, 3411–3417. (h) McKechnie, J. S.; Maier, C. A.; Bersted, B.; Paul, I. C. *J. Chem. Soc., Perkin Trans. 2* **1973**, 138–143.

(5) Scheibitz, M.; Winter, R. F.; Bolte, M.; Lerner, H.-W.; Wagner, M. *Angew. Chem., Int. Ed.* **2003**, *42*, 924–927.

(6) (a) Althoff, A.; Jutzi, P.; Lenze, N.; Neumann, B.; Stammler, A.; Stammler, H.-G. *Organometallics* **2003**, *22*, 2766–2774. (b) Uhl, W.; Hahn, I.; Jantschak, A.; Spies, T. *J. Organomet. Chem.* **2001**, 637–639, 300–303. (c) Jutzi, P.; Lenze, N.; Neumann, B.; Stammler, H.-G. *Angew. Chem., Int. Ed.* **2001**, *40*, 1424–1427.

(7) (a) Berenbaum, A.; Lough, A. J.; Manners, I. *Organometallics* **2002**, *21*, 4415–4424. (b) Calleja, G.; Carre, F.; Cerveau, G.; Labbe, P.; Coche-Guerente, L. *Organometallics* **2001**, *20*, 4211–4215. (c) Zechel, D. L.; Foucher, D. A.; Pudelski, J. K.; Yap, G. P. A.; Rheingold, A. L.; Manners, I. *J. Chem. Soc., Dalton Trans.* **1995**, 1893–1899. (d) Park, J.; Seo, Y.; Cho, S.; Whang, D.; Kim, K.; Chang, T. *J. Organomet. Chem.* **1995**, *489*, 23–25.

(8) (a) Jakle, F.; Rulkens, R.; Zech, G.; Foucher, D. A.; Lough, A. J.; Manners, I. *Chem. Eur. J.* **1998**, *4*, 2117–2128. (b) Clearfield, A.; Simmons, C. J.; Withers, H. P., Jr.; Seyferth, D. *Inorg. Chim. Acta* **1983**, *75*, 139–144.

(9) Brunner, H.; Klankermayer, J.; Zabel, M. *J. Organomet. Chem.* **2000**, *601*, 211–219.

Table 1. Molecular Structures Determined by X-ray Analysis for ER_n-Bridged [1.1]Ferrocenophanes

E	bridging group		conformation	E–Cp length average (Å)	ref
	R1	R2			
C	H or =O	H or non	<i>syn</i>	1.50, 1.47	4a
C	H	H	<i>syn</i>	1.504	4f
C	H	Me	<i>syn</i>	1.509	4c
C	H	Me	<i>syn</i>	1.513	4h
C	H	Me	<i>anti</i>	1.509	4e
B [−]	Me	Me	<i>syn</i>	1.651	5
P	Men	Men	<i>anti</i>	1.823	9
Si	Me	Me	<i>anti</i>	1.860	7c, 7d
Si	Cl	Cl	<i>anti</i>	1.829	7b
Si	Me	CC–R	<i>anti</i>	1.848	7a
Ga	Me	non	<i>anti</i>	1.9449	6a
Ga	Me	base ^a	<i>anti</i>	1.963 ^b	6a
Ga	CH(SiMe ₃) ₂	non	<i>anti</i>	1.933	6b
Sn	<i>n</i> -Bu	<i>n</i> -Bu	<i>anti</i>	2.136	8b
Sn	<i>t</i> -Bu	<i>t</i> -Bu	<i>anti</i>	2.142	8a
Sn	Mes	Mes	<i>anti</i>	2.146	8a

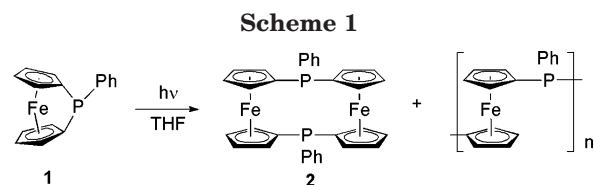
^a Base: ether, pyridine, pyrimidine, quinoxaline, pyridine, and dioxane. ^b An average value of all base adducts.

anti isomer is rigid and not able to relieve that repulsion, while the *syn* isomer is flexible and can easily twist to relieve it. The other is the repulsion between the two ER_n groups, which is conceivable only in the *syn* isomer. To take a CH₂-bridged complex in Table 1 as an example, the former repulsion in the *anti* isomer is substantial because the two CH₂ bridges form very short Cp–ER_n bonds, leading to a close approach of the α- and α'-hydrogens. In contrast, the latter repulsion in the corresponding *syn* isomer is subtle because it is practically between the hydrogen atoms of the CH₂ bridges. Therefore, the *syn*-conformation is preferable for the CH₂-bridged complex, as is actually the case (Table 1). An example that exhibits the opposite preference is an SnBu₂-bridged complex, in which the SnBu₂ bridges form fairly long Cp–ER_n bonds and have bulky butyl groups (see Table 1).

On the basis of the above perspective, a PR-bridged complex is in a delicate situation because the Cp–P bond length (ca. 1.80–1.84 Å) is in a range where the *syn*–*anti* preference is switched, as shown in Table 1. Brunner et al. have reported PMen-bridged [1.1]ferrocenophane (Men = menthyl) adopting an *anti*-conformation, but they did not mention its relative stability in comparison with the corresponding *syn* isomer, nor did they try to prepare the *syn* isomer.⁹ However, the *syn* isomer of phosphorus-bridged [1.1]ferrocenophane is worth preparing because it can be utilized as a novel bidentate chelate, which has two phosphorus donor atoms that are doubly bridged by the two ferrocene units, and thus can be expected to serve as a novel supporting ligand for metal-catalyzed transformations.

Our group has recently reported the ring-opening polymerization of PPh-bridged [1]ferrocenophane induced by UV–vis irradiation.¹⁰ In addition to polymeric products, dimers were isolated from the reaction mixture, though their yields were low. Here we report the details of their molecular structures, *syn*–*anti* preference, and coordination behavior to a metal fragment.

(10) Mizuta, T.; Onishi, M.; Miyoshi, K. *Organometallics* **2000**, *19*, 5005–5009.



Results and Discussion

Isolation of [1.1]Ferrocenophane. Phosphorus-bridged [1]ferrocenophane is known to undergo a ring-opening reaction driven by its highly strained ring structure.^{11,12} We have previously reported that the UV–vis irradiation of PhP-bridged [1]ferrocenophane, **1**, induces a ring-opening reaction to give dimer **2** as well as polymeric products, as shown in Scheme 1.¹⁰ Before the direct separation of **2** from the polymeric products, the phosphorus centers were sulfurized by a reaction with elemental sulfur in order to prevent oxidation by air. The subsequent separation using silica gel column chromatography afforded yellow and orange dimers **3** in ca. 9% yield each. The X-ray structure of the former yellow dimer is shown in Figure 2, where two ferrocene units are linked through phosphorus atoms to form a [1.1]ferrocenophane framework with a centric symmetry. The two phosphorus bridging groups are arranged in an *anti*-disposition, with two phenyl groups located at *exo*-positions. The main structural features of a [1.1]ferrocenophane molecule are usually given by four essential angles: twist, rotation, tilt, and bridge angles (see Figure 3).^{4c} The small tilt angle of 2.91(7)° for *anti*-**3** indicates that each ferrocene unit consists of almost parallel Cp rings. The twist angle also has a small value of 2.91(7)°, which is exactly the same as the tilt angle due to the centric symmetry, thereby

(11) (a) Butler, I. R.; Cullen, W. R.; Einstein, F. W. B.; Rettig, S. J.; Willis, A. J. *Organometallics* **1983**, *2*, 128–135. (b) Seyferth, D.; Withers, H. P., Jr. *Organometallics* **1982**, *1*, 1275–1282. (c) Withers, H. P., Jr.; Seyferth, D.; Fellmann, J. D.; Garrou, P. E.; Martin, S. *Organometallics* **1982**, *1*, 1283–1288. (d) Osborne, A. G.; Whiteley, R. H.; Meads, R. E. *J. Organomet. Chem.* **1980**, *193*, 345–357. (e) Stoeckli-Evans, H.; Osborne, A. G.; Whiteley, R. H. *J. Organomet. Chem.* **1980**, *194*, 91–101.

(12) For example, see: (a) Hierso, J.-C.; Lacassin, F.; Broussier, R.; Amardeil, R.; Meunier, P. *J. Organomet. Chem.* **2004**, *689*, 766–769. (b) Paquet, C.; Cyr, P. W.; Kumacheva, E.; Manners, I. *Chem. Commun.* **2004**, 234–235. (c) Mizuta, T.; Onishi, M.; Nakazono, T.; Nakazawa, H.; Miyoshi, K. *Organometallics* **2002**, *21*, 717–726. (d) Wang, X. S.; Winnik, M. A.; Manners, I. *Macromolecules* **2002**, *35*, 9146–9150. (e) Cao, L.; Massey, J. A.; Peckham, T. J.; Winnik, M. A.; Manners, I. *Macromol. Chem. Phys.* **2001**, *202*, 2947–2953. (f) Stepnicka, P.; Base, T. *Inorg. Chem. Commun.* **2001**, *4*, 682–687. (g) Cao, L.; Manners, I.; Winnik, M. A. *Macromolecules* **2001**, *34*, 3353–3360. (h) Evans, C. E. B.; Lough, A. J.; Grondy, H.; Manners, I. *New J. Chem.* **2000**, *24*, 447–453. (i) Cao, L.; Winnik, M. A.; Manners, I. *J. Inorg. Organomet. Polym.* **1998**, *8*, 215–224. (j) Herberhold, M.; Hertel, F.; Milius, W.; Wrackmeyer, B. *J. Organomet. Chem.* **1999**, *582*, 352–357. (k) Peckham, T. J.; Massey, J. A.; Honeyman, C. H.; Manners, I. *Macromolecules* **1999**, *32*, 2830–2837. (l) Honeyman, C. H.; Peckham, T. J.; Massey, J. A.; Manners, I. *J. Chem. Soc., Chem. Commun.* **1996**, 2589–2590. (m) Mizuta, T.; Yamasaki, T.; Nakazawa, H.; Miyoshi, K. *Organometallics* **1996**, *15*, 1093–1100. (n) Podlaha, J.; Stepnicka, P.; Ludvik, J.; Cisarova, I. *Organometallics* **1996**, *15*, 543–550. (o) Honeyman, C. H.; Foucher, D. A.; Dahmen, F. Y.; Rulkens, R.; Lough, A. J.; Manners, I. *Organometallics* **1995**, *14*, 5503–5512. (p) Butler, I. R.; Cullen, W. R.; Rettig, S. J.; White, A. S. C. *J. Organomet. Chem.* **1995**, *492*, 157–164. (q) Cullen, W. R.; Rettig, S. J.; Zheng, T. C. *J. Organomet. Chem.* **1993**, *452*, 97–103. (r) Butler, I. R. *Polyhedron* **1992**, *11*, 3117–3121. (s) Butler, I. R.; Cullen, W. R.; Rettig, S. J. *Organometallics* **1987**, *6*, 872–880. (t) Butler, I. R.; Cullen, W. R.; Kim, T. J.; Rettig, S. J.; Trotter, J. *Organometallics* **1985**, *4*, 972–980. (u) Butler, I. R.; Cullen, W. R.; Einstein, F. W. B.; Willis, A. C. *Organometallics* **1985**, *4*, 603–604. (v) Butler, I. R.; Cullen, W. R. *Organometallics* **1984**, *3*, 1846–1851.

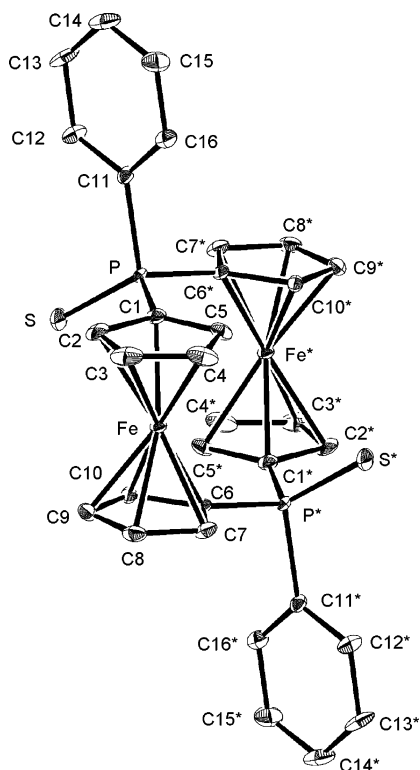


Figure 2. ORTEP drawing of *anti-3* with 50% thermal ellipsoids. Selected bond distances (Å) and angles (deg): S–P 1.9549(5), P–C1, 1.794(1), P–C6* 1.800(1), P–C11 1.824(1), S–P–C1 114.23(5), S–P–C6* 113.30(5), C1–P–C6* 110.88(6). Symmetry transformation used to generate equivalent (asterisked) atoms: $(-x, -y+1, -z)$.

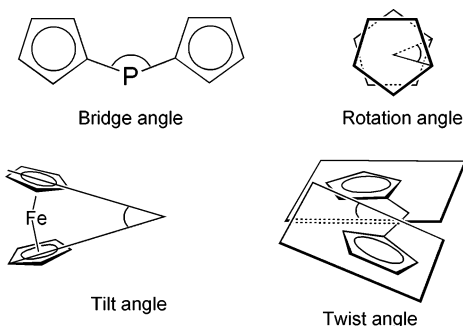


Figure 3. Description of the four essential angles in a [1.1]-ferrocenophane molecule.^{4c}

indicating the coplanarity of the two Cp rings bonding to the same phosphorus center.

A molecular structure for the other dimer **3** is shown in Figure 4, where the dimer adopts a *syn*-conformation with C_2 symmetry. A significant steric repulsion is anticipated at first glance between both sulfur atoms of *syn-3*, but actually *syn-3* avoids it by adopting a significantly large twist angle of $42.5(1)^\circ$ to sufficiently separate the sulfur atoms from each other. In addition, the two Cp rings of each ferrocene unit are tilted by $8.2(1)^\circ$ so as to enlarge the separation of the two sulfur atoms.

syn-3 thus obtained was desulfurized by treatment with Si_2Cl_6 in refluxing benzene.¹³ The ^{31}P NMR signal of the desulfurized product, **2**, was observed at -29.7

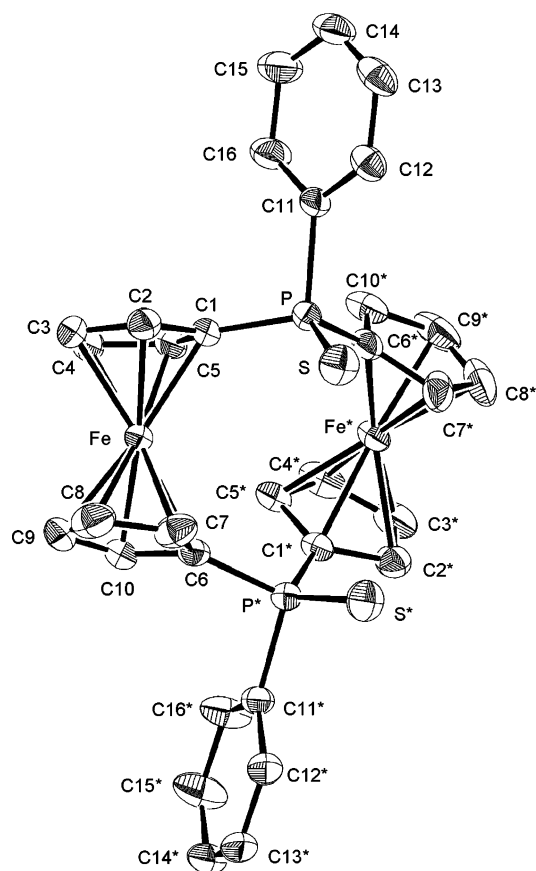


Figure 4. ORTEP drawing of *syn-3* with 50% thermal ellipsoids. Selected bond distances (Å) and angles (deg): S–P 1.9421(6), P–C1, 1.803(2), P–C6* 1.782(2), P–C11 1.825(2), S–P–C1 114.28(7), S–P–C6* 114.63(6), C1–P–C6* 109.21(8). Symmetry transformation used to generate equivalent (asterisked) atoms: $(-x, y, -z+0.5)$.

ppm. The *syn* structure of the product was confirmed by X-ray analysis, as shown in Figure 5. Similar treatment was also applied to the desulfurization of *anti-3* in the hopes of getting the corresponding *anti-2*. However, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the product showed a chemical shift almost identical to that of *syn-2*, suggesting that an *anti*-to-*syn* isomerization had taken place during the desulfurization reaction in refluxing benzene. To confirm that the product was not *anti-2* but *syn-2*, the desulfurized product of *anti-3* was sulfurized again. The $^{31}\text{P}\{^1\text{H}\}$ NMR chemical shift of the resulfurized product was found identical to that of *syn-3*. Since refluxing in benzene probably induced the isomerization, desulfurization of *anti-3* was also carried out at room temperature using $\text{CF}_3\text{SO}_3\text{Me}/\text{P}(\text{NMe}_2)_3$.¹⁴ However, because of the poor solubility of the product in the usual laboratory solvents, its spectroscopic characterization was unsuccessful as it was. Thus, the product was characterized as the resulfurized form, which turned out to give spectroscopic data identical to those of *anti-3*, demonstrating that the *anti*-conformation is retained during the present desulfurization of *anti-3*.

Improvement of the Yield of *syn-2*. The molecular structure of *syn-2* shown in Figure 5 suggests a potential utility as a novel diphosphine chelate in which two lone

(13) (a) Naumann, K.; Zon, G.; Mislow, K. *J. Am. Chem. Soc.* **1969**, *91*, 7012–7023. (b) Naumann, K.; Zon, G.; Mislow, K. *J. Am. Chem. Soc.* **1969**, *91*, 7023–7030.

(14) Omelankzuk, J.; Mikolajczyk, M. *Tetrahedron. Lett.* **1984**, *25*, 2493–2496.

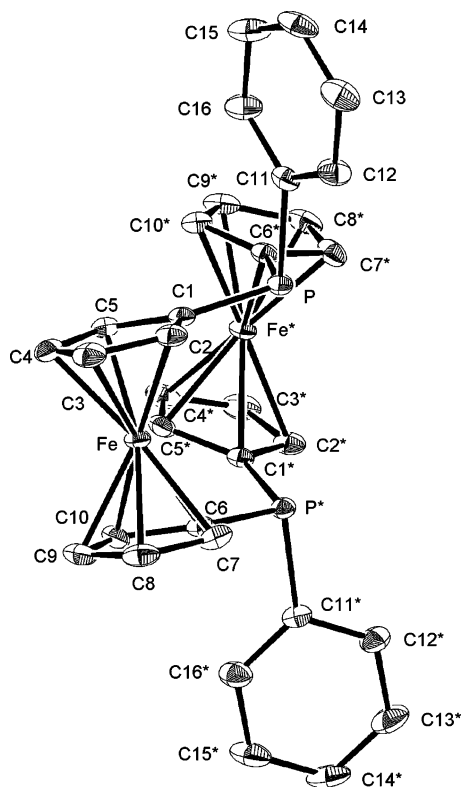
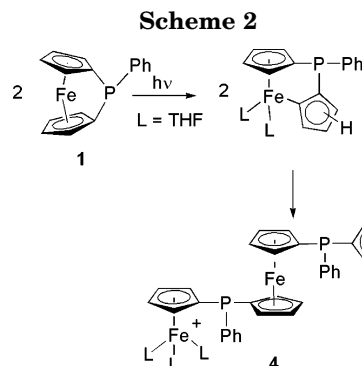


Figure 5. ORTEP drawing of *syn*-**2** with 50% thermal ellipsoids. Selected bond distances (Å) and angles (deg): P–C1, 1.826(1), P–C6* 1.810(1), P–C11 1.849(1), C1–P–C6* 105.96(6), C1–P–C11 98.29(6), C6*–P–C11 100.63(6). Symmetry transformation used to generate equivalent (asterisked) atoms: $(-x+1, y, -z+1.5)$.

pairs on the phosphorus atoms are nicely disposed for coordination to a metal. However, the yield of *syn*-**2** in the photolysis described above is too low to perform preparative scale studies. For SiR₂-bridged [1]ferrocenophane, a transition-metal-catalyzed ring-opening reaction gives [1.1]ferrocenophane in high to moderate yields.^{7a,15–17} However, the addition of a palladium(0) complex such as Pd(PPh₃)₄ to a solution of **1** did not give any desired products, probably because of the strong metal coordination expected for the starting **1** as well as for the products derived from it.

Formation of the cyclic dimer **2** from **1** is a side reaction of the polymerization (Scheme 1). We have demonstrated that the photolytic ring-opening reaction proceeds through the cleavage of the Cp–Fe bond, as shown in Scheme 2.¹⁸ The major reaction that follows is a successive intermolecular coupling between some sorts of ring-opened intermediates, leading eventually to the polymeric products. On the other hand, the dimer **2** is probably formed through an intramolecular head-to-tail ring-closure of the dimeric intermediate **4**. It is



therefore expected that high-dilution conditions may enhance the latter intramolecular ring-closure of **4**. THF in Scheme 2 acts as a strongly donating solvent that facilitates formation of the ring-opened intermediates, primarily leading to polymeric products. Conversely, if a less donating solvent is employed, formation of the ring-opened intermediates is suppressed to lead to a low concentration of the intermediate **4**, which has a greater chance of undergoing the intramolecular ring-closure of **4**. Ether was chosen as such a less donating solvent. Actually, the photolysis in ether proceeded slowly, taking a few hours for complete consumption of the starting **1**, while the reaction in THF was completed within 10 min. Separation of the sulfurized dimer following the procedures described above gave a *syn*–*anti* mixture of **3** in about 2 times the yield. In addition, the desulfurization in refluxing benzene has been confirmed to accompany the *anti*-to-*syn* isomerization. Thus, a crude mixture of *syn*- and *anti*-**2** obtained by the above modified photolysis was heated overnight in toluene at a higher temperature to further improve the yield of *syn*-**2**. In this case, without sulfurization, *syn*-**2** could be isolated directly by an Al₂O₃ column in 32% yield.

Preparation of Cobalt Complex. To explore the structural properties of *syn*-**2** coordinated to a transition metal fragment, Co(II) was selected as a tetrahedral metal center that tolerates a relatively wide range of bite angles formed by diphosphine chelates, 96.3(1)° for [CoCl₂(dppp)],¹⁹ 107.87(3)° for [CoCl₂(dppf)],²⁰ and 114.57(6)° for [CoCl₂{MeN(CH₂CH₂PPh₂)₂}].²¹

syn-**2** was allowed to react with CoCl₂ in THF to give green CoCl₂(*syn*-**2**) (**5**) in an almost quantitative yield. The molecular structure of **5** determined by X-ray analysis is shown in Figure 6, where *syn*-**2** coordinates to CoCl₂ to form a tetrahedral coordination sphere. The two phosphorus donor atoms of *syn*-**2** are doubly linked with two ferrocene units, which occupy the front and back spaces of the coordination plane defined by a CoP₂ core. The bite angle P–Co–P is 95.62(2)°, which is much smaller than the ideal tetrahedral angle of 109.5°. It is noteworthy that the bite angle of *syn*-**2** in **5** is also much smaller than the 107.87(3)° angle found in the corresponding dppf complex possessing a single ferrocene linker. For dppf coordinating to the CoCl₂ fragment, two Cp rings of the ferrocene unit are approximately eclipsed

(15) Reddy, N. P.; Choi, N.; Shimada, S.; Tanaka, M. *Chem. Lett.* **1996**, 649–650.

(16) (a) Ni, Y.; Rulkens, R.; Pudelski, J. K.; Manners, I. *Macromol. Rapid Commun.* **1995**, *16*, 637–641. (b) Zechel, D. L.; Hultsch, K. C.; Rulkens, R.; Balaishis, D.; Ni, Y.; Pudelski, J. K.; Lough, A. J.; Manners, I. *Organometallics* **1996**, *15*, 1972–1978. (c) Gomez-Elipe, P.; Resendes, R.; McDonald, P. M.; Manners, I. *J. Am. Chem. Soc.* **1998**, *120*, 8348–8356.

(17) Peckham, T. J.; Lough, A. J.; Manners, I. *Organometallics* **1999**, *18*, 1030–1040.

(18) Mizuta, T.; Imamura, Y.; Miyoshi, K. *J. Am. Chem. Soc.* **2003**, *125*, 2068–2069.

(19) dppp = 1,3-bis(diphenylphosphino)propane. Heinze, K.; Huttner, G.; Zsolnai, L.; Schober, P. *Inorg. Chem.* **1997**, *36*, 5457–5469.

(20) dppf = 1,1'-bis(diphenylphosphino)ferrocene. Park, T.-J.; Huh, S.; Kim, Y.; Jun, M.-J. *Acta Crystallogr. Sect. C* **1999**, *C55*, 848–850.

(21) Wang, M.; Yu, X.; Shi, Z.; Qian, M.; Jin, K.; Chen, J.; He, R. *J. Organomet. Chem.* **2002**, *645*, 127–133.

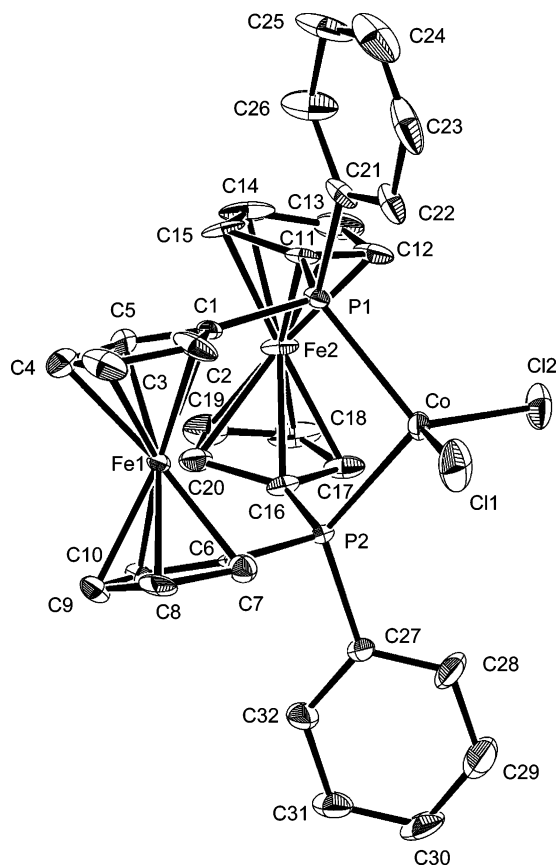
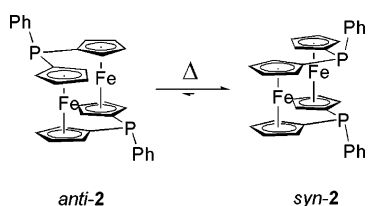


Figure 6. ORTEP drawing of **5** with 50% thermal ellipsoids. Selected bond distances (Å) and angles (deg): Co–Cl1 2.221(1), Co–Cl2 2.2381(9), Co–P1 2.3947(9), Co–P2 2.3728(9), P1–C1 1.806(3), P1–C11, 1.791(3), P1–C21, 1.818(3), P2–C6 1.775(3), P2–C16 1.793(3), P2–C27 1.820(3), P1–Co–P2 95.62(3), Cl1–Co–Cl2 111.38(4), Co–P1–C1 112.9(1), Co–P1–C11 109.3(1), Co–P1–C21 119.3(1), C1–P1–C11 107.5(2), Co–P2–C6 110.6(1), Co–P2–C16 109.8(1), C6–P2–C16 109.4(2).

Scheme 3



and tilted by 6.1° , with their spacing increasing toward the P atoms. The latter tilting in a slightly opened “clam” contributes to the bite angle being closer to the ideal tetrahedral angle. On the other hand, because the two phosphorus atoms of *syn-2* are doubly linked with the two ferrocene units, the clam-like tilting is expected to be rather difficult for *syn-2*. Actually, the two ferrocene units of **5** adopt smaller tilt angles of 3.0° and 5.7° .

***syn-anti* Preference of **2**.** *anti-2* was almost completely converted to *syn-2* upon simple heating in toluene, while *syn-2* gave a trace amount of *anti-2* under similar conditions (Scheme 3). These results indicate thermodynamic stability of *syn-2* over *anti-2*. Although the molecular structure of *anti-2* has not yet been determined, its structure is expected to be similar to that of *anti-3*. The twist, rotation, tilt, and bridge angles

Table 2. Geometrical Parameters of Phosphorus-Bridged [1.1]Ferrocenophanes

	<i>anti-3</i>	<i>syn-3</i>	<i>syn-2</i>	5	
Angles (deg)					
bridge angle	110.88(6)	109.21(8)	105.96(6)	107.5(2)	109.4(2)
twist angle	2.91(7)	42.47(10)	24.81(7)	21.1(2)	20.9(2)
tilt angle	2.91(7)	8.2(1)	3.68(7)	3.0(2)	5.7(2)
rotation angle	50.3	−34.8	−17.6	16.1	−10.4
Distances (Å)					
C(Cp)–P ^a	1.797	1.793	1.818	1.791	
H(C5)⋯H(C10 [*]) ^{b,c}	1.82	2.49	2.05	1.95 ^d	2.05 ^e
H(C5)⋯H(C5 [*]) ^{b,c}		2.08	2.22	2.36 ^f	
P⋯P ^{*c}	4.847(1)	4.623(1)	3.758(1)	3.532(1)	

^a An average value. ^b Distances are estimated assuming an ideal geometry with a C–H length of 1.08 Å. ^c Symmetry transformations used to generate equivalent (asterisked) atoms: (−*x*, −*y*+1, −*z*) for *anti-3*, (−*x*, *y*, −*z*+0.5) for *syn-3*, and (−*x*+1, *y*, −*z*+1.5) for *syn-2*. ^d A distance between H(C5) and H(C15). ^e A distance between H(C10) and H(C20). ^f A distance between H(C5) and H(C20).

of *anti-3* and of *syn-2* are given in Table 2. The small twist angle of $2.91(7)^\circ$ for *anti-3* indicates that the two Cp rings bound to the same phosphorus bridge are almost coplanar, with the two α -H(Cp) atoms, H(C5) and H(C10^{*}), being in close proximity. Moreover, the short C(Cp)–bridge distance of 1.797 Å also contributes to their short H(C5)⋯H(C10^{*}) separation of 1.82 Å, which suggests a substantial steric repulsion present between them.^{4,22–24}

On the other hand, *syn-2* adopts a wider twist angle of $24.81(7)^\circ$ and therefore has a longer α -H⋯ α -H distance of 2.05 Å, leading in turn to a smaller H⋯H repulsion than that of *anti-2*. In addition, the steric repulsion between the two PPh bridging groups is expected to be small in *syn-2* because their *endo*-positions are occupied with lone pairs (see Figure 5), the bulkiness of which is negligible from a stereochemical point of view, though with a slight electrostatic repulsion being anticipated between the lone pairs.^{25,26} Consequently, the observed thermodynamic preference of *syn-2* over *anti-2* can be understood rationally.

The conversion of *anti-2* to *syn-2* proceeds upon heating, while the *syn-anti* interconversion is reported to be very rapid for the CH₂-bridged [1.1]ferrocenophane at room temperature.^{23,24} The energy barrier for the latter is estimated to be 28 kJ/mol by low-temperature NMR measurements,²⁴ and it is supported by a molecular mechanics calculation.²³ On the other hand, for the conversion of *anti-2* to *syn-2*, one of the two phosphorus centers must invert its configuration, as shown in Scheme 3. An energy barrier for the inversion of a trivalent phosphorus center is reported to be ca. 125–146 kJ/mol,²⁷ which is responsible for the prolonged heating necessary for the *anti-2* to *syn-2* conversion.

(22) Karlsson, A.; Löwendahl, M.; Hilmersson, G.; Davidsson, Ö.; Ahlberg, P. *J. Phys. Org. Chem.* **1996**, *9*, 436–438.

(23) Rudzinski, J. M.; Osawa, E. *J. Phys. Org. Chem.* **1993**, *6*, 107–112.

(24) Löwendahl, M.; Davidsson, Ö.; Ahlberg, P. *J. Chem. Res., Synop.* **1993**, 40–41.

(25) Sztaray, B.; Szalay, P. G. *J. Am. Chem. Soc.* **1997**, *119*, 11926.

(26) Becker, G.; Golla, W.; Grobe, J.; Klinkhammer, K. W.; Le Van, D.; Maulitz, A. H.; Mundt, O.; Oberhammer, H.; Sachs, M. *Inorg. Chem.* **1999**, *38*, 1099.

(27) Quin, L. D. *A Guide to Organophosphorus Chemistry*; John Wiley & Sons: New York, 2000; pp 272–306.

Experimental Section

General Remarks. All reactions were carried out under an atmosphere of dry nitrogen using Schlenk tube techniques. All solvents were dried and purified by distillation: CH₂Cl₂ was distilled from P₂O₅; benzene, toluene, ether, and THF were distilled from sodium/benzophenone; and hexane was distilled from sodium metal. These purified solvents were stored under an N₂ atmosphere. Other reagents were used as received. PPh-bridged [1]ferrocenophane **1** was prepared according to previously described methods.^{9d,12l,28}

NMR spectra were recorded on a JEOL LA-300 spectrometer. ¹H and ¹³C NMR chemical shifts were reported relative to Me₄Si and were determined by reference to the residual solvent peaks. ³¹P NMR chemical shifts are reported relative to H₃PO₄ (85%), which was used as an external reference. Elemental analyses were performed with a Perkin-Elmer 2400CHN elemental analyzer.

Photolysis was carried out with Pyrex-glass-filtered emission from a 400 W mercury arc lamp (Riko-Kagaku Sangyo UVL-400P). The emission lines (nm) used and their relative intensities (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).

Preparation of Sulfurized Dimers *anti*-3 and *syn*-3. A solution of **1** (508 mg, 1.74 mmol) in THF (40 mL) was irradiated with a mercury arc lamp. To the suspension thus obtained was added elemental sulfur (276 mg). After the suspension was stirred for a day, the solvent was removed. The oily residue was dissolved in CH₂Cl₂ and loaded into a silica gel column (3 cm i.d. × 18 cm). Elution with CH₂Cl₂ gave light yellow *anti*-3 as the first band and orange *syn*-3 as the third band. After the solvent was removed in vacuo, *anti*-3 (52 mg, 9%) and *syn*-3 (52 mg, 9%) were obtained from their respective fractions.

***anti*-3.** ¹H NMR (300.4 MHz, CDCl₃): δ 4.54 (br, 4H, fc), 4.79 (br, 4H, fc), 4.92 (br, 4H, fc), 5.56 (br, 4H, fc), 7.13–7.23 (m, 6H, Ph), 7.46 (m, 4H, Ph). ¹³C{¹H} NMR (75.45 MHz, CDCl₃): δ 71.8 (d, *J*_{PC} = 11 Hz, fc), 73.5 (d, *J*_{PC} = 9 Hz, fc), 73.8 (d, *J*_{PC} = 15 Hz, fc), 74.7 (d, *J*_{PC} = 9 Hz, fc), 78.9 (d, *J*_{PC} = 97 Hz, *ipso*-fc), 128.0 (d, *J*_{PC} = 12 Hz, Ph), 129.4 (d, *J*_{PC} = 11 Hz, Ph), 130.2 (d, *J*_{PC} = 3 Hz, Ph). ³¹P{¹H} NMR (121.5 MHz, in CDCl₃): δ 40.5. Anal. Calcd for C₃₂H₂₆Fe₂P₂S₂: C, 59.28; H, 4.04. Found: C, 59.36; H, 3.75.

***syn*-3.** ¹H NMR (300.4 MHz, CDCl₃): δ 4.56 (br, 4H, fc), 4.67 (br, 8H, fc), 5.42 (br, 4H, fc), 7.15–7.30 (m, 6H, Ph), 7.40 (m, 4H, Ph). ¹³C{¹H} NMR (75.45 MHz, CDCl₃): δ 71.6 (d, *J*_{PC} = 11 Hz, fc), 72.0 (d, *J*_{PC} = 9 Hz, fc), 74.9 (d, *J*_{PC} = 11 Hz, fc), 76.7 (d, *J*_{PC} = 11 Hz, fc), 79.4 (d, *J*_{PC} = 97 Hz, *ipso*-fc), 128.0 (d, *J*_{PC} = 12 Hz, Ph), 129.8 (d, *J*_{PC} = 11 Hz, Ph), 130.3 (d, *J*_{PC} = 3 Hz, Ph), 139.3 (d, *J*_{PC} = 88 Hz, *ipso*-Ph). ³¹P{¹H} NMR (121.5 MHz, in CDCl₃): δ 37.7. Anal. Calcd for C₃₂H₂₆Fe₂P₂S₂: C, 59.28; H, 4.04. Found: C, 58.84; H, 3.80.

Desulfurization of *syn*-3. An excess amount of Si₂Cl₆ was added to *syn*-3 (125 mg, 0.193 mmol) dissolved in benzene (100 mL). The mixture was refluxed for a day, then cooled to room temperature, and a 30% aqueous NaOH solution (20 mL) was added. The organic layer was washed with water, then dried over anhydrous magnesium sulfate and filtered. The solvent was removed, and the residue was recrystallized from CH₂Cl₂/hexane. The product was washed with hexane and ether and then dried in vacuo to give yellow *syn*-2 (96 mg, 85%). ¹H NMR (300.4 MHz, CDCl₃): δ 4.42 (br, 4H, fc), 4.46 (br, 4H, fc), 4.57 (br, 4H, fc), 4.80 (br, 4H, fc), 7.10 (m, 6H, Ph), 7.18–7.24 (m, 4H, Ph). ¹³C{¹H} NMR (75.45 MHz, CDCl₃): δ 70.8 (s, fc), 71.1 (d, *J*_{PC} = 4 Hz, fc), 72.0 (s, fc), 75.3 (t, *J*_{PC} = 18 Hz, fc), 127.8 (s, Ph), 127.9 (t, *J*_{PC} = 3 Hz, Ph), 131.6 (t, *J*_{PC} = 11 Hz, Ph). ³¹P{¹H} NMR (121.5 MHz, in CDCl₃): δ –29.7. Anal.

Table 3. Crystallographic Data

	<i>anti</i> -3	<i>syn</i> -3
formula	C ₃₂ H ₂₆ Fe ₂ P ₂ S ₂	C ₃₂ H ₂₆ Fe ₂ P ₂ S ₂
cryst color, habit	orange, plate	orange, plate
cryst syst	triclinic	monoclinic
space group	P1 (#2)	C2/c (#15)
<i>a</i> (Å)	7.7460(2)	11.729(3)
<i>b</i> (Å)	8.6840(4)	12.655(3)
<i>c</i> (Å)	10.7830(4)	19.330(4)
α (deg)	72.269(2)	
β (deg)	80.518(3)	104.86(2)
γ (deg)	75.220(2)	
<i>V</i> (Å ³)	665.03(4)	2773.0(10)
<i>Z</i>	1	4
temp (K)	200	300
μ(Mo Kα) (cm ⁻¹)	13.90	13.33
diffractometer	MacScience DIP2030 Imaging Plate	MacScience MXC3-κ
no. of reflns		
measd	2917	4470
obsd	2830	3355
(<i>I</i> > 3.00σ(<i>I</i>))		
no. variables	225	225
<i>p</i> -factor	0.1050	0.0670
residuals ^a :	0.025; 0.054	0.029; 0.043
<i>R</i> ^b , <i>R</i> _w ^c		
largest diff peak/ hole (e/Å ³)	0.28/–0.45	0.45/–0.24
	<i>syn</i> -2	5
formula	C ₃₂ H ₂₆ Fe ₂ P ₂	C ₃₅ H ₃₂ CoCl ₅ Fe ₂ P ₂
cryst color, habit	yellow, plate	green, cubic
cryst syst	monoclinic	monoclinic
space group	C2/c (#15)	P2 ₁ / <i>n</i> (#14)
<i>a</i> (Å)	24.5570(3)	11.4290(1)
<i>b</i> (Å)	6.1060(1)	17.2090(2)
<i>c</i> (Å)	19.1840(3)	18.3380(1)
α (deg)		
β (deg)	121.140(1)	102.922(1)
γ (deg)		
<i>V</i> (Å ³)	2462.05(7)	3515.41(6)
<i>Z</i>	4	4
temp (K)	200	200
μ(Mo Kα) (cm ⁻¹)	13.28	17.76
diffractometer	MacScience DIP2030 Imaging Plate	MacScience
no. of reflns		
measd	3184	8080
obsd	2748	7358
(<i>I</i> > 3.00σ(<i>I</i>))		
no. variables	216	425
<i>p</i> -factor	0.1020	0.2000
residuals ^a :	0.029; 0.052	0.055; 0.139
<i>R</i> ^b , <i>R</i> _w ^c		
largest diff peak/ hole (e/Å ³)	0.38/–0.48	1.11/–0.79

^a Function minimized: $\sum w(|F_o| - |F_c|)^2$ where $w = 1/[\sigma^2(F_o)] = [\sigma_c^2(F_o) + p^2 F_o^2/4]^{-1}$. $\sigma_c(F_o)$ = esd based on counting statistics, *p* = *p*-factor. ^b $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^c $R_w = [(\sum w(|F_o| - |F_c|)^2) / \sum w F_o^2]^{1/2}$.

Calcd for C₃₂H₂₆Fe₂P₂: C, 65.79; H, 4.49. Found: C, 65.53; H, 4.78.

Desulfurization of *anti*-3 with Si₂Cl₆. *anti*-3 (129 mg, 0.199 mmol) was treated similarly with Si₂Cl₆ in the manner described for *syn*-3 to give a yellow product. The spectroscopic data of the product were identical to those of *syn*-2, indicating that the major product is *syn*-2 (91 mg, 78%).

Desulfurization of *anti*-3 with CF₃SO₃Me/P(NMe₂)₃. To *anti*-3 (244 mg, 0.376 mmol) dissolved in CH₂Cl₂ (30 mL) was added CF₃SO₃Me (120 μL, 1.06 mmol). The mixture was stirred for 3 h at room temperature. The volatiles were removed in vacuo. Next, P(NMe₂)₃ (170 μL, 0.935 mmol) was again added to the residue dissolved in CH₂Cl₂ at room temperature. The mixture was stirred for 3 h, and the volatiles were then

(28) Seyferth, D.; Withers, H. P., Jr. *J. Organomet. Chem.* **1980**, *185*, C1.

removed in vacuo. The residue was washed with CH_2Cl_2 /ether and with pure ether and dried in vacuo to give *anti-2* (214 mg, 97.4%). Anal. Calcd for $\text{C}_{32}\text{H}_{26}\text{Fe}_2\text{P}_2$: C, 65.79; H, 4.49. Found: C, 65.74; H, 4.83.

Since the product was almost insoluble in common organic solvents, spectroscopic data could not be obtained at all. Its characterization was therefore performed as the sulfide of *anti-2*. *anti-2* suspended in CH_2Cl_2 was treated with excess sulfur. After stirring, the solution became homogeneous. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of this solution gave only one singlet at 40.5 ppm, which was identical to that of the starting *anti-3*.

Improved Method for the Synthesis of *syn-2*. A solution of **1** (972 mg, 3.33 mmol) in ether (100 mL) was irradiated with a mercury arc lamp for 3 h. The precipitate was washed with toluene/ether (1:2) and then dried in vacuo. The product suspended in toluene (80 mL) was refluxed overnight. After the solvent was removed in vacuo, the residue was dissolved in CH_2Cl_2 and then loaded into an Al_2O_3 column. *syn-2* eluted with CH_2Cl_2 was collected, and the solvent was removed in vacuo to give *syn-2* as a yellow powder (314 mg, 32%).

Preparation of Cobalt Complex with *syn-2*. *syn-2* (354 mg, 0.606 mmol), CoCl_2 (98 mg, 0.755 mmol), and THF (30 mL) were placed into a Schlenk tube and stirred for 1 day. The green precipitate formed was washed with THF and ether and then dried in vacuo to give $\text{CoCl}_2(\textit{syn-2})$ (417 mg, 96%). Anal. Calcd for $\text{C}_{32}\text{H}_{26}\text{Cl}_2\text{CoFe}_2\text{P}_2$: C, 53.83; H, 3.67. Found: C, 53.45; H, 3.37.

X-ray Crystallography. A suitable crystal was mounted on a glass fiber for *syn-2*, *syn-3*, *anti-3*, and **5**. Measurements were made on a Mac Science DIP2030 imaging plate area detector for *syn-2*, *anti-3*, and **5** and on a Mac Science MXC3- κ for *syn-3*. The data were collected to a maximum 2θ value of

55° for *syn-2*, *anti-3*, and **5** and 60° for *syn-3*. Cell parameters and intensities for the reflection were estimated using the program packages of MacDENZO.²⁹ The structure was solved by direct methods and expanded using Fourier techniques. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included for all crystals and refined except for **5**. All calculations were performed using the teXsan crystallographic software package from the Molecular Structure Corporation.³⁰ Crystal data and refinement details are summarized in Table 3.

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Supporting Information Available: Tables giving bond lengths and angles, and positional and thermal parameters for *syn-2*, *syn-3*, *anti-3*, and **5**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(29) Gewirth, D. (with the cooperation of the program authors Otwinowski, Z. and Minor, W.) *MacDENZO* in The MacDenzo Manual-A Description of the Programs DENZO, XDISPLAYF, and SCALEPACK; Yale University: New Haven, CT, 1995.

(30) *teXsan*, Single-Crystal Structure Analysis Software, Version 1.6; Molecular Structure Corporation: The Woodlands, TX, 1993.