Articles

Synthesis of Dinuclear Complexes Bearing Metalloporphyrin−Phosphine Hybrid Ligands and Their Catalytic Activity toward Hydrosilylation of Ketones

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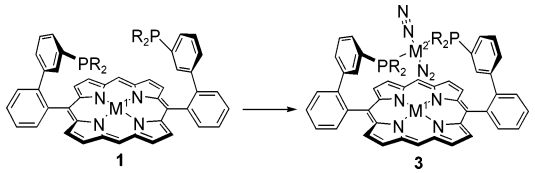
A new type of metalloporphyrin−phosphine hybrid ligand (**1**) has been designed and synthesized. Reactions of some transition metal complexes such as $PdCl_2$, $PtCl_2$, and $[RhCl(CO)_2]_2$ with a zinc porphyrin−phosphine ligand (**1**; M^1 = Zn) afford the corresponding dinuclear complexes (**2**) bearing the hybrid ligand. The zinc porphyrin−phosphine compound (**1**; M^1 = Zn, R = Ph) has been found to work as an effective ligand for Rh(I)- or Ir(I)-catalyzed hydrosilylation of ketones to give the corresponding alcohols after acid hydrolysis.

Introduction

Up until now, many types of mononuclear and polynuclear dinitrogen (N_2) complexes of various transition metals have been prepared, and some of them have been known to liberate ammonia (NH_3) or hydrazine (NH_2NH_2) by protonolysis with inorganic acids such as H_2SO_4 and HCl.[1,2] Recently, one of the authors has reported the formation of NH_3 by ruthenium-assisted protonation of coordinated N_2 on the W atom with H_2 under mild reaction conditions.[3] As an extension of this multimetallic approach for nitrogen fixation, we have envisaged to design a new type of metalloporphyrin−phosphine hybrid ligand (**1**)[4] and the corresponding dinuclear N_2 complexes (**3**) bearing this hybrid ligand,

Scheme 1



as shown in Scheme 1, although some N_2 complexes of porphyrin have already been prepared, where N_2 is coordinated on the central metal of porphyrin.[5,6] It is expected that the metalloporphyrin moiety in **3** induces intramolecular electron and energy transfer of the excitation energy into the metal center, where the conversion of solar energy into chemical potentials in the form of a charge-separated state takes place, because the metalloporphyrin moiety has a light-harvesting antenna system.[7,8] As a result, the properties of the light-driven energy migration and transfer of **1** are considered to change the coordination mode of N_2 on the metal in **3**.[9] Unfortunately, we have not yet succeeded in preparing N_2 complexes **3** with a metalloporphyrin−phosphine hybrid ligand, but we could prepare some transition

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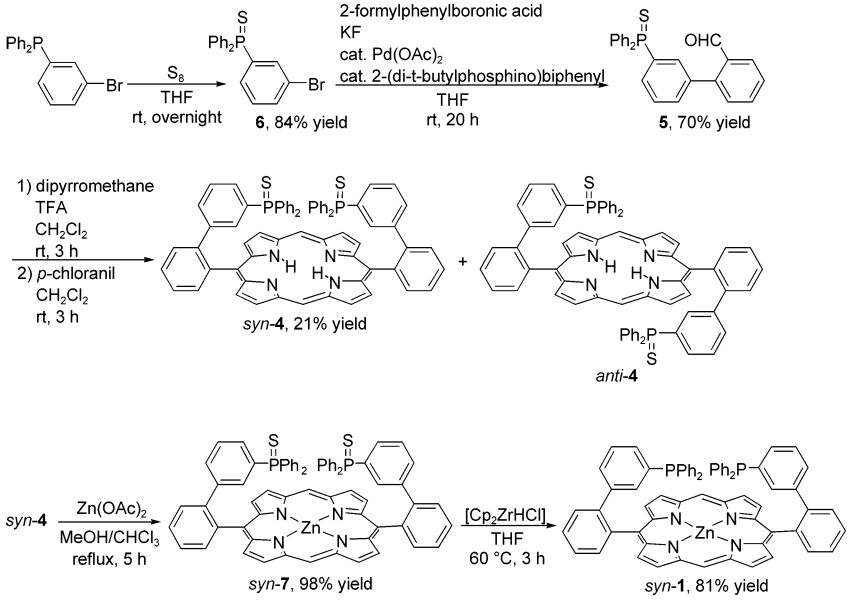
Scheme 2



metal complexes (**2**) bearing this hybrid ligand. Here, we describe the method for the preparation of some transition metal complexes (**2**) bearing the hybrid ligand and their catalytic activity toward rhodium(I)- and iridium(I)-catalyzed hydrosilylation of some ketones.

Results and Discussion

Preparation of the Zinc Porphyrin−Phosphine Hybrid Ligand (*syn*-1). The porphyrin-phosphinothioyl hybrid ligand (**4**) was prepared by treatment of 3′-(diphenylphosphinothioyl)biphenyl-2-carbaldehyde (**5**), which was obtained easily from the reaction of 3-(diphenylphosphinothioyl)bromobenzene (**6**) with 2-formylphenylboronic acid in the presence of a catalytic amount of $Pd(OAc)_2$ and 2-(di-*tert*-butylphosphino)biphenyl at room temperature for 20 h (70% isolated yield based on **6**),[10] with dipyrromethane in the presence of trifluoroacetic acid (TFA), followed by oxidation with *p*-chloranil (Scheme 2).[11] Although a mixture of two isomers of **4** was formed with the isomer ratio 1:1, only the *syn* isomer (*syn*-**4**) was isolated in 21% isolated yield based on **4** by flash chromatography. Treatment of *syn*-**4** with $Zn(OAc)_2$ at reflux temperature for 5 h in $MeOH/CHCl_3$ gave the corresponding zinc porphyrin−phosphinothioyl hybrid ligand (*syn*-**7**) in 98% isolated yield.[12] The structure of *syn*-**7** is unambiguously clarified by X-ray crystallography, an ORTEP drawing of *syn*-**7** being shown in Figure 1. Selected bond lengths and angles of *syn*-**7** are listed in Tables 1 and 2, respectively. Finally, treatment of *syn*-**7** with an excess amount of $[Cp_2ZrHCl]$ gave the reduced phosphine, *syn*-**1**, in 81% isolated yield based on *syn*-**7**.[13] Thus, *syn*-**1** was prepared in 10% overall isolated yield based on **6**.

Preparation of Dinuclear Complexes Bearing *syn*-1. The coordinated properties of *syn*-**1** were first examined with a platinum complex because the isomeric structures (*trans* or *cis*) are easily determined by the magnitude of $J^{195}_{Pt-^{31}P}$ in $^{31}P\{^1H\}$ NMR.[14,15] Treatment of platinum(II) complex $[PtCl_2(PhCN)_2]$ with *syn*-**1** at room temperature for 5 h in CH_2Cl_2 gave the corresponding dinuclear complex (**2a**) in 30% isolated yield (Scheme 3) with complete selectivity. The $^{31}P\{^1H\}$ NMR spectrum of **2a** (17.6 ppm in $CDCl_3$) was accompanied by its ^{195}Pt satellite with a $J^{195}_{Pt-^{31}P}$ value of 2598 Hz, indicating the *trans* geometry of two phosphorus atoms in **2a**. Similar treatment of palladium(II) complex $[PdCl_2(MeCN)_2]$ with *syn*-**1** at room temperature for 7 h in benzene afforded the corresponding dinuclear complex **2b** in 49% isolated yield with complete selectivity. Furthermore, the reaction of $[RhCl(CO)_2]_2$ with *syn*-**1** in a 1:2 molar ratio at room temperature for 1 h in tetrahydrofuran (THF) afforded the dinuclear complex **2c** in 20% isolated yield. The IR spectrum of **2c** exhibited an absorption at 1973 cm^{-1} ($\nu_{C=O}$). Unfortunately, when an equimolar mixture of tungsten N_2 complex *trans*-$[W(N_2)_2(PMePh_2)_4]$[16] and *syn*-**1** was stirred at room temperature for 1 h in THF, no formation of

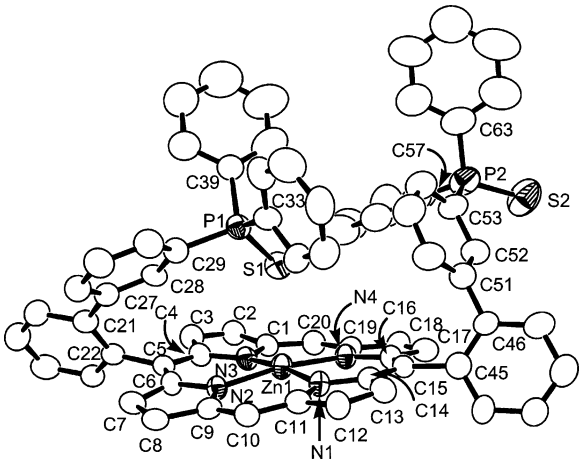


Figure 1. Molecular structure of *syn*-**7**.

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Table 1. Selected Bond Lengths (Å) for *syn*-7

Zn(1)−N(1)	2.041(8)	C(1)−C(2)	1.43(1)
Zn(1)−N(2)	2.025(8)	C(2)−C(3)	1.36(1)
Zn(1)−N(3)	2.056(8)	C(3)−C(4)	1.45(1)
Zn(1)−N(4)	2.042(8)	C(4)−C(5)	1.39(1)
P(1)−S(1)	1.956(4)	C(5)−C(6)	1.39(1)
P(2)−S(2)	1.946(5)	C(6)−C(7)	1.46(1)
P(1)−C(29)	1.80(1)	C(7)−C(8)	1.34(1)
P(1)−C(33)	1.80(1)	C(8)−C(9)	1.43(1)
P(1)−C(39)	1.80(1)	C(9)−C(10)	1.41(1)
P(2)−C(53)	1.80(1)	C(10)−C(11)	1.37(1)
P(2)−C(57)	1.80(1)	C(11)−C(12)	1.43(1)
P(2)−C(63)	1.80(1)	C(12)−C(13)	1.35(1)
N(1)−C(11)	1.39(1)	C(13)−C(14)	1.45(1)
N(1)−C(14)	1.35(1)	C(14)−C(15)	1.39(1)
N(2)−C(6)	1.37(1)	C(15)−C(16)	1.42(1)
N(2)−C(9)	1.38(1)	C(16)−C(17)	1.45(1)
N(3)−C(1)	1.37(1)	C(17)−C(18)	1.34(1)
N(3)−C(4)	1.37(1)	C(18)−C(19)	1.43(1)
N(4)−C(16)	1.37(1)	C(19)−C(20)	1.40(1)
N(4)−C(19)	1.36(1)	C(28)−C(29)	1.39(1)
C(1)−C(20)	1.38(1)	C(15)−C(45)	1.51(1)
C(5)−C(22)	1.51(1)	C(45)−C(46)	1.38(1)
C(21)−C(22)	1.41(1)	C(46)−C(51)	1.51(1)
C(21)−C(27)	1.48(1)	C(51)−C(52)	1.36(1)
C(27)−C(28)	1.40(1)	C(52)−C(53)	1.42(2)

Table 2. Selected Angles (deg) for *syn*-7

N(1)−Zn(1)−N(2)	90.9(3)	S(1)−P(1)−C(29)	114.0(3)
N(2)−Zn(1)−N(3)	88.4(3)	S(1)−P(1)−C(33)	112.5(4)
N(1)−Zn(1)−N(3)	172.8(3)	S(1)−P(1)−C(39)	111.7(4)
N(1)−Zn(1)−N(4)	88.5(3)	C(29)−P(1)−C(33)	107.1(5)
N(2)−Zn(1)−N(4)	171.0(3)	C(29)−P(1)−C(39)	106.3(5)
N(3)−Zn(1)−N(4)	91.1(3)	C(33)−P(1)−C(39)	104.7(5)
Zn(1)−N(1)−C(11)	125.7(6)	S(2)−P(2)−C(53)	113.6(4)
Zn(1)−N(1)−C(14)	127.8(7)	S(2)−P(2)−C(57)	113.8(5)
Zn(1)−N(2)−C(6)	127.0(7)	S(2)−P(2)−C(63)	113.0(5)
Zn(1)−N(2)−C(9)	126.4(6)	C(53)−P(2)−C(57)	104.1(6)
Zn(1)−N(3)−C(1)	124.8(6)	C(53)−P(2)−C(63)	106.4(6)
Zn(1)−N(3)−C(4)	126.0(6)	C(57)−P(2)−C(63)	105.1(7)
Zn(1)−N(4)−C(16)	127.5(7)	C(1)−C(2)−C(3)	107.0(9)
Zn(1)−N(4)−C(19)	125.5(6)	C(1)−C(20)−C(19)	128.1(9)
C(1)−N(3)−C(4)	107.1(8)	C(2)−C(1)−C(20)	125.5(9)
C(6)−N(2)−C(9)	106.5(8)	C(2)−C(3)−C(4)	107.0(9)
C(11)−N(1)−C(14)	106.5(8)	C(3)−C(4)−C(5)	125.7(9)
C(16)−N(4)−C(19)	107.0(8)	C(4)−C(5)−C(6)	124.4(9)
N(1)−C(11)−C(10)	125.2(9)	C(5)−C(6)−C(7)	125.8(9)
N(1)−C(11)−C(12)	108.8(9)	C(6)−C(7)−C(8)	108.3(9)
N(1)−C(14)−C(13)	110.1(9)	C(7)−C(8)−C(9)	106.6(8)
N(1)−C(14)−C(15)	125.8(9)	C(8)−C(9)−C(10)	125.2(9)
N(2)−C(6)−C(5)	125.9(9)	C(9)−C(10)−C(11)	127.3(9)
N(2)−C(6)−C(7)	108.2(9)	C(10)−C(11)−C(12)	126.0(9)
N(2)−C(9)−C(8)	110.3(8)	C(11)−C(12)−C(13)	108.2(9)
N(2)−C(9)−C(10)	124.3(9)	C(12)−C(13)−C(14)	106.2(9)
N(3)−C(1)−C(2)	109.9(9)	C(13)−C(14)−C(15)	123.9(9)
N(3)−C(1)−C(20)	124.5(9)	C(14)−C(15)−C(16)	124.3(9)
N(3)−C(4)−C(3)	108.9(9)	C(15)−C(16)−C(17)	125.0(9)
N(3)−C(4)−C(5)	125.4(9)	C(16)−C(17)−C(18)	105.5(9)
N(4)−C(16)−C(15)	125.2(9)	C(17)−C(18)−C(19)	109.0(1)
N(4)−C(16)−C(17)	109.7(9)	C(18)−C(19)−C(20)	126.3(9)
N(4)−C(19)−C(18)	108.8(9)	C(4)−C(5)−C(22)	118.7(9)
N(4)−C(19)−C(20)	124.9(9)	C(6)−C(5)−C(22)	116.6(9)
P(1)−C(29)−C(28)	119.6(7)	C(5)−C(22)−C(21)	119.6(8)
C(14)−C(15)−C(45)	119.4(9)	C(22)−C(21)−C(27)	123.1(9)
C(16)−C(15)−C(45)	116.3(9)	C(21)−C(27)−C(28)	122.4(9)
C(15)−C(45)−C(46)	123.0(9)	C(27)−C(28)−C(29)	122.6(9)
C(45)−C(46)−C(51)	122.1(9)	C(51)−C(52)−C(53)	121.4(1)
C(46)−C(51)−C(52)	120.6(1)	P(2)−C(53)−C(52)	119.3(9)

the corresponding novel N_2 complex was observed even by $^{31}P\{^1H\}$ NMR.

Catalytic Reactivity toward Hydrosilylation of Ketones. To obtain some information on the catalytic activity of the dinuclear complexes **2** where *syn*-**1** works as a ligand, we examined the rhodium- and iridium-catalyzed hydrosilylation of some ketones because we have previously investigated the rhodium-, iridium-, and ruthenium-catalyzed hydrosilylation of ketones in detail.[17] The formation of the corresponding dinuclear complex was confirmed by $^{31}P\{^1H\}$ NMR in the reaction of $[RhCl(COD)]_2$ or $[IrCl(COD)]_2$ with *syn*-**1** in $CDCl_3$ at room temperature for 30 min. In the case of the Rh complex, one doublet peak was observed at 27.6 (J_{Rh-P} = 146 Hz) ppm, and in the case of the Ir complex, one singlet peak was observed at 18.7 ppm. Thus, only one isomer was quantitatively formed in both cases. This fact indicates that the complexes formed in situ are suitable to investigate their catalytic activity toward hydrosilylation without further purification. Treatment of acetophenone (0.20 mmol) with diphenylsilane (0.60 mmol) in the presence of a catalytic amount of $[RhCl(COD)]_2$ or $[IrCl(COD)]_2$ (0.001 mmol; 0.5 mol %) and ligand *syn*-**1** (0.002 mmol; 1 mol %) at room temperature for 24 h in anhydrous THF afforded 1-phenylethanol in 53% or 26% GLC yield after acid hydrolysis, respectively (Table 3; runs 1 and 2; Scheme 4). Similarly, rhodium-

Scheme 3

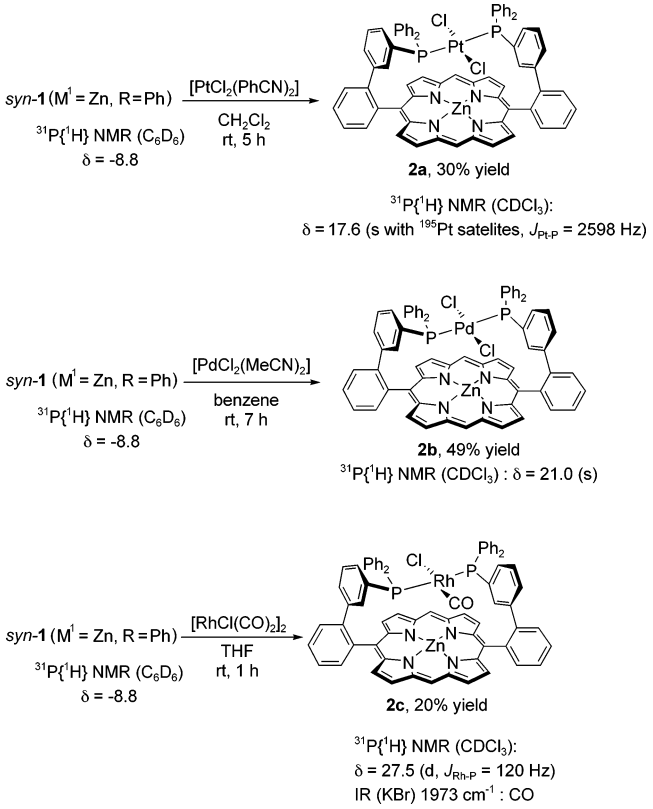

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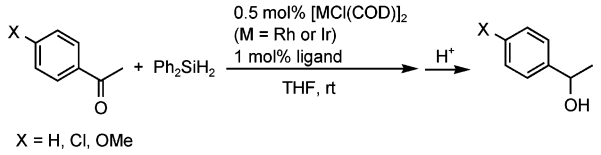
Table 3. Rhodium- or Iridium-Catalyzed Hydrosilylation of Acetophenones[a]

run	X	catalyst	ligand	reaction time (h)	yield (%)[b]
1	H	$[RhCl(COD)]_2$	*syn*-**1**	24	53
2	H	$[IrCl(COD)]_2$	*syn*-**1**	24	26
3	Cl	$[RhCl(COD)]_2$	*syn*-**1**	24	82
4	OMe	$[RhCl(COD)]_2$	*syn*-**1**	24	18
5	H	$[RhCl(COD)]_2$	dppf	24	73
6	H	$[RhCl(COD)]_2$	dppe	24	36
7	H	$[RhCl(COD)]_2$	dppp	24	54
8	H	$[RhCl(COD)]_2$		24	0
9	H	$[IrCl(COD)]_2$		24	0
10	H	$[RhCl(COD)]_2$	*syn*-**1**	8	41
11[c]	H	$[RhCl(COD)]_2$	*syn*-**1**	8	38
12[d]	H	$[RhCl(COD)]_2$	*syn*-**1**	8	44

[a] All the reactions of acetophenones (0.20 mmol) with diphenylsilane (0.60 mmol) were carried out in the presence of $[M(COD)Cl]_2$ (M = Rh or Ir) (0.001 mmol) and ligand (0.002 mmol) in THF (5 mL) at room temperature. [b] GLC yield. [c] In the dark. [d] The reaction mixture was irradiated with a high-pressure Hg lamp without a slit.

Scheme 4



catalyzed hydrosilylation of substituted acetophenones such as *p*-chloroacetophenone and *p*-methoxyacetophenone with diphenylsilane proceeded to give the corresponding alcohols in 82% and 18% GLC yields, respectively (Table 3; runs 3 and 4). For comparison, typical bidentate diphosphines such as dppf (1,1′-bis(diphenylphosphino)ferrocene), dppe (1,2-bis(diphenylphosphino)ethane), and dppp (1,3-bis(diphenylphosphino)propane) were used as ligands for the rhodium-catalyzed hydrosilylation of acetophenone under the same reaction conditions (Table 3; runs 5−7). No reaction proceeded in the absence of phosphine ligands in both cases (Table 3; runs 8 and 9). These results indicate that *syn*-**1** works as a suitable diphosphine ligand for rhodium- and iridium-catalyzed hydrosilylation of ketones. To investigate the effect of light, the catalytic hydrosilylation of acetophenone by using *syn*-**1** as ligand was carried out in the dark (Table 3; runs 10−12), where the catalytic reaction proceeded smoothly. On the other hand, when the reaction mixture was irradiated with a high-pressure Hg lamp (450 W) without a slit, the catalytic reaction was not accelerated at all. Further work is currently in progress aimed at finding new catalytic activity.

Conclusion

In summary, we have developed a new route to the porphyrin−phosphine hybrid ligand (*syn*-**1**) and prepared the novel rhodium-, palladium-, and platinum−zinc dinuclear complexes bearing *syn*-**1**. The molecular structure of porphyrin−phosphinothioyl hybrid ligand *syn*-**7** is unambiguously clarified by X-ray crystallography. The compound *syn*-**1** has been revealed to work as a ligand for Rh- and Ir-catalyzed hydrosilylation of ketones.

Experimental Section

General Methods. ^1H NMR (400, 300, and 270 MHz) and $^{31}P\{^1H\}$ NMR (161.7 MHz) spectra were recorded using $CDCl_3$ or C_6D_6 as solvent. GLC analyses were performed on a Shimadzu GC-14B instrument equipped with a flame ionization detector using a 25 m × 0.25 mm CBP 10 fused silica capillary column. Elemental analyses were performed at Microanalytical Center of Kyoto University. High-resolution mass spectra and low-resolution mass spectra were measured on a JEOL JMS600H mass spectrometer. UV−visible spectra were recorded on a Shimadzu Multispec-1500 spectrometer. IR spectra were recorded on an FT-IR spectrometer. All reactions were carried out under a dry nitrogen atmosphere. Solvents were dried by the usual methods and distilled before use. Unless otherwise noted, all manipulations were done by use of Schlenk techniques. 2-Formylphenylboronic acid, 2-(di-*tert*-butylphosphino)biphenyl, $Zn(OAc)_2$, $[Cp_2ZrHCl]$, $Pd(OAc)_2$, $[RhCl(CO)_2]_2$, $[RhCl(COD)]_2$, $[IrCl(COD)]_2$, acetophenone, diphenylsilane, dppf, dppe, and dppp were commercial products. 3-(Diphenylphosphinyl)bromobenzene,[18] dipyrromethane,[19] $PtCl_2(PhCN)_2$,[20] and $PdCl_2(MeCN)_2$[21] were prepared according to reported procedures.

3-(Diphenylphosphinothioyl)bromobenzene (6). In a 200 mL flask, 3-(diphenylphosphinyl)bromobenzene (9.72 g, 28.5 mmol) and elemental sulfur (1.02 g, 31.9 mmol) were stirred in THF (80 mL) at room temperature under N_2. The reaction mixture was stirred overnight, and then the reaction mixture was concentrated in vacuo. The crude mixture was purified by flash chromatography on silica gel to give a white solid (**6**) (8.90 g, 23.8 mmol; 84%): ^1H NMR ($CDCl_3$) δ 7.29 (dt, 1H, J = 3.2 and 7.8 Hz), 7.40−7.53 (m, 6H), 7.54−7.64 (m, 2H), 7.66−7.76 (m, 4H), 7.88 (dt, 1H, J = 1.4 and 13.2 Hz); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 40.0; HRMS (FAB) calcd for $C_{18}H_{14}{}^{79}BrPS$ ($M + H^+$) 372.9815, found 372.9808; calcd for $C_{18}H_{14}{}^{81}BrPS$ ($M + H^+$) 374.9796, found 374.9796. Anal. Calcd for $C_{18}H_{14}BrPS$: C, 57.92; H, 3.78. Found: C, 58.73; H, 3.85.

3′-(Diphenylphosphinothioyl)biphenyl-2-carbaldehyde (5). In a 100 mL flask, 3-(diphenylphosphinothioyl)-bromobenzene (**6**) (8.90 g, 23.8 mmol), $Pd(OAc)_2$ (117 mg, 0.523 mmol), 2-(di-*tert*-butylphosphino)biphenyl (301 mg, 1.01 mmol), KF (4.07 g, 70.0 mmol), and 2-formylphenylboronic acid (3.81 g, 25.4 mmol) were stirred in THF (50 mL) at room temperature for 20 h under N_2. The reaction mixture was then diluted with diethyl ether (100 mL) and poured into a separatory funnel. The reaction mixture was washed with aqueous 1 N NaOH (50 mL × 3), and the aqueous layers were extracted with diethyl ether (50 mL × 3). The combined organic layers were washed with brine, dried over anhydrous $MgSO_4$, and concentrated in vacuo. The crude mixture was purified by flash chromatography on silica gel to give a white solid (**5**) (6.61 g, 16.6 mmol; 70%): ^1H NMR ($CDCl_3$) δ 7.38−7.65 (m, 11H), 7.73−7.80 (m, 6H), 7.99 (dd, 1H, J = 1.0 and 7.8 Hz), 9.90 (s, 1H); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 40.4 (s). Anal. Calcd for $C_{25}H_{19}OPS$: C, 75.36; H, 4.81. Found: C, 75.31; H, 5.00.

***syn*-5,15-Bis[3′-(diphenylphosphinothioyl)biphenyl-2-yl]porphyrin (*syn*-4).** In a 1 L flask, 3′-(diphenylphosphinothioyl)biphenyl-2-carbaldehyde (**5**) (2.04 g, 5.12 mmol) and dipyrromethane (0.752 g, 5.15 mmol) were dissolved in CH_2Cl_2 (500 mL) under N_2, and then TFA (0.55 mL, 7.13 mmol) was added slowly. The reaction mixture was stirred at room temperature for 3 h, and then *p*-chloranil (1.29 g, 4.07 mmol) was added to it. After the reaction mixture was further stirred at room temperature for another 20 h, it was concen-

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(19) Wang, Q. M.; Bruce, D, W. *Synlett* **1995**, 1267.
(20) Braunstein, P.; Bender, R.; Jud, J. *Inorg. Synth.* **1987**, *26*, 345.
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trated in vacuo. The crude mixture was purified by flash chromatography on silica gel to give a purple solid (*syn*-**4**) (607 mg, 0.547 mmol; 21%), which was recrystallized from CH_2Cl_2/*n*-hexane: ^{1}H NMR ($CDCl_3$) δ 6.27 (dt, 8H, J = 3.2 and 7.6 Hz), 6.42−6.47 (m, 6H), 6.57 (dd, 8H, J = 7.6 and 13.4 Hz), 6.81 (dd, 2H, J = 7.6 and 13.4 Hz), 7.29 (d, 2H, J = 6.8 Hz), 7.70−7.86 (m, 10H), 8.04 (d, 2H, J = 6.8 Hz) 8.91 (d, 4H, J = 4.8 Hz), 9.21 (d, 4H, J = 4.8 Hz), 10.09 (s, 2H); ^{31}P{^{1}H} NMR ($CDCl_3$) δ 40.1 (s); UV/vis ($CHCl_3$) λ_{max} (log ϵ) 369 (3.24), 414 (5.41), 440 (4.21), 507 (4.10), 540 (3.65), 580 (3.66), 635 (3.36) nm. Anal. Calcd for $C_{68}H_{48}N_4P_2S_2{\cdot}CH_2Cl_2$ (*syn*-**4**·CH_2Cl_2): C, 73.20; H, 4.45; N, 4.95. Found: C, 72.88; H, 4.60; N, 4.73.

Representative data of *anti*-**4** are as follows:[22] ^{1}H NMR ($CDCl_3$) δ 9.97 (s, 2H); ^{31}P{^{1}H} NMR ($CDCl_3$) δ 40.4 (s).

***syn*-{5,15-Bis[3′-(diphenylphosphinothioyl)biphenyl-2-yl]porphyrinato}zinc(II) (*syn*-7).** In a 50 mL flask, *syn*-5,-15-bis[3′-(diphenylphosphinothioyl)biphenyl-2-yl]porphyrin (*syn*-**4**) (33.9 mg, 0.0324 mmol) dissolved in $CHCl_3$ (20 mL) was added to a saturated methanol solution with zinc acetate (5 mL), and the solution was stirred at reflux temperature for 5 h under N_2. The reaction mixture was poured into water, and the resulting mixture was extracted with $CHCl_3$ (20 mL × 3). The organic layer was washed with water (40 mL × 2), dried over anhydrous $MgSO_4$, and concentrated in vacuo to give a purple solid (*syn*-**7**) (35.3 mg, 0.0318 mmol; 98%), which was recrystallized from CH_2Cl_2/*n*-hexane: ^{1}H NMR ($CDCl_3$) δ 6.15 (t, 2H, J = 7.6 Hz), 6.36 (dd, 2H, J = 7.6 and 13.2 Hz), 6.43 (dd, 8H, J = 7.6 and 13.2 Hz), 6.63 (dt, 8H, J = 2.0 and 7.6 Hz), 6.74 (dt, 4H, J = 2.0 and 7.6 Hz), 6.98 (d, 2H, J = 13.2 Hz), 7.17 (d, 2H, J = 7.6 Hz), 7.74 (t, 4H, J = 7.6 Hz), 7.84 (t, 2H, J = 7.6 Hz), 8.29 (d, 2H, J = 7.6 Hz), 8.94 (d, 4H, J = 4.4 Hz), 9.21 (d, 4H, J = 4.4 Hz), 10.06 (s, 2H); ^{31}P{^{1}H} NMR ($CDCl_3$) δ 39.1 (s); UV/vis ($CHCl_3$) λ_{max} (log ϵ) 313 (4.56), 420 (5.51), 547 (4.43), 622 (4.07) nm. Anal. Calcd for $C_{68}H_{46}N_4P_2S_2Zn{\cdot}2CH_2Cl_2$ (*syn*-**7**·$2CH_2Cl_2$): C, 65.66; H, 3.94; N, 4.38. Found: C, 65.63; H, 4.07; N, 4.30.

***syn*-{5,15-Bis(3′-diphenylphosphinylbiphenyl-2-yl)-porphyrinato}zinc(II) (*syn*-1).** In a 20 mL flask, *syn*-{5,15-bis[3′-(diphenylphosphinothioyl)biphenyl-2-yl]porphyrinato}-zinc(II) (*syn*-**7**) (43.8 mg, 0.0394 mmol) and [Cp_2ZrHCl] (63.2 mg, 0.245 mmol) were stirred in THF (5 mL) at 60 °C for 3 h under N_2. The reaction mixture was concentrated in vacuo and purified by flash chromatography on silica gel under N_2 to give a purple solid (*syn*-**1**) (33.5 mg, 0.0320 mmol; 81%): ^{1}H NMR (C_6D_6) δ 6.08 (t, 2H, J = 7.8 Hz), 6.22−6.38 (m, 14H), 6.54 (t, 8H, J = 7.8 Hz), 7.29 (d, 2H, J = 7.8 Hz), 7.38 (t, 2H, J = 7.8 Hz), 7.56 (t, 2H, J = 7.8 Hz), 7.70 (d, 2H, J = 7.8 Hz), 7.78 (d, 2H, J = 7.8 Hz), 7.90 (d, 2H, J = 7.8 Hz), 9.01 (d, 4H, J = 4.4 Hz), 9.09 (d, 4H, J = 4.4 Hz), 9.89 (s, 2H); ^{31}P{^{1}H} NMR (C_6D_6) δ −8.8 (s); LRMS (FAB) calcd for $C_{68}H_{46}N_4ZnP_2$ (*syn*-**1**) 1046, found 1046; UV/vis ($CHCl_3$) λ_{max} (log ϵ) 418 (5.50), 458 (4.46), 498 (4.42), 544 (4.44), 620 (4.26) nm.

Preparation of Dinuclear Complexes Bearing *syn*-1. 2a. In a 20 mL flask, *syn*-{5,15-bis(3′-diphenylphosphanylbiphenyl-2-yl)porphinato}zinc(II) (*syn*-**1**) (56.4 mg, 0.0539 mmol) and $PtCl_2(PhCN)_2$ (23.7 mg, 0.0502 mmol) were stirred in dichloromethane (6 mL) at room temperature for 5 h. The solvent was then removed under vacuum. The residue was recrystallized from $CHCl_3$/*n*-hexane to give a purple solid (**2a**) (20.1 mg, 0.0153 mmol; 30%): ^{1}H NMR ($CDCl_3$) δ 6.18 (br, 2H), 6.25−6.46 (br, 10H), 7.51−7.78 (m, 22H), 7.92 (d, 2H, J = 8.0 Hz), 8.45 (br, 4H), 8.15 (br, 4H), 9.97 (s, 2H); ^{31}P{^{1}H} NMR ($CDCl_3$) δ 17.7 (s with ^{195}Pt satellites, J_{Pt-P} = 2598 Hz). Anal. Calcd for $C_{68}H_{46}N_4Cl_2P_2PtZn{\cdot}2CHCl_3$ (**2a**·$2CHCl_3$): C, 54.20; H, 3.12; N, 3.61. Found: C, 54.44; H, 3.41; N, 3.84.

2b. In a 20 mL flask, *syn*-{5,15-bis(3′-diphenylphosphanyl-biphenyl-2-yl)porphinato}zinc(II) (*syn*-**1**) (42.1 mg, 0.0402 mmol) and $PdCl_2(MeCN)_2$ (10.0 mg, 0.0385 mmol) were stirred in benzene (8 mL) at room temperature for 8 h. The solvent was then removed under vacuum. The residue was recrystallized from CH_2Cl_2/*n*-hexane to give a purple solid (**2b**) (23.0 mg, 0.0188 mmol; 49%): ^{1}H NMR ($CDCl_3$) δ 5.93 (br, 2H), 6.17 (br, 8H), 6.32−6.46 (m, 2H), 6.91 (br, 10H), 7.16 (t, 2H, J = 7.0 Hz), 7.68−7.91 (m, 10H), 8.43 (d, 2H, J = 7.2 Hz), 8.66 (d, 4H, J = 3.6 Hz), 8.90 (br, 4H), 9.82 (s, 2H); ^{31}P{^{1}H} NMR ($CDCl_3$) δ 21.0 (s). Anal. Calcd for $C_{68}H_{46}N_4Cl_2P_2PdZn{\cdot}2CH_2Cl_2$ (**2b**·$2CH_2Cl_2$): C, 60.33; H, 3.62; N, 4.02. Found: C, 60.23; H, 3.85; N, 3.65.

2c. In a 20 mL flask, *syn*-{5,15-bis(3′-diphenylphosphanyl-biphenyl-2-yl)porphyrinato}zinc(II) (*syn*-**1**) (38.8 mg, 0.0371 mmol) and $[RhCl(CO)_2]_2$ (7.6 mg, 0.0196 mmol) were stirred in THF (5 mL) at room temperature for 1 h. The solvent was then removed under vacuum. The residue was recrystallized from CH_2Cl_2/*n*-hexane to give a purple solid (**2c**) (9.1 mg,

Table 4. Crystallographic Data for *syn*-7

formula	$C_{70}H_{50}N_4Cl_4P_2S_2Zn$
fw	1280.45
cryst size (mm)	0.60 x 0.40 x 0.10
cryst syst	triclinic
space group	$P\bar{1}$ (#2)
cryst color	black
a (Å)	11.9579(3)
b (Å)	12.3233(3)
c (Å)	22.1029(5)
α (deg)	106.002(2)
β (deg)	97.916(2)
γ (deg)	92.123(1)
V (Å^3)	3091.4(1)
Z	2
d_{calc} (g cm^{-1})	1.375
F(000)	1316.00
μ_{calc} (cm^{-1})	7.35
no. of unique data	11527
no. of data used ($I > 3\sigma(I)$)	5136
no. of params refined	798
R^a	0.075
$R_w{}^b$	0.084
goodness of fit indicator	1.55
max. residuals (e A^{-3})	0.66

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o{}^2]^{1/2}$.

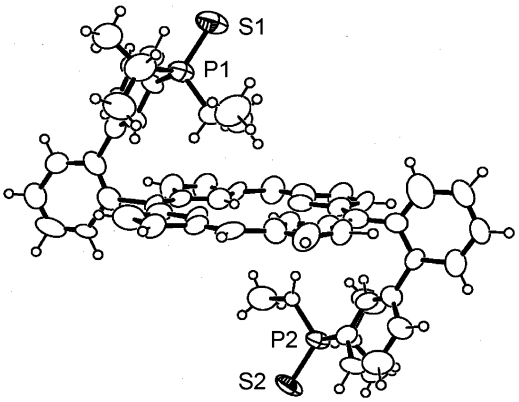
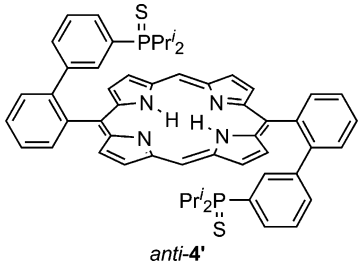


Figure 2. Molecular structure of *anti*-**4′**.

(22) Separately, we have confirmed the molecular structure of *anti*-**4′** (see below and Figure 2) by X-ray crystallography. Saito M.; Nishibayashi, Y.; Uemura, S. Unpublished results.



anti-**4'**

0.0075 mmol; 20%): ^{1}H NMR ($CDCl_3$) δ 5.86 (t, 2H, J = 4.8 Hz), 6.21 (br, 8H), 6.80 (dd, 2H, J = 6.8 and 14.0 Hz), 6.93 (t, 10H, J = 7.6 Hz), 7.10 (t, 2H, J = 7.6 Hz), 7.68−7.89 (m, 10H), 8.41 (d, 2H, J = 6.4 Hz), 8.63 (d, 4H, J = 4.4 Hz), 8.89 (d, 4H, J = 4.4 Hz), 9.82 (s, 2H); ^{31}P{^{1}H} NMR ($CDCl_3$) δ 27.5 (d, J_{Rh-P} = 120 Hz); IR (KBr) 1973 cm^{-1} ν(C═O); UV/vis ($CHCl_3$) λ_{max} (log ϵ) 424 (5.62), 550 (4.42), 624 (4.15) nm. Anal. Calcd for $C_{69}H_{46}ON_4ClP_2RhZn\cdot 2CH_2Cl_2$ (**2c**·$2CH_2Cl_2$): C, 61.67; H, 3.64; N, 4.05. Found: C, 61.84; H, 4.14; N, 3.83.

General Procedure for Rhodium- or Iridium-Catalyzed Hydrosilylation of Ketones. A typical experimental procedure for the hydrosilylation of ketones by using $[RhCl(COD)]_2$ and *syn*-**1** is as follows. In a 20 mL flask were placed $[RhCl(COD)]_2$ (0.001 mmol; 0.5 mol %) and *syn*-**1** (0.002 mmol; 1 mol %) under N_2. Anhydrous THF (5 mL) and then acetophenone (0.02 mmol) were added. Diphenylsilane (0.60 mmol) was added slowly, and the reaction mixture was stirred at room temperature for 24 h. Methanol (1 mL) was slowly added, and the mixture was stirred for 1 h. After gas evolution ceased, 1 N aqueous HCl (5 mL) was added to the reaction mixture. The reaction mixture was washed with brine (10 mL) and extracted with diethyl ether (10 mL × 3). The organic layer was dried over anhydrous $MgSO_4$. For the GLC analysis, cyclododecane was added as an internal standard.

X-ray Crystallographic Studies of *syn*-7. Black crystals of *syn*-**7** suitable for X-ray analysis were obtained by recrystallization from CH_2Cl_2/*n*-hexane. A single crystal was sealed in a Pyrex glass capillary under N_2 atmosphere and used for data collection. All measurements were made on a Rigaku RAXIS imaging plate area detector with graphite-monochromated Mo Kα radiation. Details of crystal and data collection parameters are summarized in Table 4. The positions of nonhydrogen atoms were determined by direct methods (SIR92) and subsequent Fourier syntheses (DIRDIF99).

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Supporting Information Available: Crystallographic data of *syn*-**7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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