Synthesis and Ligand Properties of 1-Phosphaethenyl-2-phosphanylferrocenes

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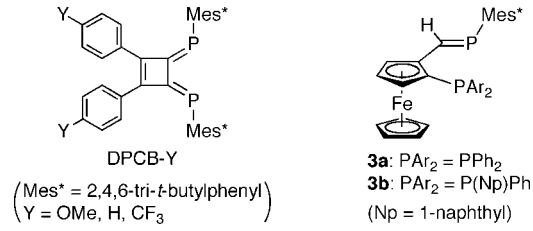
(*S*)-1-Phosphaethenyl-2-diarylphosphanylferrocenes with planar chirality (Fc(CH═PMes*)PAr_2: PAr_2 = PPh_2 (**3a**), P(1-naphthyl)Ph (**3b**)) are prepared in high yields from optically active 2-phosphanylferrocenecarboxaldehydes by the phospha-Peterson reactions with Mes*P(Li)$SiMe_3$ in THF. The stereochemistry of **3b** is determined by X-ray diffraction analysis. Compounds **3a** and **3b** readily react with $[PtMe_2(\mu\text{-}SMe_2)]_2$ in Et_2O to afford dimethyl complexes with bidentate coordination of these ligands ($PtMe_2$(L): L = **3a** (**4a**), **3b** (**4b**)). The X-ray structure of **4b** reveals almost identical trans-influence of the phosphaethenyl and phosphanyl groups, showing comparable σ-donating abilities of those components. Treatment of **3a** and **3b** with $[Pd(\eta^3\text{-allyl})(\mu\text{-Cl})]_2$ in CH_2Cl_2 in the presence of AgOTf forms the corresponding π-allyl complexes $[Pd(\eta^3\text{-allyl})(L)]OTf$ (L = **3a** (**5a**), **3b** (**5b**)), respectively, which are mixtures of diastereomers with endo- and exo-oriented π-allyl ligands. Complex **5a** catalyzes hydroamination of 1,3-cyclohexadiene with aniline in toluene in the presence of 5 Å molecular sieves at room temperature, giving *N*-cyclohexen-3-ylaniline in 84% yield.

Introduction

Recent advances in transition metal catalysis have been largely dependent on the development of supporting ligands, because ligand properties dominate the catalytic performance of transition metal complexes. While phosphanes, imines, and pyridine derivatives are most widely used, new types of ligands with unique electronic properties have recently emerged. For example, N-heterocyclic carbenes (NHCs) are extremely strong σ-donors, which have enabled versatile transformations of aryl chlorides in palladium-catalyzed reactions.[1] NHCs have led to notable improvements in the Grubbs-type olefin metathesis catalysts as well.[2] More recently, phosphaalkenes with a P═C double bond have been examined as new entries of supporting ligands.[3] We have reported highly efficient catalyses using 1,2-diaryl-3,4-diphosphinidenecyclobutenes as bidentate phosphaalkene ligands (DPCB-Y, Chart 1).[4] Representative examples include dehydrative allylation with allylic alcohols (Pd),[5] cyclodehydration of *cis*-2-butene-1,4-diol with active methylene compounds (Pd),[6] hydroamination of 1,3-dienes with aniline (Pd),[7] conjugate addition of benzyl carbamate to α,β-unsaturated ketones (Pd),[8] and *Z*-selective hydrosilylation of alkynes (Ru).[9] This paper reports the synthesis and coordination chemistry of 1-phosphaethenyl-2-phosphanylferrocenes with planar chirality (**3a**, **b**), which have been prepared aiming at the following points: (1) direct comparison of the ligand properties of phosphaalkene and phosphane, (2) application of phosphaalkene ligands to catalytic asymmetric reactions.

Chart 1



Phosphaalkenes adopt end-on coordination with transition metals via two types of orbital interactions, σ-donation and π-back-donation.[3] The most remarkable feature of phosphaalkenes is the extremely low-lying π^* orbital of the P═C bond, which induces strong π-back-donation. We recently documented that DPCB-Y forms extended π-conjugated systems with platinum via highly efficient $d\pi-p\pi$ interactions (i.e., π-back-donation).[10] The π-conjugation stabilizes DPCB-Y complexes especially in low-valent oxidation states to a great extent, and this unique ligand property is a key to the high catalytic activities

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(1) (a) *N-Heterocyclic Carbenes in Synthesis*; Nolan, S. P., Ed.; Wiley-VCH: Weinheim, 2006. (b) Enders, D.; Niemeier, O.; Henseler, A. *Chem. Rev.* **2007**, *107*, 5606.

(2) *Handbook of Metathesis*; Grubbs, R. H., Ed.; Wiley-VCH: Weinheim, 2003.

(3) (a) Le Floch, P. *Coord. Chem. Rev.* **2006**, *250*, 627. (b) Mathey, F. *Angew. Chem., Int. Ed.* **2003**, *42*, 1578. (c) Mathey, F. *J. Organomet. Chem.* **2002**, *646*, 15. (d) Weber, L. *Angew. Chem., Int. Ed.* **2002**, *41*, 563.

(4) (a) Ozawa, F.; Yoshifuji, M. *Dalton Trans.* **2006**, 4987. (b) Ozawa, F.; Yoshifuji, M. C. R. *Chimie* **2004**, *7*, 747.

(5) (a) Ozawa, F.; Okamoto, H.; Kawagishi, S.; Yamamoto, S.; Minami, T.; Yoshifuji, M. *J. Am. Chem. Soc.* **2002**, *124*, 10968. (b) Ozawa, F.; Ishiyama, T.; Yamamoto, S.; Kawagishi, S.; Murakami, H.; Yoshifuji, M. *Organometallics* **2004**, *23*, 1698. (c) Murakami, H.; Minami, T.; Ozawa, F. *J. Org. Chem.* **2004**, *69*, 4482.

(6) Murakami, H.; Matsui, Y.; Ozawa, F.; Yoshifuji, M. *J. Organomet. Chem.* **2006**, *691*, 3151.

(7) Minami, T.; Okamoto, H.; Ikeda, S.; Tanaka, R.; Ozawa, F.; Yoshifuji, M. *Angew. Chem., Int. Ed.* **2001**, *40*, 4501.

(8) Jensen, R. S.; Umeda, K.; Okazaki, M.; Ozawa, F.; Yoshifuji, M. *J. Organomet. Chem.* **2007**, *692*, 286.

(9) (a) Nagao, M.; Asano, K.; Umeda, K.; Katayama, H.; Ozawa, F. *J. Org. Chem.* **2005**, *70*, 10511. (b) Hayashi, A.; Yoshitomi, T.; Umeda, K.; Okazaki, M.; Ozawa, F. *Organometallics* **2008**, *27*, 2321.

(10) (a) Hayashi, K.; Nakatani, M.; Hayashi, A.; Takano, M.; Okazaki, M.; Toyota, K.; Yoshifuji, M.; Ozawa, F. *Organometallics* **2008**, *27*, 1970.

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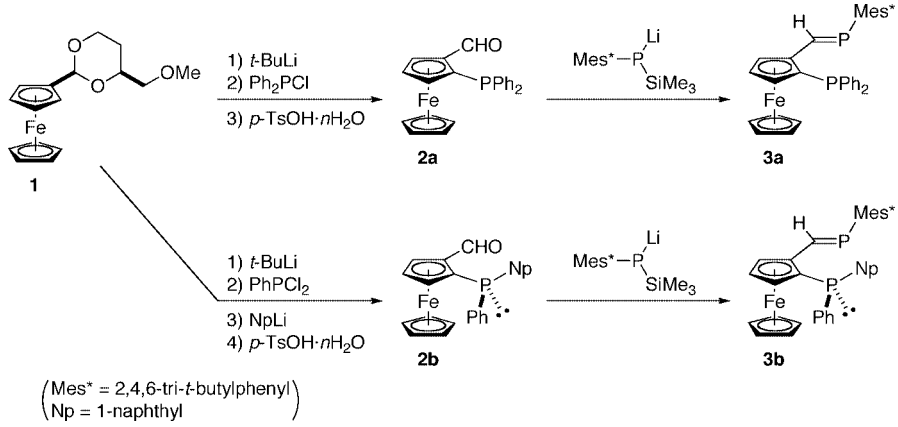
Scheme 1. Synthetic Routes to Chiral 1-Phosphaethenyl-2-phosphanylferrocenes



of DPCB-Y complexes.[4] On the other hand, although the σ-donating ability is another important ligand property, this information for phosphaalkenes has been limited. Phosphaethene ($H_2C{=}PH$) bears lone-pair electrons at an orbital level close to phosphane (PH_3).[11] However, since the 3s orbital is predominant in the lone-pair orbital,[3a] phosphaalkenes are generally regarded as moderate σ-donors, considerably weaker than phosphanes.

We previously tried to estimate the σ-donating ability of DPCB-Y ligands by comparison of the structural data of $PtMe_2$(DPCB-Y) with diphosphane analogues.[12] In this study, we prepared new bidentate ligands **3a** and **3b**, having both phosphaalkene and phosphane moieties as coordination sites, to compare the σ-donating abilities of those components more precisely in the same molecule. For constructing such molecules, the phosphaalkene moiety should be attached to an unsaturated hydrocarbon system to secure the thermodynamic stability of the P=C bond via π-conjugation.[3a] We therefore employed a 2-phosphanylferrocenyl group as the counterpart of the phosphaethenyl group for taking advantage of accessibility of the ferrocene-based precursors **2a** and **2b** (Scheme 1).[13,14] Since the asymmetric synthesis of these precursors has recently been established, we were able to successfully prepare the desired compounds **3a** and **3b** in enantiomerically pure forms.

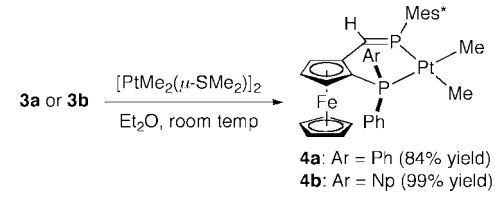
Results and Discussion

Preparation of 1-Phosphaethenyl-2-phosphanylferrocenes. Scheme 1 outlines the synthetic routes to **3a** and **3b**. Compound **2a** (S_{Fc}) as the precursor of **3a** was prepared from the chiral acetal **1** according to a procedure developed by Kagan et al.[13] Treatment of **2a** with Mes*P(Li)$SiMe_3$ in THF at room temperature led to the phospha-Peterson reaction,[15] giving **3a**, which was isolated in 78% yield as a red solid. Similarly, compound **3b**, having a *P*-chiral 1-naphthyl(phenyl)phosphanyl group, was prepared in 94% yield from corresponding ferrocenecarboxaldehyde **2b**. The enantioselective synthesis of **2b** was accomplished by a method reported by Chen et al.[14]

Compounds **3a** and **3b** were identified by NMR spectroscopy, mass spectrometry, and elemental analysis. Each compound showed one set of NMR signals assignable to a single stereoisomer. The $^{31}P\{^1H\}$ NMR signals were observed as two sets of doublets in typical regions of ferrocenylphosphanes (δ −22.8 (**3a**), −30.0 (**3b**)) and phosphaalkenes (δ 247.8 (**3a**), 248.5 (**3b**)). In the ^1H NMR spectra, a vinylic proton signal arising from the phosphaethenyl group appeared at δ 8.18 with a $^2J_{PH}$ coupling of 24 Hz for both compounds; the chemical shift and coupling constant are consistent with the *E*-configuration of the phosphaethenyl group.[16]

The stereochemistry of **3b** (S_{Fc},R_P) was uniquely determined by X-ray diffraction analysis (space group $P2_12_12_1$). Figure 1 shows the crystal structure, which consists of two rotamers around the phosphaethenyl−ferrocene bond (C1−C2 (**A**), C46−C47 (**B**)). The Mes* group is bonded to the P=C bond in vertical orientation. The 1-naphthyl and phenyl groups in the phosphanyl group are situated in axial and equatorial positions, respectively. Since the two ortho *t*-Bu groups of the Mes* group are observed equivalently at δ 1.25 in the ^1H NMR spectrum measured at room temperature, these rotamers are interconverted in an NMR time scale by bond rotation in solution.

Preparation and Structures of Dimethylplatinum(II) Complexes. Compounds **3a** and **3b** readily reacted with $[PtMe_2(\mu\text{-}SMe_2)]_2$ in Et_2O at room temperature to give dimethyl complexes **4a** and **4b**, respectively (eq 1), which were isolated as red crystals, fairly stable to air and moisture. While the free ligand **3a** decomposed upon electrochemical oxidation, complex **4a** exhibited a reversible one-electron oxidation wave ($E_{1/2}$ = 0.34 V vs Fc^+/Fc, ΔE = 0.13 V) in the cyclic voltammogram recorded in CH_2Cl_2 in the presence of Bu_4NBF_4 (0.1 M) at room temperature.



(1)

Complex **4b** adopts a square-planar configuration around the platinum (Figure 2).[17a] The six-membered chelate ring comprised of Pt, P1, C3, C4, C5, and P2 atoms also has planarity,[17b] while the ferrocene unit inclines slightly from the chelate ring (ca. 11°). The P1−Pt−P2 angle is 94.31(3)°, the value of which

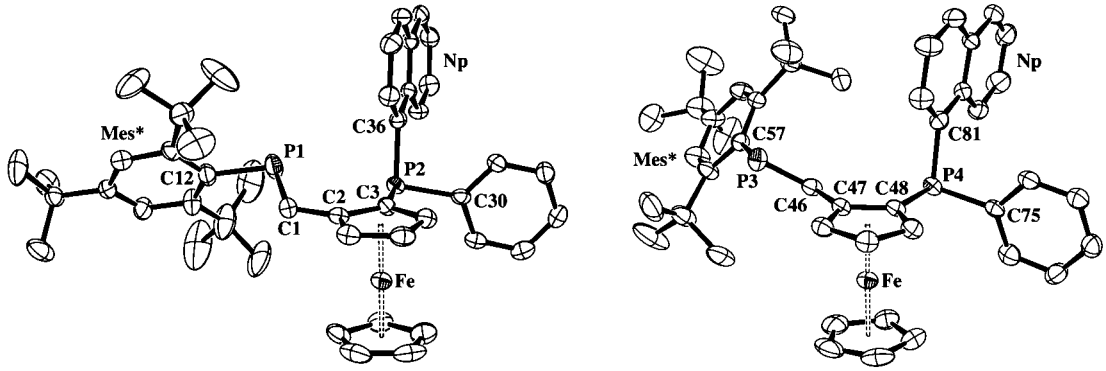
(11) (a) Lacombe, S.; Gonbeau, D.; Cabioch, J.-L.; Pellerin, B.; Denis, J.-M.; Pfister-Guillouzo, G. *J. Am. Chem. Soc.* **1988**, *110*, 6964. (b) Bock, H.; Bankmann, M. *Angew. Chem., Int. Ed.* **1986**, *25*, 265.

(12) Ozawa, F.; Kawagishi, S.; Ishiyama, T.; Yoshifuji, M. *Organometallics* **2004**, *23*, 1325.

(13) Riant, O.; Samuel, O.; Flessner, T.; Taudiene, S.; Kagan, H. B. *J. Org. Chem.* **1997**, *62*, 6733.

(14) (a) Chen, W.; Roberts, S. M.; Whittall, J.; Steiner, A. *Chem. Commun.* **2006**, 2916. See also:(b) Chen, W.; Mbafor, W.; Roberts, S. M.; Whittall, J. *J. Am. Chem. Soc.* **2006**, *128*, 3922. (c) Chen, W.; McCormack, P. J.; Mohammed, K.; Mbafor, W.; Roberts, S. M. *Angew. Chem., Int. Ed.* **2007**, *46*, 4141.

(15) Yam, M.; Chong, J. H.; Tsang, C.-W.; Patrick, B. O.; Lam, A. E.; Gates, D. P. *Inorg. Chem.* **2006**, *45*, 5225, and references therein.



rotamer **A** rotamer **B**

Figure 1. Molecular structures of two rotamers of **3b**. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg) are as follows: [**A**] P1−C1 = 1.668(5), P1−C12 = 1.871(4), C1−C2 = 1.471(6), P2−C3 = 1.811(4), P2−C30 = 1.862(4), P2−C36 = 1.839(4), C1−P1−C12 = 103.5(2), P1−C1−C2= 125.2(3), C12−P1−C1−C2 = −178.1(4), C1−C2−C3−P2 = −3.1(7). [**B**] P3−C46 = 1.673(5), P3−C57 = 1.854(4), C46−C47 = 1.457(6), P4−C48 = 1.810(4), P4−C75 = 1.853(4), P4−C81 = 1.845(4), C46−P3−C57 = 105.0(2), P3−C46−C47 = 121.7(4), C57−P3−C46−C47 = 178.4(3), C46−C47−C48−P4 = −1.6(6).

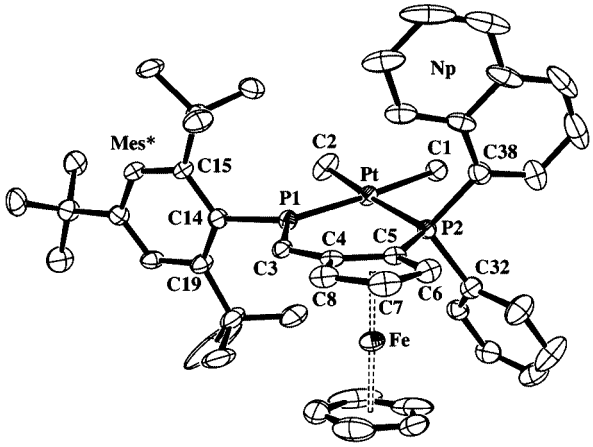


Figure 2. Molecular structure of **4b**·Et_2O. Hydrogen atoms and Et_2O molecule are omitted for clarity. Selected bond distances (Å) and angles (deg): Pt−C1 = 2.105(4), Pt−C2 = 2.102(4), Pt−P1 = 2.2358(9), Pt−P2 = 2.2706(9), P1−C3 = 1.668(4), P1−C14 = 1.842(4), C3−C4 = 1.456(5), P2−C5 = 1.819(4), P2−C32 = 1.836(4), P2−C38 = 1.847(4), C1−Pt−C2 = 84.01(16), P1−Pt−P2 = 94.31(3), C1−Pt−P1 = 176.29(11), C2−Pt−P2 = 172.95(11), C3−P1−C14=108.23(18),C4−C3−P1=125.2(3),C14−P1−C3−C4 = 179.7(3), C3−C4−C5−P2 = 9.0(6), P1−C3−C4−C8 = 169.4(3), Pt1−P2−C5−C6 = −167.9(3), C3−P1−C14−C15 = −92.0(3), C3−P1−C14−C19 = 92.2(3).

is notably larger than those of $PtMe_2$(DPCB) (82.85(4)°) and $PtMe_2$(DPCB-OMe) (83.33(3)°),[12] but almost identical to that of $PtMe_2$(dppp) (94.30(3)°), having a six-membered chelate structure.[18] The Mes* group is perpendicular to the coordination plane. Unlike the free ligand **3b**, no bond-rotation causing the exchange of ortho *t*-Bu signals (δ 1.49 and 1.80) was observed in the ^{1}H NMR spectrum.

Interestingly, the two Pt−Me bonds of **4b** are almost identical in length, showing very similar trans-influence of the phosphaethenyl and phosphanyl groups. Considering the minimal π-bonding character of the Pt−Me bond, it is convincing that the trans-influence mainly reflects the σ-donating abilities of trans ligands.[19] Accordingly, it is concluded that the C═PMes* group has almost identical σ-donating ability to the P(Np)Ph group. This conclusion is consistent with the ^{13}C{^{1}H} NMR data of **4a** and **4b**, showing two methyl−carbon signals with comparable chemical shifts and $^1J_{PtC}$ couplings: (**4a**) δ 2.2 (666 Hz), 6.0 (626 Hz); (**4b**) δ 3.4 (670 Hz), 6.1 (629 Hz).

Table 1 lists the structural data of **4b** and the related DPCB-Y and diphosphane complexes. While the Pt−Me lengths range from 2.074(3) to 2.113(3) Å, the average deviation from the mean bond distance (2.099 Å) is very small (0.009 Å). Accordingly, it is likely that the σ-donating ability of phosphaalkene is essentially comparable to that of phosphane, and the slightly shorter Pt−Me distances of DPCB-Y complexes are ascribed mainly to substituent effects.

Preparation and Catalytic Properties of (π-Allyl)palladium(II) Complexes. As a preliminary attempt at finding the utility of chiral phosphaalkene ligands in catalytic asymmetric reactions, **3a** and **3b** were introduced to (π-allyl)palladium complexes (eq 2). However, the resulting **5a** and **5b** were mixtures of diastereomers with the π-allyl ligands in endo and exo orientations toward the ferrocene unit (endo/exo = 1/1 (**5a**), 1/0.8 (**5b**)). Thus, no stereoselectivity was observed for the complexation of **3a** and **3b** with the Pd(η^3-allyl) entity. For example, the ^{31}P{^{1}H} NMR spectrum of **5a** exhibited two pairs of doublets at δ 13.3 and 178.1 ($^2J_{PP}$ = 74 Hz) and 13.2 and 180.0 ($^2J_{PP}$ = 72 Hz) in almost the same intensities. Further structure assignment was performed by ^{1}H NMR analysis.

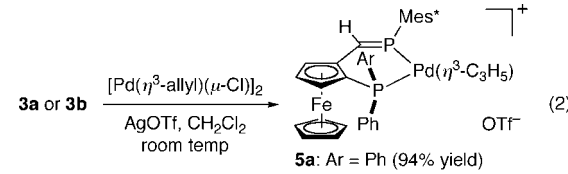


Table 2 summarizes the NMR data of **5a** together with the NOE correlations observed by NOESY. Because of the restricted

(16) (a) Yoshifuji, M.; Toyota, K.; Inamoto, N. *Tetrahedron Lett.* **1985**, *26*, 1727. (b) Yoshifuji, M.; Toyota, K.; Inamoto, N. *Tetrahedron Lett.* **1985**, *26*, 6443. (c) Yoshifuji, M.; Toyota, K.; Matsuda, I.; Niitsu, T.; Inamoto, N.; Hirotsu, K.; Higuchi, T. *Tetrahedron* **1988**, *44*, 1363. (d) Appel, R.; Menzel, J.; Knoch, F.; Volz, P. Z. *Anorg. Allg. Chem.* **1986**, *534*, 100. (e) Gudimetla, V. B.; Rheingold, A. L.; Payton, J. L.; Peng, H.; Simpson, M. C.; Protasiewicz, J. D. *Inorg. Chem.* **2006**, *45*, 4895.

(17) (a) The sum of the four angles around platinum is 360.0°. (b) The sum of the six vertical angles of the chelate ring is 718.8°.

(18) Thomas, J. C.; Peters, J. C. *J. Am. Chem. Soc.* **2003**, *125*, 8870.

(19) Appleton, T. G.; Bennett, M. A. *Inorg. Chem.* **1978**, *17*, 738, and references therein.

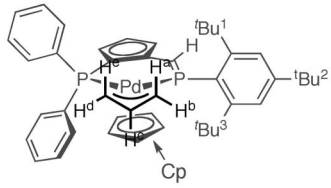
(20) Smith, D. C., Jr.; Haar, C. M.; Stevens, E. D.; Nolan, S. P.; Marshall, W. J.; Moloy, K. G. *Organometallics* **2000**, *19*, 1427.

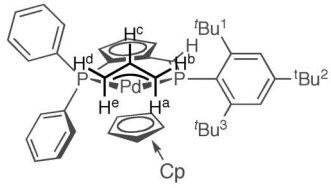
Table 1. Bond Distances and Angles (deg) of Dimethylplatinum(II) Complexes

	bond distance (Å)		bond angle (deg)		
compound	Pt−C	Pt−P	P−Pt−C	C−Pt−C	P−Pt−P
4b	2.105(4)	2.2358(9)	176.3(1)	84.0(2)	94.31(3)
	2.102(4)	2.2706(9)	173.0(1)		
$PtMe_2$(DPCB)[a]	2.093(3)	2.2909(8)	178.5(1)	85.1(2)	82.85(4)
$PtMe_2$(DPCB-OMe)[a]	2.089(4)	2.2948(7)	177.8(1)	85.9(2)	83.33(3)
	2.074(3)	2.2878(8)	177.8(1)		
$PtMe_2$(dppp)[b]	2.102(3)	2.2714(8)	174.94(9)	86.0(1)	94.30(3)
	2.113(3)	2.2724(8)	175.99(10)		
$PtMe_2$(dpmcp)[c]	2.109(5)	2.261(1)	174.8(2)	[d]	95.39(5)
	2.106(6)	2.265(1)	174.7(2)		

[a] DPCB = 1,2-diphenyl-3,4-bis{(2,4,6-tri-*tert*-butylphenyl)phosphinidene}cyclobutene: ref 12. [b] Ref 18. [c] dpmcp = 1,1-bis(diphenylphosphanylmethyl)cyclopropane: ref 20. [d] Not reported.

Table 2. ^{1}H NMR Chemical Shifts and NOE Correlations for 5a[a]

endo isomer	assign	H^a	H^b	H^c	H^d	H^e	*t*-Bu^1	*t*-Bu^2	*t*-Bu^3	Cp
	δ	3.85	4.55	6.01	4.66	3.21	1. 27	1.35	1.72	4.07
	H^a		○	−	−	○	○	−	−	−
	H^b	○		○	−	−	−	−	○	−
	H^c	−	○		○	−	−	−	○	−
	H^d	−	−	○		○	−	−	−	−
	H^e	○	−	−	○			−	−	−
	t-Bu^1	○	−	−	−	−		−	−	−
	t-Bu^2	−	−	−	−	−	−		−	−
	t-Bu^3	−	○	○	−	−	−	−		○
	Cp	−	−	−	−	−	−	−	○	

exo isomer	assign	H^a	H^b	H^c	H^d	H^e	*t*-Bu^1	*t*-Bu^2	*t*-Bu^3	Cp
	δ	3.68	4.49	5.54	4.55	3.23	1.04	1.37	1.80	4.26
	H^a		○	−	−	○	−	−	○	○
	H^b	○		○	−	−	○	−	○	−
	H^c	−	○		○	−	○	−	−	−
	H^d	−	−	○		○	−	−	−	−
	H^e	○	−	−	○		−	−	−	−
	t-Bu^1	−	○	○	−	−		−	−	−
	t-Bu^2	−	−	−	−	−	−		−	−
	t-Bu^3	○	○	−	−	−	−	−		○
	Cp	○	−	−	−	−	−	−	○	

[a] The data were accumulated at room temperature in CD_2Cl_2 on a 400 MHz NMR instrument. The NOE correlations were examined by NOESY.

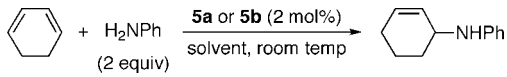
rotation of the Mes* group, all *t*-Bu signals appeared as independent singlet peaks well separated from one another. Among them, the signals at δ 1.72 and 1.80 showed cross-peaks with the signals of the nonsubstituted Cp at δ 4.07 and 4.26, respectively, and therefore they were assigned to *t*-Bu^3 groups in each isomer. The *t*-Bu^3 signal at δ 1.72 had an NOE correlation with the central proton signal of the allyl ligand (H^c) at δ 6.01, indicating the endo orientation of the allyl ligand. On the other hand, the other isomer showed no NOE correlation between *t*-Bu^3 (δ 1.80) and H^c (δ 5.54) signals. Instead, the H^c proton (δ 5.54) was correlated with the *t*-Bu^1 group (δ 1.04) on the opposite side of the nonsubstituted Cp ring. Consequently, this isomer was assigned to the exo form.

Next, the catalytic performance of **5a** and **5b** was investigated in hydroamination of 1,3-cyclohexadiene with aniline. While this reaction has been examined using diphosphane-coordinated palladium complexes, the catalytic activity is modest, and the reaction generally takes several days for completion at room temperature.[21,22] On the other hand, we have already reported that the DPCB-OMe complex [Pd(η^3-allyl)(DPCB-OMe)]OTf exhibits an exceptionally high catalytic activity, affording the

(21) (a) Johns, A. M.; Utsunomiya, M.; Incarvito, C. D.; Hartwig, J. F. *J. Am. Chem. Soc.* **2006**, *128*, 1828. (b) Lober, O.; Kawatsura, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2001**, *123*, 4367. (c) Hartwig, J. F. *Pure Appl. Chem.* **2004**, *76*, 507.

(22) (a) Taube, R. In *Applied Homogenerous Catalysis with Organometallic Compounds, Vol. 1*; Cornils, B., Herrmann, W. A., Eds.; VCH: Weinheim, 1996; p 507. (b) Müller, T. E.; Beller, M. *Chem. Rev.* **1998**, *98*, 675.

Table 3. Hydroamination of 1,3-Cyclohexadiene with Aniline Catalyzed by 5a and 5b[a]

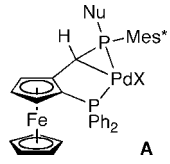


entry	catalyst	solvent	additive[b]	time (h)	yield (%)[c]	ee (%)[d]
1	**5a**	toluene		43	45	8
2	**5a**	Et_2O		96	31	21
3	**5a**	THF		100	55	0
4	**5a**	CH_2Cl_2		126	0	
5	**5a**	toluene	MS3A	49	72	1
6	**5a**	toluene	MS4A	44	76	0
7	**5a**	toluene	MS5A	49	84	3
8	**5b**	toluene	MS5A	53	61	0

[a] The reactions were performed with 1,3-cyclohexadiene (0.5 mmol), aniline (1.0 mmol), catalyst (0.01 mmol, 2 mol %), and solvent (1 mL) at room temperature. [b] 100 mg/mL of activated molecular sieves was added. [c] Determined by GLC using tridecane as an internal standard. [d] Determined by HPLC using a chiral stationary phase column (Daicel Chiralpak AD-H).

hydroamination product in nearly quantitative yield within 3−5 h under the same reaction conditions.[7]

Table 3 summarizes the results for **5a** and **5b**. Unlike the DPCB-OMe catalyst, the catalytic activity of **5a** was modest, and the reaction did not reach completion in several kinds of solvents (entries 1−4). Follow-up experiments using ^{31}P NMR revealed the occurrence of degradation of palladium species under catalytic conditions. Thus, when **5a** was treated with aniline (40 equiv) in toluene in the presence of 1,3-cyclohexadiene (20 equiv) at room temperature, the signals of **5a** disappeared within 1 h, and instead two sets of signals assignable to the endo and exo isomers of (η^3-cyclohexenyl)palladium intermediate appeared at δ 12.3 and 178.8 (each doublet, J_{PP} = 74 Hz) and δ 11.7 and 181.5 (each doublet, J_{PP} = 70 Hz), respectively, in a 1:2 ratio. Subsequently, these signals gradually decreased for 2 days to be replaced by new singlets at δ 13.4 and 72.0 with the same intensities. Based on the similarity of the chemical shift to analogous compounds previously reported,[23] the signal at δ 72.0 is assignable to a pallada-phosphacyclopropane (**A**, see the possible structure shown below) formed by addition of a nucleophile (Nu), very probably aniline or water. Therefore, we added molecular sieves to the catalytic solution and examined palladium complexes. As a result, it was found that the degradation of (η^3-cyclohexenyl)palladium species could be prevented to a considerable extent. Thus, a mixture of **5a**, 1,3-cyclohexadiene (20 equiv), and aniline (40 equiv) was stirred for 2 days at room temperature in the presence of MS5A (100 mg/mL). The $^{31}P\{^1H\}$ NMR spectrum revealed that 49% of the (η^3-cyclohexenyl)palladium complex remains together with **A**.



A

In accordance with the NMR observations described above, the yield of catalytic hydroamination product was clearly improved by addition of molecular sieves to the system (entries 5−8 in Table 2). Particularly, the reaction using **5a** and MS5A led to 84% yield of the product, while no remarkable asymmetric induction was observed as expected from the nonselective formation of the endo and exo isomers of (π-allyl)palladium complexes.

Conclusion

Using the newly prepared, ferrocene-based ligands bearing both phosphaalkene and phosphane moieties as coordination sites (**3a** and **3b**), we confirmed that the phosphaethenyl and diarylphosphanyl groups exhibit almost identical trans-influence toward Pt−Me bonds. This finding is consistent with the comparable lone-pair orbital levels of phosphaethene and phosphane, previously estimated by ab initio MO calculations.[12] On the other hand, it was also observed that the ferrocene-based phosphaalkene ligands are rather unstable in palladium-catalyzed hydroamination of 1,3-cyclohexadiene with aniline and readily undergo addition of a nucleophile to give a pallada-phosphacyclopropane as a catalytically inactive species. Although this undesirable process could be restrained to a considerable extent by addition of molecular sieves to the catalytic system, the observed catalytic performance was still far from the DPCB-OMe catalyst. Through the previous studies, we were convinced that the occurrence of extended π-conjugation over the 1,2-diaryl-3,4-diphosphinidenecyclobutene skeleton is crucial not only for the chemical stability but also for the high catalytic activity of DPCB-Y complexes. In this sense, the ferrocene unit was unfit as the counterpart of the phosphaalkene moiety. Further development of new phosphaalkene ligands especially for asymmetric catalysis is underway in this research group.

Experimental Section

General Considerations. All manipulations of air- and/or moisture-sensitive compounds were carried out under a nitrogen or argon atmosphere using standard Schlenk techniques. Toluene and hexane were distilled from sodium benzophenone ketyl and stored over activated molecular sieves (MS4A). $CDCl_3$ was purified by passing through an alumina column, degassed by freeze−pump−thaw cycles, and stored over MS4A. CD_2Cl_2 was dried over calcium hydride, transferred under vacuum, and stored over MS4A. Dehydrated Et_2O, THF, and CH_2Cl_2 were purchased (Wako) and used as received. 1,3-Cyclohexadiene and aniline were distilled prior to use. $[PtMe_2(\mu\text{-}SMe_2)]_2$ and $[Pd(\eta^3\text{-}C_3H_5)(\mu\text{-}Cl)]_2$ were prepared according to the literature.[24,25]

NMR spectra were recorded on a Bruker Avance 400 spectrometer. Chemical shifts are reported in δ, referenced to ^1H (of residual protons) and ^{13}C signals of deuterated solvents as internal standards or to the ^{31}P signal of 85% H_3PO_4 as an external standard. Cyclic voltammetry was performed with a BAS ALS600C electrochemical analyzer. Optical rotation was measured on a SEPA-200 polarimeter. Enantiomer excess of hydroamination product was determined by HPLC using a Daicel Chiralpak AD-H column and hexane as an eluting solvent. HRMS and elemental analysis were performed by the ICR Analytical Laboratory, Kyoto University.

Preparation of 2-Phosphanyl-1-phosphaethenylferrocenes (3a,b). A typical procedure is reported for **3a**. To a solution of Mes*PH_2 (2,4,6-tri-*tert*-butylphenylphosphane) (0.209 g, 0.75 mmol) in THF (20 mL) was added *n*-BuLi (1.58 M in hexane, 0.47 mL, 0.75 mmol) at −78 °C. The mixture was stirred for 15 min, warmed to room temperature, and stirred further for 30 min.

(23) (a) Liang, H.; Nishide, K.; Ito, S.; Yoshifuji, M. *Tetrahedron Lett.* **2003**, *44*, 8297. (b) Jouaiti, A.; Geoffrey, M.; Bernardinelli, G. *Chem. Commun.* **1996**, 437. (c) van der Sluis, M.; Beverwijk, V.; Termaten, A.; Gavrilova, E.; Bickelhaupt, F.; Kooijman, H.; Veldman, N.; Spek, A. L. *Organometallics* **1997**, *16*, 1144.

(24) Scott, J. D.; Puddephatt, R. J. *Organometallics* **1983**, *2*, 1643.

(25) Tatsuno, Y.; Yoshida, T.; Otsuka, S. *Inorg. Synth.* **1990**, *28*, 343.

Me_3SiCl (0.095 mL, 0.75 mmol) was added, and after 30 min, *n*-BuLi (1.58 M in hexane, 0.47 mL, 0.75 mmol) was slowly added. The mixture was stirred for 30 min at room temperature and then cooled to −78 °C. To this solution, a solution of 2-diphenylphosphanylferrocenecarboxaldehyde (**2a**, 0.199 g, 0.50 mmol) in THF (10 mL) was added dropwise. The solution was gradually warmed to room temperature and stirred until no trace of **2a** was detected by TLC. Me_3SiCl (0.095 mL, 0.75 mmol) was added, and the reaction mixture was stirred for 15 min and concentrated to dryness under vacuum. The resulting residue was subjected to flash column chromatography (SiO_2, hexane/CH_2Cl_2 = 90/10) to give **3a** as a red solid in 78% yield (0.258 g, 0.39 mmol). Similarly, compound **3b** was obtained as a red solid from (S_{Fe},R_P)-2-(1-naphthylphenylphosphanyl)ferrocenecarboxaldehyde (**2b**) in 94% yield.

3a. Mp: 83−85 °C. $[\alpha]_D^{20}$ = +636 (*c* 0.182, $CHCl_3$). ^1H NMR ($CDCl_3$, 20 °C): δ 1.34 (s, 9H), 1.38 (br, 18H), 3.90 (s, 1H), 4.06 (s, 5H), 4.50 (virtual triplet, J_{app} = 2.5 Hz, 1H), 5.06 (s, 1H), 7.03−7.10 (m, 2H), 7.15−7.21 (m, 3H), 7.33−7.40 (m, 5H), 7.48−7.55 (m, 2H), 8.18 (dd, J_{PH} = 24.2 Hz, J_{PH} = 2.7 Hz, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C): δ 31.4 (s), 33.7 (s), 33.8 (s), 34.9 (s), 38.2 (s), 67.4 (dd, J_{PC} = 17 and 3 Hz), 70.0 (s), 70.8 (s), 72.6 (d, J_{PC} = 3 Hz), 75.6 (dd, J_{PC} = 9 and 7 Hz), 92.4 (dd, J_{PC} = 25 and 23 Hz), 121.7 (s), 127.7 (s), 127.9 (d, J_{PC} = 6 Hz), 128.1 (d, J_{PC} = 8 Hz), 129.2 (s), 132.2 (d, J_{PC} = 18 Hz), 135.2 (d, J_{PC} = 21 Hz), 137.2 (d, J_{PC} = 8 Hz), 138.8 (dd, J_{PC} = 55 and 1 Hz), 139.6 (d, J_{PC} = 9 Hz), 149.2 (s), 153.7 (s), 171.4 (dd, J_{PC} = 35 and 9 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20 °C): δ −22.8 (d, J_{PP} = 15 Hz), 247.8 (d, J_{PP} = 15 Hz). HRMS (EI), *m*/*z*: calcd for $C_{41}H_{48}FeP_2$ 658.2580 $[M]^+$; found 658.2564. Anal. Calcd for $C_{41}H_{48}FeP_2$: C, 74.77; H, 7.35. Found: C, 75.10; H, 7.75.

3b. Mp: 165−168 °C. $[\alpha]_D^{20}$ = +778 (*c* 0.184, $CHCl_3$). ^1H NMR ($CDCl_3$, 20 °C): δ 1.25 (br, 18H), 1.28 (s, 9H), 3.86 (s, 1H), 4.14 (s, 5H), 4.54 (virtual triplet, J_{app} = 2.4 Hz, 1H), 5.09 (s, 1H), 7.02 (dd, *J* = 6.2 and 5.7 Hz, 1H), 7.25−7.41 (m, 8H), 7.50−7.58 (m, 2H), 7.74 (d, *J* = 8.1 Hz, 1H), 7.78 (d, *J* = 8.1 Hz, 1H), 8.11 (d, *J* = 3.3 Hz, 1H), 8.18 (dd, *J* = 24.0 and 2.9 Hz, 1H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ 31.6 (s), 34.0 (s), 34.1 (s), 35.3 (s), 38.6 (s), 68.5 (dd, J_{PC} = 16 and 3 Hz), 70.7 (s), 71.6 (s), 73.8 (d, J_{PC} = 4 Hz), 76.1 (dd, J_{PC} = 9 and 6 Hz), 93.0 (dd, J_{PC} = 25 and 23 Hz), 122.2 (s), 126.0 (d, J_{PC} = 7 Hz), 126.1 (s), 126.2 (d, J_{PC} = 2 Hz), 126.3 (s), 128.7 (d, J_{PC} = 8 Hz), 129.0 (d, J_{PC} = 1 Hz), 129.2 (s), 129.8 (s), 131.6 (s), 133.9 (d, J_{PC} = 4 Hz), 134.8 (d, J_{PC} = 21 Hz), 135.5 (d, J_{PC} = 21 Hz), 136.9 (d, J_{PC} = 8 Hz), 137.3 (d, J_{PC} = 14 Hz), 139.7 (dd, J_{PC} = 55 and 2 Hz), 149.9 (s), 154.4 (s), 172.0 (dd, J_{PC} = 35 and 9 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20 °C): δ −30.0 (d, J_{PP} = 18 Hz), 248.5 (d, J_{PP} = 18 Hz). HRMS (FAB), *m*/*z*: calcd for $C_{45}H_{50}FeP_2$ 709.2815 $[M + H]^+$; found 709.2820. Anal. Calcd for $C_{45}H_{50}FeP_2$: C, 76.27; H, 7.11. Found: C, 76.16; H, 7.17.

Preparation of Dimethylplatinum(II) Complexes (4a,b). A typical procedure is reported for **4a**. To a suspension of [$PtMe_2$(μ-SMe_2)]$_2$ (28.7 mg, 0.050 mmol) in Et_2O (5 mL) was added **3a** (65.8 mg, 0.10 mmol). The mixture was stirred at room temperature overnight. Volatile materials were removed under reduced pressure to afford a red solid, which was dissolved in a minimum amount of CH_2Cl_2, layered with pentane, and allowed to stand at 0 °C to form red crystals of **4a** in 84% yield (70 mg, 0.42 mmol). Complex **4b** was similarly prepared using **3b** instead of **3a**. Recrystallization from Et_2O gave red crystals with the composition of **4b**·Et_2O, suitable for X-ray structure analysis.

4a. Mp: 245−248 °C (dec). ^1H NMR (CD_2Cl_2, 20 °C): δ 0.46 (m, J_{PtH} = 70.6 Hz, 3H), 0.75 (m, J_{PtH} = 74.6 Hz, 3H), 1.31 (s, 9H), 1.35 (s, 9H), 1.76 (s, 9H), 4.00 (s, 5H), 4.15 (s, 1H), 4.45−4.52 (m, 2H), 7.21−7.63 (m, 9H), 7.72 (d, J_{PH} = 22.8 Hz, 1H), 7.83−7.94 (m, 2H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ 2.2 (dd, J_{PC} = 117 and 7 Hz, J_{PtC} = 666 Hz), 6.0 (dd, J_{PC} = 97 and 6 Hz, J_{PtC} = 626 Hz), 31.6 (s), 34.4 (s, J_{PtC} = 4 Hz), 35.1 (s, J_{PtC} = 5 Hz), 35.5 (s), 39.2 (s), 40.1 (s), 63.9 (dd, J_{PC} = 49 and 11 Hz), 70.3 (d, J_{PC} = 4 Hz), 71.0 (s), 73.9 (dd, J_{PC} = 74 and 16 Hz), 74.5 (virtual triplet, J_{app} = 5 Hz), 91.2 (dd, J_{PC} = 18 and 4 Hz), 123.7 (dd, J_{PC} = 39 and 7 Hz), 128.3 (dd, J_{PC} = 10 and 9 Hz), 129.5 (d, J_{PC} = 2 Hz), 130.9 (d, J_{PC} = 2 Hz), 132.4 (d, J_{PC} = 11 Hz, J_{PtC} = 11 Hz), 136.1 (d, J_{PC} = 12 Hz, J_{PtC} = 20 Hz), 137.8 (d, J_{PC} = 46 Hz, J_{PtC} = 14 Hz), 145.8 (dd, J_{PC} = 51 and 4 Hz, J_{PtC} = 30 Hz), 152.0 (s), 155.1 (d, J_{PC} = 2 Hz), 155.6 (s). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ 4.6 (d, J_{PP} = 19 Hz, J_{PtP} = 1714 Hz), 210.2 (d, J_{PP} = 19 Hz, J_{PtP} = 1953 Hz). HRMS (FAB), *m*/*z*: calcd for $C_{43}H_{54}FeP_2{}^{195}Pt$ 883.270 $[M + H]^+$, found 883.269. Anal. Calcd for $C_{43}H_{54}FeP_2Pt$: C, 58.44; H, 6.16. Found: C, 58.12; H, 6.22.

4b. Mp: >300 °C. ^1H NMR (CD_2Cl_2, 20 °C): δ 0.45 (m, J_{PtH} = 72.2 Hz, 6H), 1.34 (s, 9H), 1.49 (s, 9H), 1.80 (s, 9H), 3.81 (s, 5H), 4.18 (s, 1H), 4.36 (virtual triplet, J_{app} = 2.5 Hz, 1H), 4.48 (s, 1H), 7.19 (t, J_{HH} = 7.8 Hz, 1H), 7.34−7.49 (m, 3H), 7.55−7.70 (m, 5H), 7.78−7.91 (m, 3H), 8.15−8.30 (m, 3H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ 3.4 (dd, J_{PC} = 117 and 6 Hz, J_{PtC} = 670 Hz), 6.1 (dd, J_{PC} = 96 and 6 Hz, J_{PtC} = 629 Hz), 31.5 (s), 34.2 (s), 35.4 (s, J_{PtC} = 12 Hz), 35.6 (s), 39.5 (s), 40.0 (s), 67.9 (dd, J_{PC} = 47 and 10 Hz), 70.4 (d, J_{PC} = 5 Hz), 71.0 (s), 72.1 (dd, J_{PC} = 16 and 7 Hz), 75.4 (virtual triplet, J_{app} = 5 Hz), 91.4 (dd, J_{PC} = 20 and 6 Hz), 123.7 (d, J_{PC} = 7 Hz), 123.9 (d, J_{PC} = 7 Hz), 124.5 (d, J_{PC} = 9 Hz), 125.7 (s), 126.2 (s), 127.8 (d, J_{PC} = 11 Hz), 128.5 (d, J_{PC} = 10 Hz), 129.0 (dd, J_{PC} = 6 and 4 Hz), 129.2 (s), 130.8 (s), 131.3 (s), 131.6 (d, J_{PC} = 5 Hz, J_{PtC} = 9 Hz), 132.7 (d, J_{PC} = 45 Hz), 133.5 (d, J_{PC} = 12 Hz), 134.7 (d, J_{PC} = 7 Hz), 134.8 (d, J_{PC} = 48 Hz), 137.3 (d, J_{PC} = 13 Hz, J_{PtC} = 26 Hz), 146.1 (dd, J_{PC} = 49 and 3 Hz, J_{PtC} = 30 Hz), 152.1 (s), 155.5 (d, J_{PC} = 28 Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ 1.8 (d, J_{PP} = 18 Hz, J_{PtP} = 1685 Hz), 209.5 (d, J_{PP} = 18 Hz, J_{PtP} = 1964 Hz). HRMS (FAB), *m*/*z*: calcd for $C_{47}H_{56}FeP_2{}^{195}Pt$ 933.285 $[M]^+$; found 933.284. Anal. Calcd for $C_{47}H_{56}FeP_2Pt \cdot C_4H_{10}O$: C, 60.77; H, 6.60. Found: C, 60.74; H, 6.62.

Preparation of (π-Allyl)palladium(II) Complexes (5a,b). A typical procedure is reported for **5a**. [Pd(η^3-allyl)(μ-Cl)]$_2$ (18.9 mg, 0.050 mmol) and **3a** (65.9 mg, 0.10 mmol) were dissolved in CH_2Cl_2 (2 mL) at room temperature. The solution was cooled to 0 °C, and AgOTf (30.8 mg, 0.12 mmol) was added. The mixture was stirred at room temperature for 2 h. A white precipitate of AgCl formed in the system was removed by filtration through a Celite pad. The filtrate was concentrated to dryness, and the resultant residue was washed with hexane (3 mL × 3) and dried under vacuum to afford [Pd(η^3-allyl)(**3a**)]OTf (**5a**) in 94% yield (89.9 mg, 0.094 mmol) as a purple solid, which was analytically pure. Similarly, complex **5b** was obtained as a purple solid in 87% yield.

5a (1:1 mixture of endo and exo isomers). Mp: 231−234 °C (dec). HRMS (FAB), *m*/*z*: calcd for $C_{45}H_{54}O_3F_3P_2SFe^{106}Pd$ 955.161 $[M + H]^+$; found 955.161. Anal. Calcd for $C_{45}H_{53}F_3FeO_3P_2PdS$: C, 56.59; H, 5.59. Found: C, 56.19; H, 5.77. The NMR data of each isomer are as follows.

Endo isomer. ^1H NMR (CD_2Cl_2, 20 °C): δ 1.27 (s, 9H), 1.35 (s, 9H), 1.72 (s, 9H), 3.21 (t, *J* = 11.9 Hz, 1H), 3.85 (t, *J* = 12.8 Hz, 1H), 4.07 (s, 5H), 4.55 (2H), 4.66 (t, *J* = 6.2 Hz, 1H), 4.78 (s, 1H), 4.89 (q, *J* = 2.4 Hz, 1H), 6.01 (septet, *J* = 6.9 Hz, 1H), 7.20 (dd, *J* = 12.1 and 7.7 Hz, 2H), 7.36−7.86 (m, 10H), 7.91 (d, *J* = 25.8 Hz, 1H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C): 13.3 (d, J_{PP} = 74 Hz), 178.1 (d, J_{PP} = 74 Hz).

Exo isomer. ^1H NMR (CD_2Cl_2, 20 °C): 1.04 (s, 9H), 1.37 (s, 9H), 1.80 (s, 9H), 3.23 (t, *J* = 12.0 Hz, 1H), 3.68 (t, *J* = 11.7 Hz, 1H), 4.26 (s, 5H), 4.44 (s, 1H), 4.49 (t, *J* = 6.7 Hz, 1H), 4.55 (1H), 4.76 (s, 1H), 4.92 (q, *J* = 2.4 Hz, 1H), 5.54 (septet, *J* = 6.7 Hz, 1H), 7.12 (dd, *J* = 12.2 and 7.8 Hz), 7.36−7.86 (m, 10H), 7.87 (d, *J* = 26.1 Hz, 1H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ 13.2 (d, J_{PP} = 72 Hz), 180.0 (d, J_{PP} = 72 Hz).

5b (1:0.8 mixture of endo and exo isomers). Mp: 164−167 °C (dec). HRMS (FAB), *m*/*z*: calcd for $C_{48}H_{55}FeP_2{}^{106}Pd$ 855.216 $[M + H]^+$; found 855.217. Anal. Calcd for $C_{49}H_{55}F_3FeO_3P_2PdS$: C,

Table 4. Crystallographic Data for 3b and 4b·Et$_2$O

	3b	**4b·Et$_2$O**
formula	$C_{45}H_{50}FeP_2$	$C_{51}H_{66}FeOP_2Pt$
fw	708.64	1007.92
cryst size, mm	0.50 × 0.10 × 0.04	0.30 × 0.20 × 0.04
cryst syst	orthorhombic	orthorhombic
space group	$P2_12_12_1$ (#19)	$P2_12_12_1$ (#19)
a (Å)	14.550(3)	10.46390(10)
b (Å)	15.300(3)	17.2101(2)
c (Å)	34.447(7)	25.5495(3)
V (Å^3)	7669(3)	4601.08(9)
Z	8	4
d_{calcd} (g cm^{-3})	1.228	1.455
μ(Mo Kα) (mm^{-1})	0.507	3.457
temp (K)	173(2)	113(2)
θ range (deg)	3.49−27.48	2.28−28.54
no. of reflns collected	62 571	49 777
no. of unique reflns	17494 (R_{int} = 0.0790)	11538 (R_{int} = 0.0504)
transmn factor	0.7857−0.9800	0.4236−0.8741
no. of reflections with $I > 2\sigma(I)$	13 618	10 485
no. of variables	891	522
goodness-of-fit on F^2	1.049	1.003
final R indices ($I > 2\sigma(I)$)	R_1 = 0.0659, wR_2 = 0.1383	R_1 = 0.0287, wR_2 = 0.0665
R indices (all data)	R_1 = 0.0905, wR_2 = 0.1531	R_1 = 0.0348, wR_2 = 0.0688

58.55; H, 5.51. Found: C, 58.33; H, 5.69. The NMR data of each isomer are as follows.

Endo isomer. ^{1}H NMR (CD_2Cl_2, 20 °C): δ 1.20 (s, 9H), 1.35 (s, 9H), 1.70 (s, 9H), 3.07 (t, J = 11.7 Hz, 1H), 4.07 (s, 5H), 4.12 (t, J = 12.8 Hz, 1H), 4.45 (s, 1H), 4.51 (br, 1H), 4.69 (br, 1H), 4.79 (s, 1H), 4.88 (m, 1H), 5.95 (septet, J = 6.7 Hz, 1H), 7.24 (dd, J = 13.3 and 7.2 Hz, 1H), 7.30−7.58 (m, 8H), 7.60−8.20 (m, 18H). ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C): δ 7.7 (d, J_{PP} = 72 Hz), 180.2 (d, J_{PP} = 72 Hz).

Exo isomer. ^{1}H NMR (CD_2Cl_2, 20 °C): δ 0.79 (s, 9H), 1.32 (s, 9H), 1.78 (s, 9H), 2.99 (t, J = 12.7 Hz, 1H), 3.50 (t, J_{PH} = 11.7 Hz, 1H), 4.29 (s, 5H), 4.30 (s, 1H), 4.33 (br, 1H), 4.59 (br, 1H), 4.79 (s, 1H), 4.88 (m, 1H), 5.39 (septet, J = 6.8 Hz, 1H), 7.03 (dd, J = 12.8 and 7.2 Hz, 1H), 7.30−7.58 (m, 8H), 7.60−8.20 (m, 18H). ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C): δ 8.9 (d, J_{PP} = 73 Hz), 182.7 (d, J_{PP} = 73 Hz).

Catalytic Hydroamination. To a Schlenk tube containing catalyst **5a** (9.5 mg, 0.01 mmol) were added successively 1,3-cyclohexadiene (48 μL, 0.50 mmol), toluene (1.0 mL), tridecane (20 μL, GLC standard), and aniline (0.091 mL, 1.0 mmol). The mixture was stirred at room temperature and examined by GLC. The reaction solution was concentrated and subjected to flash column chromatography (SiO_2, 70/1 = hexane/AcOEt), affording *N*-cyclohexen-3-ylaniline as colorless oil. The enantiomer excess of the product was determined by chiral HPLC (Daicel Chiralpak AD-H, hexane, flow rate = 0.17 mL/min, t_R = 71.8 (major) and 78.7 min (minor)).

X-ray Diffraction Analysis of 3b and 4b·Et$_2$O. The X-ray diffraction studies were performed on a Rigaku Mercury CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71070 Å). The intensity data were collected at 173 K (**3b**) or 113 K (**4b**·Et$_2$O) and corrected for Lorentz and polarization effects and absorption (numerical). The structure was solved by direct methods (SHELXS-97) and refined on F^2 against all reflections (SHELXL-97).[26] Further information has been deposited with the Cambridge Crystallographic Data Centre (CCDC-699610 and -699611). A summary of the data is given in Table 4.

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Supporting Information Available: Crystallographic data for **3b** and **4b**·Et$_2$O in cif format. This material is available free of charge via the Internet://pus.acs.org.

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(26) Sheldrick, G. M. *SHELX-97*; University of Göttingen: Germany, 1997.