Stereoselective Synthesis and Coordination Behavior of Phosphorus-Bridged [1.1]Ferrocenophanes

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Chlorination with HCl of a mixture of *syn*- and *anti*-P(NEt_2)-bridged [1.1]ferrocenophane **3** derived from [Fe{(η^5-C_5H_4)PCl(NEt_2)}$_2$] **2** accompanied facile *anti*-to-*syn* conversion to give the *syn* isomer of PCl-bridged [1.1]ferrocenophane *syn*-**4** selectively in 90% yield, and treatment of *syn*-**4** with PhLi, Me_3SiCH_2Li, or *p*-TolMgBr afforded the corresponding diarylated or dialkylated compounds *syn*-**5** to *syn*-**7**. Reactions of *syn*-**5** with [$PdCl_2$(COD)], [$PdMe_2$(TMEDA)], and $NiCl_2$ gave respectively four-coordinate [$PdCl_2$(*syn*-**5**)], [$PdMe_2$(*syn*-**5**)], and [$NiCl_2$(*syn*-**5**)] complexes, the former two of which had a distorted square-planar structure with the latter adopting a tetrahedral geometry. In addition, *syn*-**5** acted as a bridging ligand toward piano-stool Mn carbonyl complex fragments to give a novel dinuclear complex, [{Cp′Mn(CO)$_2$}$_2$(μ-*syn*-**5**)] (Cp′ = $C_5H_4CH_3$).

Introduction

Diphosphines have been widely used as a common chelate ligand in transition-metal complexes. Most of them reported so far are those whose two P atoms are linked with a single chain. On the other hand, such double-chained diphosphines as shown in Figure 1 are considerably limited in number,[1−3] although they are expected to have some significant structural effects on the metal complex formation. For example, they may coordinate to a transition metal more tightly through the double chelate effect. In addition, each P atom has one substituent R forced to reside at the front side of the metal center (Figure 1), and therefore, elaborate structural modulations are possible around the metal center with various R groups. Furthermore, the chelate chains, if they carry bulky substituent(s), will act as protecting groups against the axial coordination to the metal.

Several metal complexes with double-chained diphosphines have been synthesized so far and characterized by X-ray analysis.[1,4] However, such diphosphines are usually obtained as a mixture of two stereoisomers (*syn*- and *anti*-forms, see Chart 1). It is noteworthy in this respect that stereoselective synthetic methods have been developed for 1,*n*-diphosphacycloalkanes by Alder et al.[3] and for 1,5,3,7-diazadiphosphacyclooctane derivatives by Karasik et al.[1a−c]

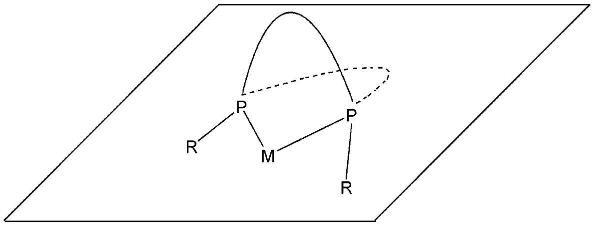
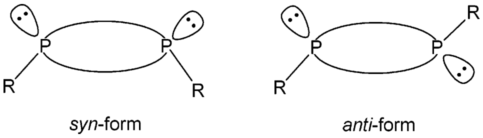


Figure 1. Schematic representation of a double-chained diphosphine and its metal complex fragment.

Chart 1



We reported previously that P-bridged [1.1]ferrocenophane, one of the double-chained diphosphines, was obtained as a byproduct in photoinduced oligomerization of P-bridged [1]-ferrocenophane.[5] It has two P atoms linked doubly with two 1,1′-ferrocenediyl moieties, and its *anti* isomer isomerizes upon heating to the *syn* isomer, useful as a bidentate chelate. In this paper, we report an alternative and stereoselective synthetic route designed rationally to the double-chained P-bridged [1.1]-ferrocenophanes having various substituents on the P atoms, and their coordination behavior to metal fragments is also reported.

Results and Discussion

Synthesis and Characterization of P(NEt_2)-Bridged [1.1]-Ferrocenophane, *anti*- and *syn*-3. The synthetic route to P-bridged [1.1]ferrocenophanes is shown in Schemes 1 and 2. It is sensible to introduce an NEt_2 group on each P atom in advance, since the P−NEt_2 group is readily converted to the

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(1) (a) Karasik, A. A.; Bobrov, S. V.; Nikonov, G. N.; Pisarevskii, A. P.; Litvinov, I. A.; Dokuchaev, A. S.; Struchkov, Y. S.; Enikeev, K. M. *Russ. J. Coord. Chem.* **1995**, *21*, 551−561. (b) Karasik, A. A.; Krashilina, A. V.; Gubaidullin, A. T.; Litvinov, I. A.; Cherkasov, V. K.; Sinyashin, O. G.; Abakumov, G. A. *Russ. Chem. Bull.* **2000**, *49*, 1782−1788. (c) Karasik, A. A.; Naumov, R. N.; Sinyashin, O. G.; Belov, G. P.; Novikova, H. V.; Lönnecke, P.; Hay-Hawkins, E. *J. Chem. Soc., Dalton Trans.* **2003**, 2209−2214. (d) Kane, J. C.; Wong, E. H.; Yap, G. P.; Rheingold, A. L. *Polyhedron* **1999**, *18*, 1183−1188.

(2) (a) Brooks, P. J.; Gallagher, M. J.; Sarroff, A.; Bowyer, M. *Phosphorus, Sulfur Silicon* **1989**, *44*, 235−247. (b) Toto, S. D.; Arbuckle, B. W.; Bharadwaj, P. K.; Doi, J. T.; Musker, W. K. *Phosphorus, Sulfur Silicon* **1991**, *56*, 27−38.

(3) Alder, R. W.; Ganter, C.; Gil, M.; Gleiter, R.; Harris, C. J.; Harris, S. E.; Lange, H.; Orpen, A. G.; Taylor, P. N. *J. Chem. Soc., Perkin Trans. 1* **1998**, 1643−1655.

(4) (a) Cucciolito, M. E.; Felice, V. D.; Orabona, I.; Panunzi, A.; Ruffo, F. *Inorg. Chim. Acta* **2003**, *343*, 209−216. (b) Arbuckle, B. W.; Musker, W. K. *Polyhedron* **1991**, *10*, 415−419.

(5) (a) Mizuta, T.; Imamura, Y.; Miyoshi, K.; Yorimitsu, H.; Oshima, K. *Organometallics* **2005**, *24*, 990−996. (b) Mizuta, T.; Onishi, M.; Miyoshi, K. *Organometallics* **2000**, *19*, 5005−5009. (c) Mizuta, T.; Imamura, Y.; Miyoshi, K. *J. Am. Chem. Soc.* **2003**, *125*, 2068−2069.

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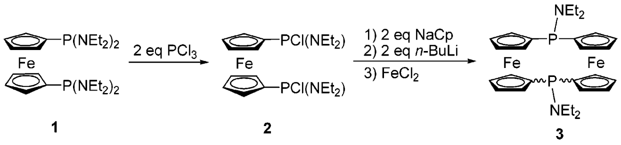
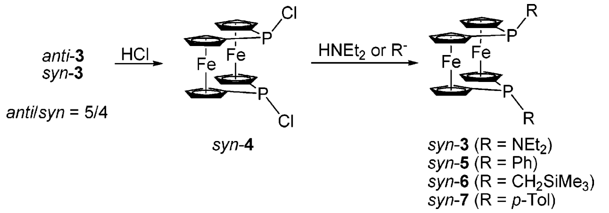
Scheme 1



Scheme 2



P−Cl group, with which various R groups are in turn introduced on the P atoms. The starting material chosen is thus the ferrocene derivative **1**, having a $P(NEt_2)_2$ group on each C_5H_4 ring. The reaction of **1** with PCl_3 yielded the dichlorinated compound **2** as a mixture of diastereomers. Compound **2** thus obtained was then allowed to react with NaCp to connect each P atom with a ferrocenediyl fragment, followed by deprotonation with *n*-BuLi, and then complexation with $FeCl_2$ was performed to obtain **3**. In the $^{31}P\{^1H\}$ NMR spectrum of **3**, two signals were observed at 43.6 and 41.9 ppm in an intensity ratio of ca. 5:4, indicating the presence of two types of phosphorus compounds. Repeated recrystallization yielded a small amount of the pure major product, X-ray analysis of which revealed it to be $P(NEt_2)$-bridged [1.1]ferrocenophane with an *anti* conformation, *anti*-**3** (Figure 2). Comparison of the NMR data indicates that the minor product is a *syn* isomer of **3** (*syn*-**3**). Since isolation of *syn*-**3** from the mixture was unsuccessful, it was characterized finally on the basis of spectroscopic data of pure *syn*-**3** prepared separately from *syn*-**4** in Scheme 2 (vide infra). A $^{13}C\{^1H\}$ NMR spectrum of *syn*-**3** showed a characteristic virtual coupling due to a through-space coupling of the two P centers in close proximity;[3,6] four of the five C_5H_4-carbon signals each appeared as a virtual triplet and the remaining one a singlet, whereas *anti*-**3** showed three doublets, one singlet, and one triplet due to its five C_5H_4 carbons.

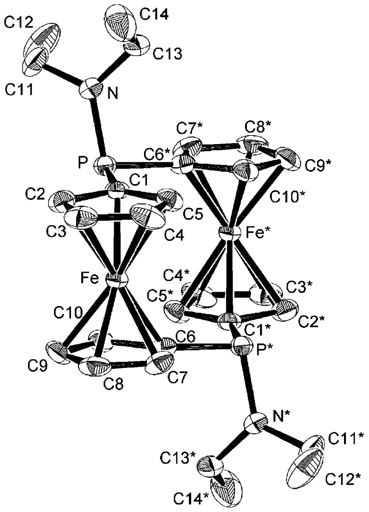


Figure 2. ORTEP drawing of *anti*-**3** with 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): P−N 1.694(2), P−C(1) 1.814(2), P−C(6*) 1.831(2), N−P−C(1) 100.75(10), N−P−C(6*) 101.53(9), C(1)−P−C(6*) 106.04(9). Symmetry transformation used to generate equivalent (asterisked) atoms: $(-x + 1.5, -y + 0.5, -z)$.

Crystal Structure of *anti*-3. The molecular structure of *anti*-**3** is shown in Figure 2, where two ferrocenediyl units are linked through two $P(NEt_2)$ bridging groups to form a [1.1]ferrocenophane framework with an *anti* conformation. Each half of the molecule is related by an inversion center. The twist angle, i.e., the dihedral angle between the two C_5H_4 planes connected to the same P atom, is 2.43(10)°, and so the two C_5H_4 planes are nearly coplanar. Similar small twist angles are observed for most of the *anti* isomers of heteroatom-bridged [1.1]ferrocenophanes known to date,[7] indicating that coplanarity of the two C_5H_4 rings is an inherent property of the *anti* isomers. The bridge angle of the two ferrocene units, i.e., the angle of C(1)−P(1)−C(6*), is 106.04(9)°, close to a tetrahedral angle. The P···P distance of 4.88 Å is too large for the through-space P−P coupling to emerge.

Synthesis and Characterization of PR-Bridged [1.1]Ferrocenophane. The reaction of a mixture of *anti*-**3** and *syn*-**3** with HCl in THF gave PCl-bridged [1.1]ferrocenophane **4** in 90% yield (Scheme 2). The ^1H NMR spectrum of **4** showed only four signals assignable to the C_5H_4 ring protons. In the $^{13}C\{^1H\}$ NMR spectrum, the signal of the *ipso*-C_5H_4 carbon atoms appeared as a virtual triplet with $J = 17$ Hz, indicating that the *syn* isomer of **4** (*syn*-**4**) was obtained selectively with accompanying *anti*-to-*syn* conversion. In the case of **5** (Scheme 2) reported previously, the *anti* isomer was also converted upon heating to the more stable *syn* isomer,[5a] while the *anti*-to-*syn* conversion of **4** took place readily at room temperature. Humbel et al. reported that the presence of a catalytic amount of HCl brings about a facile inversion of R^1R^2PCl at room temperature.[8] Therefore, it is highly plausible that HCl not only substitutes the NEt_2 group with the Cl atom but also catalyzes the *anti*-to-*syn* conversion, to give *syn*-**4** exclusively.

The chloride derivative *syn*-**4** is a useful precursor of P-bridged [1.1]ferrocenophanes bearing various substituents on the P atoms. For example, reactions of *syn*-**4** with $HNEt_2$, PhLi, Me_3SiCH_2Li, or *p*-TolMgBr yielded the expected diphosphines *syn*-**3**, *syn*-**5**, *syn*-**6**, and *syn*-**7**, respectively (Scheme 2). Their characterization was achieved by multinuclear NMR spectroscopy. In particular, their conformations were readily determined by $^{13}C\{^1H\}$ NMR spectroscopy. For *syn*-**6**, for example, the signal of the *ipso*-C_5H_4 carbon atoms was observed as a virtual triplet with $J = 7$ Hz, confirming its *syn* conformation. Both *syn*-**5**[5a] and *syn*-**7** behaved similarly; so did *syn*-**3** and *syn*-**4** as mentioned earlier.

Coordination Behavior of Phosphorus-Bridged [1.1]Ferrocenophane. The *syn* isomer of P-bridged [1.1]ferrocenophane is a double-chained diphosphine that has substituents R forced to reside in the coordination plane in Figure 1, when it binds as a bidentate ligand to a metal M. This structural characteristic is expected to bring about a peculiar steric effect on the metal complex formation with it. Then, reactions of some metal complexes were examined with PPh-bridged [1.1]ferrocenophane *syn*-**5** as a prototype, whose molecular structure has been already established.[5a]

Pd Complexes. The reaction of *syn*-**5** with $[PdCl_2(COD)]$[9] or $[PdMe_2(TMEDA)]$[9] at room temperature gave $[PdCl_2($*syn*-**5**$)]$ (**8**) or $[PdMe_2($*syn*-**5**$)]$ (**9**) (Scheme 3), both of which were characterized by X-ray analysis as shown in Figure 3. The selected bond distances and angles are listed in Table 1.

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(6) (a) Kilian, P.; Slawin, A. M. Z.; Woollins, J. D. *Chem. Eur. J.* **2003**, *9*, 215−222. (b) Karaçar, A.; Freytag, M.; Jones, P. G.; Bartsch, R.; Schmutzler, R. *Z. Anorg. Allg. Chem.* **2001**, *627*, 1571−1581.

(7) Ref 5a and references therein.

(8) Humbel, S.; Bertrand, C.; Darcel, C.; Bauduin, C.; Jugé, S. *Inorg. Chem.* **2003**, *42*, 420−427.

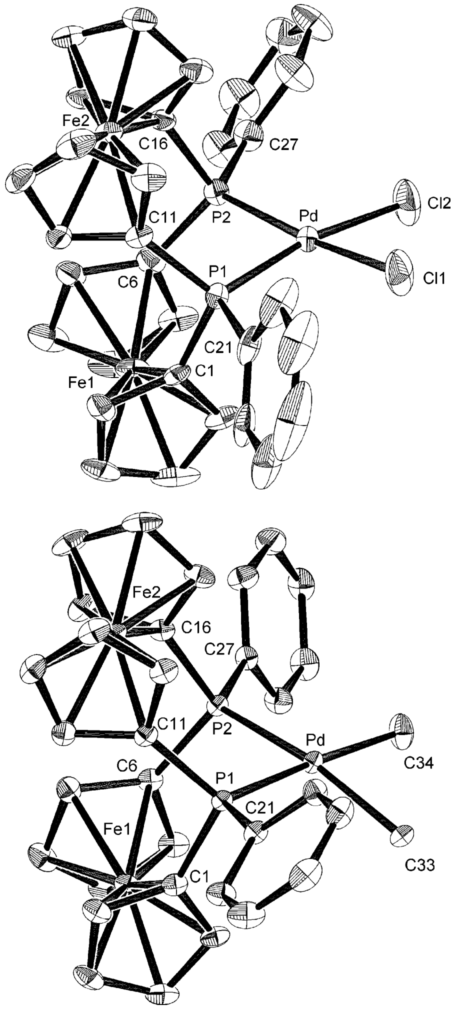
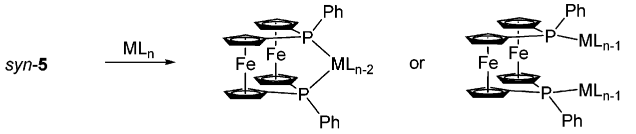


Figure 3. ORTEP drawings of **8** (top) and **9** (bottom) with 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

Scheme 3



8 (ML$_{n-2}$ = PdCl$_2$)
9 (ML$_{n-2}$ = PdMe$_2$)
10 (ML$_{n-2}$ = NiCl$_2$)

11 (ML$_{n-1}$ = Cp'Mn(CO)$_2$)

Complexes **8** and **9** both have a distorted square-planar structure around a Pd center; **8** has a dihedral angle of 11.3° between the PdP$_2$ and PdCl$_2$ planes, and **9** has one of the Me groups deviating by 0.49 Å from a least-squares plane of PdP$_2$C, leading to the corresponding dihedral angle of 13.0°. In addition, the distance (2.185(2) Å) from the Pd center to the deviating Me group (C33) is considerably larger than that (2.115(2) Å) to the other Me group (C34) in **9**. These distortions are no doubt ascribed to the steric repulsion between the Ph groups and Cl or Me ligands.

Table 1. Selected Bond Distances (Å) and Angles (deg) for 8, 9, and 10

	8	**9**^{a}	**10** Ni(1)	**10**^{b} Ni(2)
M−P(1)	2.2886(9)	2.3518(5)	2.3133(13)	2.2782(13)
M−P(2)	2.3016(9)	2.3222(5)	2.3126(13)	2.3016(13)
M−X(1)	2.331(1)	2.185(2)	2.2315(14)	2.2087(16)
M−X(2)	2.328(1)	2.115(2)	2.2098(15)	2.2167(14)
P(1)−M−P(2)	92.29(3)	91.77(2)	93.85(4)	93.20(5)
X(1)−M−X(2)	88.73(5)	83.66(9)	119.52(6)	119.55(6)
P(1)−M−X(1)	88.25(4)	91.91(5)	103.15(5)	106.28(6)
P(1)−M−X(2)	170.28(5)	175.46(7)	115.12(5)	111.39(6)
P(2)−M−X(1)	173.19(5)	166.61(5)	119.47(6)	116.56(6)
P(2)−M−X(2)	91.80(4)	92.76(7)	103.26(5)	106.73(6)
twist angle	27.2(2) 25.9(2)	22.0(1) 23.2(1)	9.23(16) 9.61(16)	18.89(21) 20.19(22)

[a] X(1) = C(33), X(2) = C(34). [b] P(1) = P(3), P(2) = P(4), X(1) = Cl(3), X(2) = Cl(4).

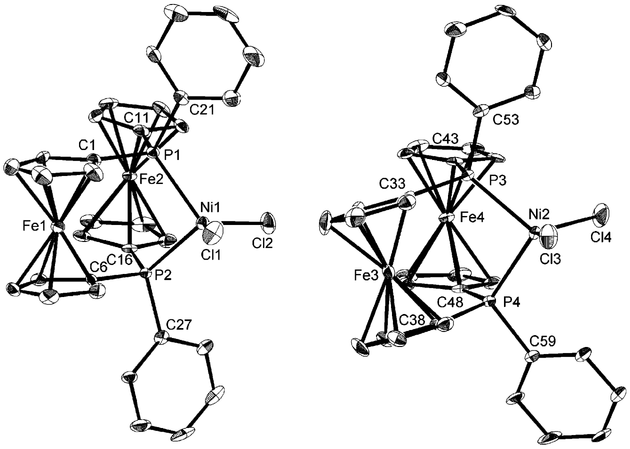


Figure 4. ORTEP drawings of two independent molecules of **10** with 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

Ni Complex. Dichlorodiphosphine nickel(II) complexes are known to adopt both tetrahedral and square-planar geometries. For example, the dppf[9] complex adopts a tetrahedral structure with the suitable P−Ni−P angle of 105.0(1)°,[10] whereas the less bulky dppp[9] complex is square-planar with the suitable P−Ni−P angle of 91.77(4)°.[11] Thus, it is of interest which geometry is adopted by the present double-chained diphosphine ligand upon coordination to a nickel(II) fragment.

The reaction of *syn*-**5** with NiCl$_2$ gave the green paramagnetic complex **10**, which was characterized by X-ray analysis as shown in Figure 4, where two independent molecules are depicted. The selected bond distances and angles are listed in Table 1. Both molecules have a considerably distorted tetrahedral geometry with P−Ni−P bite angles of 93.85(4)° and 93.20(5)°, which are comparable to those of the square-planar complexes **8** and **9** (vide supra), but are substantially smaller than an ideal tetrahedral angle. The Cl−Ni−Cl bite angles of 119.52(6)° and 119.55(6)° are on the contrary fairly larger than a tetrahedral angle. It has been established that [Ni(P−P)X$_2$] complexes having a relatively short single-chained diphosphine, such as dppm,[9] dppe,[9] and dppp, adopt a square-planar geometry with P−Ni−P bite angles close to or smaller than 90°,[11] whereas those having a longer single-chained diphosphine, such as dppb[9] and dppf, adopt a tetrahedral geometry with larger bite angles.[10] Taking the small P−Ni−P bite angle of **10** into account, some additional but opposing effect must be in action to make complex **10** exceptionally tetrahedral. If **10** adopted a square-planar geometry as expected from its narrow P−Ni−P bite angle, the two Ph groups would have to be located in the

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(9) Ligand abbreviations: COD = cycloocta-1,5-diene, TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, dppf = 1,1′-bis(diphenylphosphino)-ferrocene, dppp = 1,3-bis(diphenylphosphino)propane, dppm = 1,1-bis-(diphenylphosphino)methane, dppe = 1,2-bis(diphenylphosphino)ethane, and dppb = 1,4-bis(diphenylphosphino)butane.

(10) Casellato, U.; Ajó, D.; Valle, G.; Corain, B.; Longato, B.; Graziani, R. *J. Cryst. Spectrosc. Res.* **1988**, *18*, 583−590.

(11) Bomfim, J. A. S.; de Souza, F. P.; Filgueiras, C. A. L.; de Sousa, A. G.; Gambardella, M. T. P. *Polyhedron* **2003**, *22*, 1567−1573.

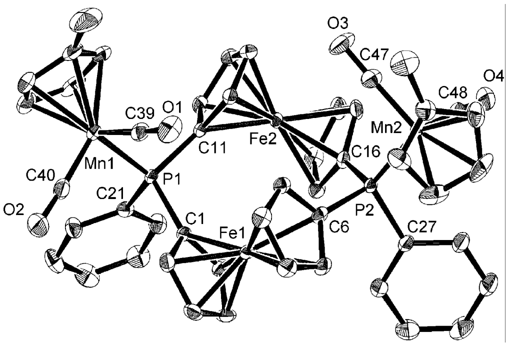

Figure 5. ORTEP drawing of **11** with 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Mn(1)−P(1) 2.2298(5), Mn(2)−P(2) 2.2328(5), P(1)−C(1) 1.812(2), P(1)−C(11) 1.819(2), P(2)−C(6) 1.817(2), P(2)−C(16) 1.830(2), P(1)−Mn(1)−C(39) 89.95(6), P(1)−Mn(1)−C(40) 95.47(7), P(2)−Mn(2)−C(47) 92.36(6), P(2)−Mn(2)−C(48) 92.07(7), Mn(1)−P(1)−C(1) 118.85(6), Mn(1)−P(1)−C(11) 108.18(6), C(1)−P(1)−C(11) 109.54(8), Mn(2)−P(2)−C(6) 108.22(6), Mn(2)−P(2)−C(16) 118.08(6), C(6)−P(2)−C(16) 111.14(8), twist angle 72.44(9), 70.41(9).

coordination plane of the Ni center because *syn*-**5** is double-chained, and thus they should exert a severe steric repulsion on the two Cl atoms like in **8**. The repulsion is, we suppose, a major reason complex **10** adopts a tetrahedral geometry, in which no such steric repulsion is anticipated, as seen in Figure 4. In contrast, the low-spin d^8 Pd complexes **8** and **9** adopt a square-planar structure in defiance of the inevitable steric repulsion mentioned above.

Mn Complex. The photochemical reaction of [Cp′Mn(CO)$_3$] (Cp′ = $C_5H_4CH_3$) with *syn*-**5** yielded the novel cyclic dinuclear Mn complex **11**, [{Cp′Mn(CO)$_2$}$_2$(μ-*syn*-**5**)], the molecular structure of which was determined by X-ray analysis as shown in Figure 5, where *syn*-**5** is acting as a bridging ligand. The twist angles of 70.41° and 72.44° are extraordinarily large compared with those of some structurally characterized [1.1]-ferrocenophanes[7,12] including *anti*-**3** (2.43°), *syn*-**5** itself (24.8°),[5a] and complexes **8**−**10** (9.2−27.2°). It has been confirmed that CH$_2$-bridged [1.1]ferrocenophane is a very flexible compound with respect to twisting of the two ferrocene units, and it readily undergoes *anti*-to-*syn* interconversion.[13,14] Therefore it is natural that the two P centers recede readily from each other by the twisting, so that the bulky Mn fragment may be accommodated on each P center, giving rise to a very large twist angle in **11** so as to avoid the steric repulsion otherwise anticipated between the two bulky Cp′Mn(CO)$_2$ moieties. ^{1}H and ^{13}C{^{1}H} NMR spectra of **11** in CDCl$_3$ were consistent with its X-ray structure.

Experimental Section

General Remarks. All reactions were carried out under an atmosphere of dry nitrogen using standard Schlenk tube techniques. Solvents were dried and distilled from sodium (hexane), sodium/benzophenone (ether, THF, and toluene), or P$_2$O$_5$ (CH$_2$Cl$_2$ and MeCN). These solvents were stored under a dry nitrogen atmosphere. The compounds [Fe{(η^5-C$_5$H$_4$)P(NEt$_2$)$_2$}$_2$] **1**,[15] *syn*-**5**,[5a] and CpNa[16] were prepared by literature procedures.

NMR spectra were recorded on a JEOL LA-300 spectrometer. ^{1}H and ^{13}C data were referenced to SiMe$_4$, and ^{31}P NMR data to 85% H$_3$PO$_4$. Photolysis was carried out with Pyrex-glass-filtered emission from a 400 W mercury arc lamp (Riko-Kagaku Sangyo UVL-400P). The emission lines in 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).

Characterization data for the new compounds prepared in this paper are given in the Supporting Information, and only ^{31}P{^{1}H} NMR data are provided below. Standard procedures[17−20] were applied to synthesize **8**−**11**; complete experimental details are also given in the Supporting Information.

Synthesis of 1,1′-Bis(diethylaminochlorophosphino)ferrocene, 2. To a solution of **1** (20.31 g, 38.0 mmol) in hexane (100 mL) was added PCl$_3$ (6.7 mL, 76.8 mmol) dropwise. After the solution was stirred overnight, the solvent was removed and the slurry was washed with cold hexane to remove phosphorus byproducts. The residue was extracted with hot hexane and dried in vacuo to give **2** as a yellow powder (12.57 g, 72%). ^{31}P{^{1}H} NMR (121.5 MHz, C$_6$D$_6$): δ 136.5 (s), 136.8 (s).

Synthesis of *exo*,*exo*-1,12-Bis(diethylamino)-1,12-diphospha-[1.1]ferrocenophane, *anti*-3 and *syn*-3. To a suspension of **2** (8.32 g, 18.0 mmol) in THF (40 mL) was added dropwise 40 mL of a THF solution of CpNa (3.19 g, 36.2 mmol) at −50 °C. After stirring for 30 min, the solution became homogeneous, and then *n*-BuLi (2.71 M hexane solution, 13.3 mL, 36.0 mmol) was added dropwise. The mixture was stirred for 30 min and then added dropwise to a suspension of FeCl$_2$ (2.40 g, 18.9 mmol) in THF (80 mL) at −50 °C. After stirring overnight, the solvent was removed in vacuo and the residue was then extracted with hot hexane. The solvent was removed in vacuo and then washed with cold hexane to give **3** (*anti*/*syn* = 5/4) (4.95 g, 48%) as a yellow powder. Recrystallization from hexane repeated several times gave a small amount of pure *anti*-**3**. ^{31}P{^{1}H} NMR (121.5 MHz, C$_6$D$_6$): δ 43.8 (s).

Isolation of pure *syn*-**3** was achieved by the reaction of *syn*-**4** prepared as below with 4 equiv of HNEt$_2$ in a MeCN/THF mixture as follows. To a solution of *syn*-**4** (573 mg, 1.14 mmol) in a mixture of THF (15 mL) and MeCN (10 mL) was added HNEt$_2$ (0.50 mL, 4.83 mmol) at room temperature. After the reaction mixture was stirred for 1 h, all volatile components were removed. Then, the residue was extracted with hexane and dried in vacuo to give *syn*-**3** as a yellow powder (461 mg, 70%). ^{31}P{^{1}H} NMR (121.5 MHz, C$_6$D$_6$): δ 41.7 (s).

Synthesis of *exo*,*exo*,*syn*-1,12-Dichloro-1,12-diphospha[1.1]-ferrocenophane, *syn*-4. To a solution of **3** (45 mg, 0.078 mmol) in ether (5 mL) was added HCl (1.0 M ether solution, 0.35 mL, 0.35 mmol) at −78 °C. The mixture was stirred for 30 min, and then the solvent was removed. The residue was extracted with toluene and dried in vacuo to give *syn*-**4** as a yellow powder (35 mg, 90%). ^{31}P{^{1}H} NMR (121.5 MHz, C$_6$D$_6$): δ 87.3 (s).

Synthesis of *exo*,*exo*,*syn*-1,12-Bis(trimethylsilylmethyl)-1,12-diphospha[1.1]ferrocenophane, *syn*-6. To a suspension of *syn*-**4** (1.06 g, 2.12 mmol) in THF was added Me$_3$SiCH$_2$Li (1.0 M solution of pentane, 4.6 mL, 4.6 mmol) at −78 °C. After stirring for 2.5 h

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(12) (a) Schachner, J. A.; Lund, C. L.; Quail, J. W.; Muller, J. *Acta Crystallogr. Sect. E* **2005**, *E61*, m682−m684. (b) Braunschweig, H.; Burschka, C.; Clentsmith, G. K. B.; Kupfer, T.; Radacki, K. *Inorg. Chem.* **2005**, *44*, 4906−4908. (c) Schachner, J. A.; Orlowski, G. A.; Quail, J. W.; Kraatz, H.-B.; Muller, J. *Inorg. Chem.* **2005**, *45*, 454−459.

(13) Rudziñski, J. M.; Osawa, E. *J. Phys. Org. Chem.* **1993**, *6*, 107−112.

(14) Löewendahl, M.; Davidsson, Ö.; Ahlberg, P. *J. Chem. Res. Synop.* **1993**, 40−41.

(15) Nifant'ev, I. E.; Boricenko, A. A.; Manzhukova, L. F.; Nifant'ev, E. E. *Phosphorus, Sulfur Silicon* **1992**, *68*, 99−106.

(16) Panda, T. K.; Gamer, M. T.; Roesky, P. W. *Organometallics* **2003**, *22*, 877−878.

(17) de Graaf, W.; Boerama, J.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Organometallics* **1989**, *8*, 2907−2917.

(18) Van Hecke, G. R.; Horrocks, W. D., Jr. *Inorg. Chem.* **1966**, *5*, 1968−1974.

(19) Meier, U. W.; Thewalt, U.; Debaerdemaeker, T.; Rieger, B. *Eur. J. Inorg. Chem.* **2004**, 3057−3062.

(20) Onaka, S.; Moriya, T.; Takagi, S.; Mizuno, A.; Furuta, H. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 1415−1427.

at room temperature, a few drops of water was added to quench the remaining Li compound and dried in vacuo. The residue was extracted with hexane and dried in vacuo to give *syn*-**6** as a yellow powder (708 mg, 55%). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ −41.7 (s).

Synthesis of *exo,exo,syn*-1,12-Bis(*p*-tolyl)-1,12-diphospha[1.1]-ferrocenophane, *syn*-7. To a solution of *syn*-**4** (259 mg, 0.517 mmol) in THF was added *p*-tolylmagnesium bromide (1.0 M THF solution, 1.3 mL, 1.3 mmol) at 0 °C. The mixture was stirred for 1 h at room temperature, and then one drop of water was added. After the solvent was removed in vacuo, the residue was dissolved in CH_2Cl_2 and then loaded on a silica gel column. A yellow band eluted with CH_2Cl_2 was collected and dried in vacuo to give *syn*-**7** as a red powder (80 mg, 25%). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ −31.8 (s).

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Supporting Information Available: Text giving complete experimental details and X-ray crystallographic data for *anti*-**3**, **8**, **9**, **10**, and **11**; X-ray data are also given in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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