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Chiral Phosphinooxazolidine Ligands for Palladium- and Platinum-Catalyzed Asymmetric Diels−Alder Reactions

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Cationic palladium (Pd)- and platinum (Pt)-phosphinooxazolidine catalysts **13a**−**c**, **15a**−**d**, **17a**−**c**, and **19a**−**c** were prepared from phosphinooxazolidine ligands **1**−**3**, MCl_2 (M = Pd and Pt), and counterions, and the activities of the catalysts in the asymmetric Diels−Alder (DA) reactions of cyclic or acyclic dienes with imide dienophiles were investigated. These catalysts demonstrated high levels of catalytic activity. The cationic Pd−POZ complex **13c** provided particularly excellent enantioselectivity (98% ee) in the DA reactions of cyclopentadiene with acryloyl-, crotonyl-, and fumaroyl-1,3-oxazolidin-2-ones (**20a**−**c**).

Introduction

The design of economical and efficient chiral ligands for highly enantioselective transformations has been a great challenge in the field of catalytic asymmetric synthesis.[1] Recently, we developed N−P type, chiral phosphinooxazoline (POZ) ligands **1** and **3** (Figure 1) and found that the Pd complex of ligand **1** works as an effective catalyst of Pd-catalyzed asymmetric allylic alkylation.[2] A major advantage of ligand **1** is that either enantiomeric form can be readily obtained from the reaction of commercially available (*R*)- or (*S*)-1,1-diphenyl(2-pyrrolidinyl)methanol with 2-(diphenylphosphino)-benzaldehyde. The enantioselective Diels−Alder reaction (DA) is an important and versatile reaction in synthetic organic chemistry. Many research groups have reported an enantioselective version that relies on a chiral catalyst.[3] However, most DA catalysts have the disadvantage of working effectively only on a specific subset of substrates. The chiral catalysts that are reported to provide high enantioselectivity in the DA reaction include copper−C_2-symmetrical bis-oxazolines,[4] copper−phosphinooxazolines,[5] copper−siam,[6] borane−BLA,[7] titanium−TADDOL[8] catalysts, and others.[9] The use of late transition metals such as palladium(Pd) and platinum(Pt) as chiral

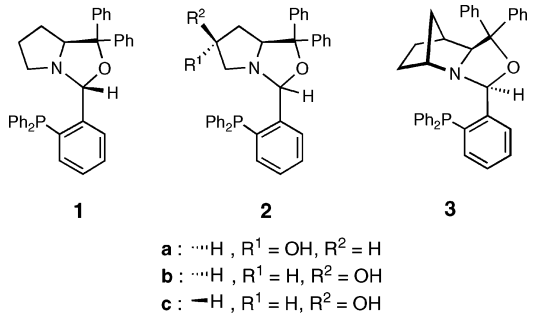

FIGURE 1. Phosphinooxazolidine Ligands.

DA catalysts has not been extensively explored. Only a few studies on Pd- or Pt-based catalysts have been reported.[10] In this paper we report a detailed investigation of the design of cationic Pd− and Pt−POZ catalysts containing POZ ligands **1**−**3**, the application of these catalysts in the enantioselective DA reaction, and the transition-state assembly of these catalysts.[11]

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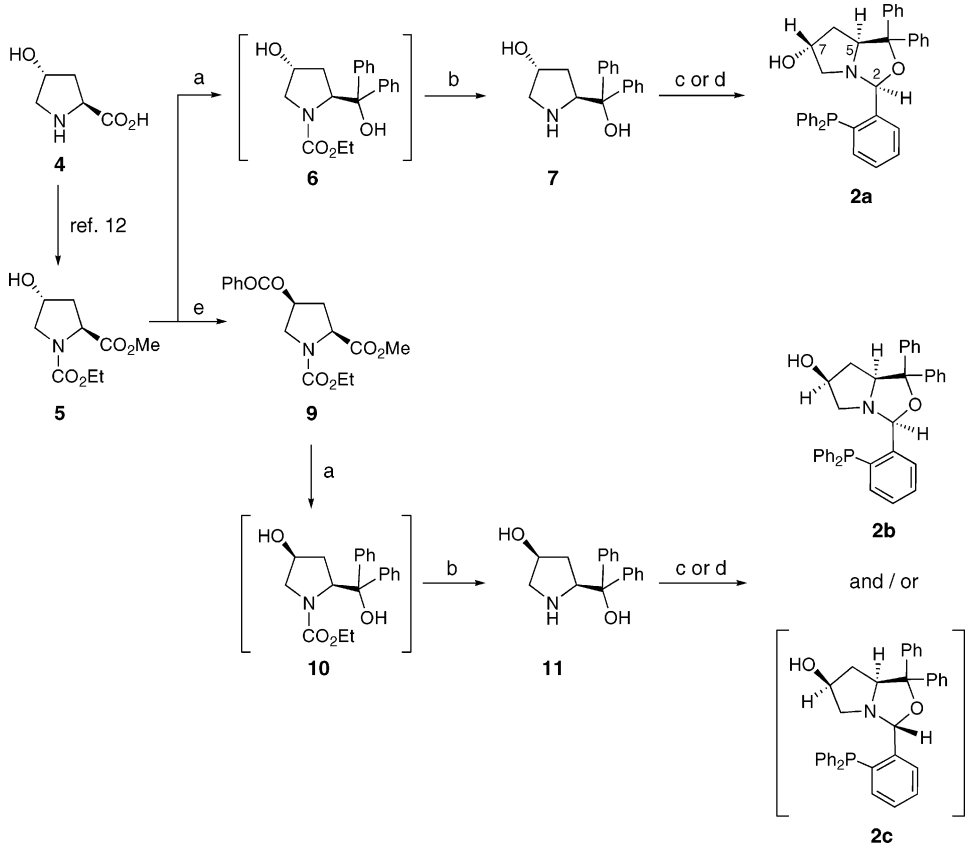
SCHEME 1. Preparation of Chiral Ligands[a]



[a] Reagents and conditions: (a) PhMgBr, THF, rt, 5 h; (b) KOH, MeOH/H_2O, 100 °C, 24 h, **7** 72%, **11** 90%; (c) 2-(diphenylphosphino)benzaldehyde **8**, *p*-TsOH, benzene, reflux, 24 h, **2a** 64%, **2b** + **2c** (1:1) 59%; (d) **8**, CSA, benzene. reflux, 24 h, **2a** 77%, **2b**:58%; (e) DIAD, Ph_3P, $PhCO_2H$, THF, 0 °C, 5 h, 90%.

Results and Discussion

Synthesis of Chiral POZ Ligands. The simplest chiral POZ ligand, **1**, and the bulkiest, **3**, were prepared by using our previously reported procedure.[2,11] The bulkier 7-hydroxy-POZ ligands **2a**–**c** were synthesized from commercially available 2,4-*trans*-4-hydroxy-L-proline **4** (Scheme 1).[12] Compound **4** was converted to ester **5**, and the prolinol **7** was isolated in good yield after a Grignard reaction and the treatment of **6** with potassium hydroxide. The condensation of **7** with 2-(diphenylphosphino)benzaldehyde **8** in the presence of *p*-TsOH or camphorsulfonic acid (CSA) afforded the 5,7-*trans* POZ ligand **2a** with yields of 55% and 77%, respectively. A Mitsunobu reaction of **5** gave benzoate **9**, inverting the oxygen configuration at the 7-position, with a 90% yield. Compound **9** was converted to the prolinol **11** by a Grignard reaction followed by the treatment of **10** with potassium hydroxide. The condensation of **11** with **8** in the presence of *p*-TsOH afforded a 1:1 mixture of 5,7-*cis* POZ **2b** and 5,7-*trans* POZ **2c** ligands with 59% yield, but a similar reaction in the presence of CSA afforded only the 5,7-*cis* ligand **2b** with 58% yield, although the reason for this is not clear. The stereochemical outcomes of **2a**, **2b**, and **2c** were evaluated by using ^{1}H NMR NOE difference spectra (NOEDS). H-2 and H-5 were enhanced in **2a** and **2b**, while the same positions were not enhanced in **2c**.

Synthesis of Chiral Pd– and Pt–POZ Complexes. We prepared the Pd– and Pt–POZ complexes from POZ ligands **1**–**3**. The chiral $PdCl_2$– and $PtCl_2$–POZ complexes **12** and **14a**,**b** were prepared in a convenient and efficient manner by the reaction of **1** (1 equiv) with $PdCl_2$ (1 equiv) or $PtCl_2$ (1 equiv), respectively (Scheme 2). Depending on the temperature, the reaction of **1** with $PdCl_2$ afforded either the *N*,*O*-acetal epimer **12** or its counterpart **14a**; at room temperature the complex **12** was formed in 95% yield with the same stereochemistry as ligand **1**, while under reflux, the epimeric complex **14a** was formed in 90% yield. Complex **12** was easily transformed to the thermodynamically stable complex **14a** in refluxing 1,2-dichloroethane (85%: **14a**/**12** = 17/3). Only the $PtCl_2$–POZ complex **14b**, which had the same stereochemistry as ligand **1**, was formed in refluxing dichloroethane, with an 80% yield. The chiral $PdCl_2$–POZ complexes **16a**–**c** were also prepared by reacting **2a**–**c** with $PdCl_2$, respectively, at both room temperature and elevated temperature, and complex **16c** was easily separated from the mixture of **16b** and **16c**. Similarly, the reaction of the ligand **3** with $PdCl_2$ gave $PdCl_2$–POZ

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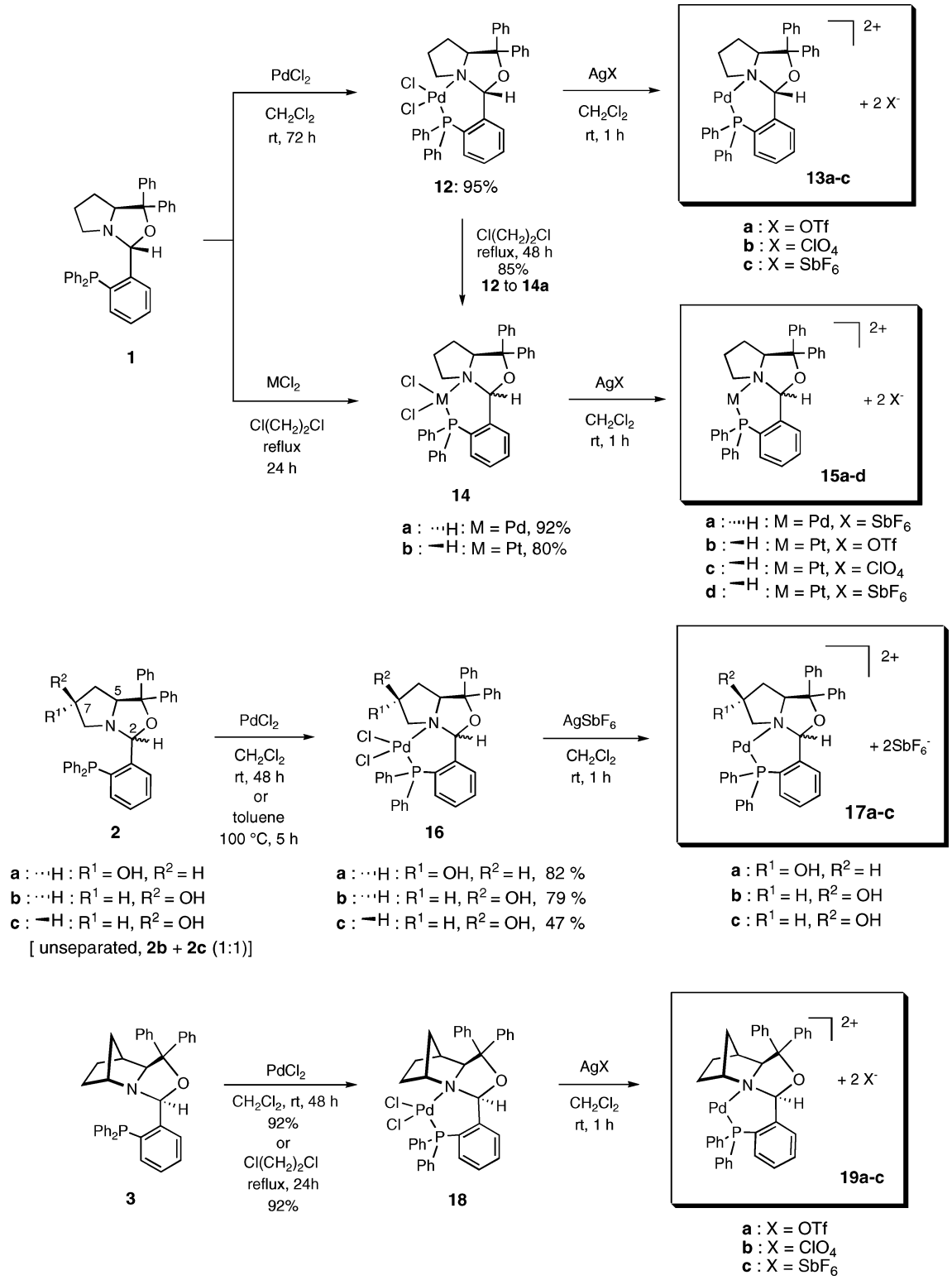
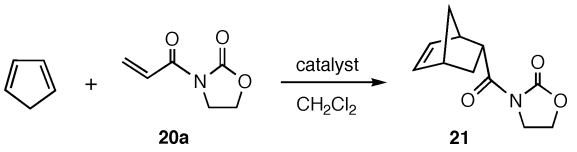
SCHEME 2. Preparations of Cationic Pd−POZ Catalysts



complex **18** as a single product in 92% yield both at room temperature and in refluxing 1,2-dichloroethane. The stereochemical outcomes of these complexes were confirmed in X-ray diffraction studies of **12**,[11] **14a**,[11] **14b**, **16b**, **16c**, and **18** (Figure 2), and in a ^{1}H NMR NOEDS experiment of **16a**. H-2 and H-5 were enhanced in 5,7-*cis* **16a** or **16b**, while they were not enhanced in 5,7-*trans* **16c**. These results also suggested the stereochemistry of **2a**−**c** determined in the ^{1}H NMR NOE experiment.

Diels−Alder Reactions. In the catalytic asymmetric DA reaction of cyclopentadiene with acryloyl-1,3-oxazolidin-2-one **20a** catalyzed by cationic catalysts **13a**−**c**, the antimonate catalyst **13c** showed superior catalytic activity to give the DA adduct **21** in high chemical yield and

TABLE 1. Diels–Alder Reaction with Cationic Catalysts



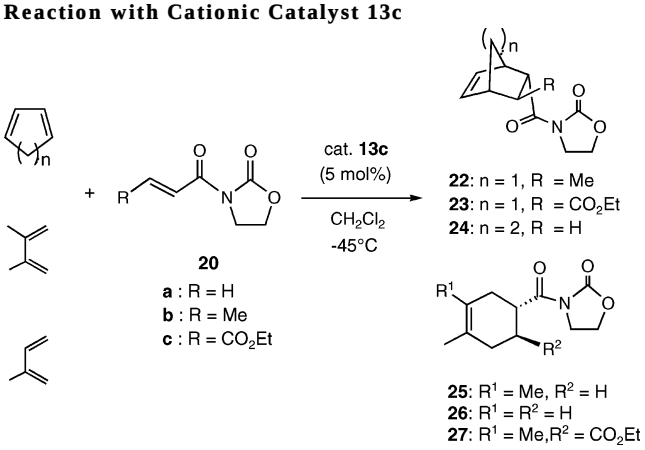
entry	catalyst (mol %)	temp (°C)/ time (h)	yield[a] (%)	endo/exo[b]	% ee[c]
1	**13c** (10)	−45/24	96	97/3	98
2	**13c** (5)	−50/22	87	97/3	97
3	**13c** (2.5)	−35/24	82	95/5	96
4	**13c** (1)	−45/48	76	97/3	94
5	**15a** (10)	−45/32	55	94/6	55
6	**15b** (10)	−45/90	37	95/5	0
7	**15c** (10)	−45/24	5	96/4	0
8	**15d** (10)	−35/36	4	95/5	0
9	**17a** (10)	−45/24	78	91/9	25
10	**17b** (10)	−45/24	75	90/10	93
11	**17c** (10)	−45/24	92	97/3	97
12	**19a** (5)	−50/24	10	96/4	16
13	**19b** (5)	−50/24	70	90/10	85
14	**19c** (5)	−50/24	87	94/6	79

[a] Isolated yields. [b] Endo/exo ratios were determined by HPLC or ^{1}H NMR. [c] Ee of endo isomers were determined by chiral HPLC, using a Daicel OD-H column (**21**: 0.5 mL/min, hexane:2-propanol = 90:10).

enantioselectivity in the range of 10 to 1 mol % (entries 1−4).[11] However, the isomeric antimonite complex **15a** was not as effective as **13c** (entry 5).[11] To test the nature of the metal, we prepared and examined the use of three cationic Pt−POZ complexes **15b**−**d**; when these catalysts were used, the chemical yields were poor and no enantioselectivity was observed (entries 6−8). Next, the catalytic abilities of the cationic 7-hydroxy−POZ complexes **17a**, **17b**, and **17c** with antimonate counterions were tested under the same reaction conditions as for **13c** (10 mol % and −45 °C; entry 1). The use of the 5,7-*trans* catalyst **17a** resulted in the formation of the DA adduct **21** in 78% yield, but with 25% ee (entry 9). Conversely, 5,7-*cis* **17b** and 5,7-*trans* **17c** showed satisfactory catalytic activity; particularly, **17c** gave DA adduct **21** in 92% and 97% ee (entries 10 and 11). The utility of the more conformationally constrained cationic POZ catalysts **19a**−**c**, in which the 2-azanorbornane ring system was fused, was also tested under the same reaction conditions as for **13c** (entries 12−14). The results indicated that both the perchlorate and antimonate catalysts, **19b** and **19c**, were effective; **19b** produced a particularly good ee. However, **19b** did not result in a higher catalytic activity than **13c**, in which the pyrrolidine ring system was fused. The above results indicate that the simplest antimonate POZ catalyst **13c** was the most effective in the DA reaction of cyclopentadiene with dienophile **20a**.

Substrate Scope. The superior cationic antimonate catalyst **13c** was then tested with a series of substituted dienophiles, such as crotonoyl-1,3-oxazolidin-2-one **20b** and fumaroyl-1,3- oxazolidin-2-one **20c** (Table 2). The reactions with 5 mol % of catalyst **13c** gave the desired DA adducts **22** and **23** in good isolated yields and with excellent enantioselectivities (**20b**: 73% yield, 98% ee, entry 1; **20c**: 95% yield, 98% ee, entry 2). Notwithstanding the work of Evans et al.,[4c] note that such enantioselectivities for **20b** and **20c** are notoriously difficult to obtain. Furthermore, the high catalytic activity of our

TABLE 2. Substrate Generality in the Diels–Alder Reaction with Cationic Catalyst 13c



entry	*n*	substrate	adduct	temp (°C)/ temp (h)	yield (%)[a]	endo/exo[b]	% ee[c] (config)
1	1	**20b**	22	−35/36	73	96/4	98 (2*R*)
2	1	**20c**	23	−35/24	95	94/6	98 (2*S*)[d]
3	2	**20a**	24	−25/48	75	95/5	93 (2*R*)[e]
4	–	**20a**	25	0/48	88	–	51 (1*R*)
5	–	**20a**	26	0/48	70	–	50 (1*R*)[f]
6	–	**20c**	27	−45/72	56	–	82 (1*R*)

[a] Isolated yields. [b] Endo/exo ratios were determined by HPLC or ^{1}H NMR. [c] Ee of endo isomers were determined by chiral HPLC, using a Daicel OD-H column. [d] After conversion to the corresponding iodolactone (I_2, KI, $NaHCO_3$, yield 63%), the ee and absolute configuration were determined by comparison with known optical rotation: $[\alpha]^{20}_D$ +39.1 (*c* 3.3; $CHCl_3$) {lit.[3] $[\alpha]^{23}_D$ −39.2 (*c* 4.65; $CHCl_3$)}. [e] After conversion to the corresponding amide [(*R*)-(+)-α-methylbenzylamine, Me_3Al, yield 60%). [f] After conversion to the corresponding benzyl ester, the absolute configuration and ee were determined by comparison with known optical rotation.[4d]

system allowed the formation of DA adduct **24** with 70% yield and 93% ee from the relatively unreactive cyclohexadiene (Table 2, entry 3). Catalyst **13c** was also used in DA reactions of acyclic dienes, 2,3-dimethyl-1,3-butadiene, and isoprene with dienophiles **20a** and **20c** (entries 4−6). However, the reaction with dienophile **20a** was sluggish and gave only DA adducts **25** and **26** in moderate chemical yield and poor enantioselectivity (68%, 51% ee, entry 4; 60%, 50% ee, entry 5). Conversely, the reaction of 2,3-dimethyl-1,3-butadiene with **20c** proceeded smoothly, even at −45 °C, giving the desired DA adduct **27** in moderate yield, but with good enantioselectivity (56% yield, 82% ee, entry 6).

Next, the DA reaction of furan with dienophile **20a** was investigated (Table 3). 7-Oxabicyclo[2.2.1]hept-2-enes formed from the DA reaction with furan are attractive intermediates in organic synthesis.[13] When furan was reacted with dienophile **20a** at room temperature, the DA adducts *endo*-**28**[13,14] and *exo*-**28** were obtained as a 4.5:1 mixture of endo/exo isomers, both of which were almost racemic (entry 1). By reducing the temperature to −30 °C, the enantioselectivity was improved remarkably to 90% ee for *endo*-**28** and 88% ee for *exo*-**28** (entry 2). Furthermore, satisfactory enantioselectivity was obtained for both the *endo*-**28** and *exo*-**28** forms at −50 °C,

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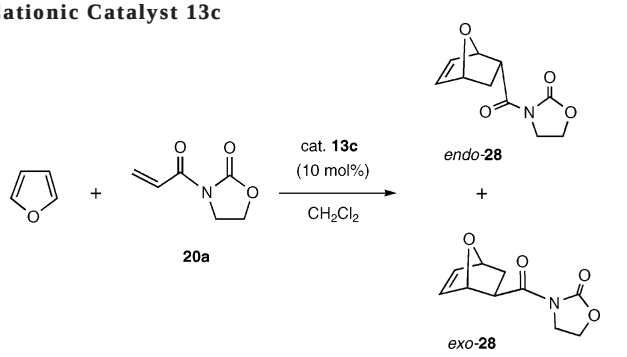
(14) Ogawa, S.; Yoshikawa, M.; Taki, T. *Chem. Commun.* **1992**, 406−408.

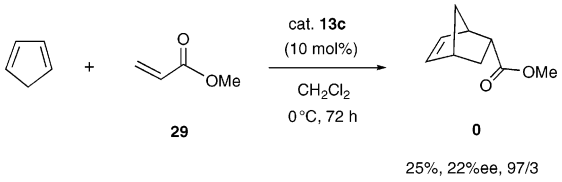
TABLE 3. Diels−Alder Reaction of Furane with Cationic Catalyst 13c



entry	temp (°C)	time (h)	yield (%)[a]	endo/exo[b]	endo % ee[c,d]	exo % ee[c,e]
1	rt	6	84	18/82	7	6
2	−30	24	76	28/72	90	88
3	−50	48	20	43/57	96	95

[a] Isolated yields. [b] Endo/exo ratios were determined by HPLC. [c] Ee were determined by chiral HPLC, using a Daicel OD-H column. [d] After conversion to the corresponding iodolactone (I_2, KI, $NaHCO_3$), the absolute configuration was determined by comparison with known optical rotation.[14] [e] The absolute configuration was not determined.

SCHEME 3. Diels−Alder Reaction with Methylacrylate as a Dienophile



although the chemical yield and diastereoselectivity were poor (entry 3). Finally, the utility of a monodentate dienophile in this reaction was tested (Scheme 3). However, the reaction with methylacrylate **29** as a monodentate dienophile was sluggish and the result indicated the importance of the bidentate activation as the dienophile.

X-ray Crystal Structure Determination. Previously we reported detailed X-ray structures of the two $PdCl_2$−POZ complexes **12** and **14a** and proposed that the marked difference in their enantioselectivity might be explained by the difference in the distortion of the planar Pd coordination and by the difference in the steric congestion of the structures.[11] We also compared X-ray analyses of the $PtCl_2$−POZ complex **14b**, which produced no enantioselectivity (entries 9−11 in Table 1), and the corresponding Pd complex **12**, which produced the highest enantioselectivity (catalyst **13c**, entries 3). As shown in Figure 2a, the structures were very similar and displayed no significant difference in the bond lengths and angles of the coordination geometries. However, the degree of distortion in the coordination geometry was notably different, as demonstrated by the dihedral angle between the two planes of N−metal−Cl1 and P−metal−Cl2 (2.3° for **14b** and 10.2° for **12**). Furthermore, the structures of **16b** and **16c** with 7-hydroxy−POZ were determined by X-ray analysis (Figure 2, parts b and c), showing that the dihedral angles are 2.4° and 3.1°, respectively.

Semiempirical PM5 Calculations.[15] We used semiempirical PM5 calculations to predict the stabilities of $PdCl_2$−POZ complexes. X-ray structures were used as the starting models and, somewhat surprisingly, the optimized geometries corresponded very well to the X-ray structures. The optimizations predict that **14a** is preferred to **12** by 6.21 kcal/mol, which is in agreement with the experimental results that **14a** is thermodynamically more stable than **12** (Scheme 2). Thus, we considered that semiempirical MO calculation using the PM5 method might be applicable for this system including transition Pd metal. As summarized in Figure 3, the results suggest that, in all cases, the [2*S*]-forms (**14a**, **16a**, and **16b**) are energetically preferred to the corresponding [2*R*]-forms (**12**, **16d**, and **16c**, respectively), and in the 7-hydroxy position, **16a** and **16d** (R^1 = OH) are preferred to **16b** and **16c** (R^2 = OH), respectively. It is very interesting that the complexes with the higher energy (**12** and **16c**) produced the high enantioselectivity (97% ee, entries 2 and 11 in Table 1) and, conversely, the complexes with the lower energy (**14a** and **16a**) resulted in low enantioselectivity (entries 5 and 9).

Conclusion

Our results demonstrate that the cationic POZ catalyst is effective in DA reactions on various substrates. Both the reactivity and enantioselectivity were influenced by the structure of the POZ and counterion. Notably, the cationic antimonate complex **13c**, derived from phosphinooxazolidine ligand **1**, $PdCl_2$, and silver hexafluoroantimonate, gave superior results. A major feature of this catalyst is that the chiral ligand **1** is readily obtained from the reaction of commercial (*R*)- or (*S*)-1,1-diphenyl-(2-pyrrolidinyl)methanol with 2-(diphenylphosphino)benzaldehyde. Additionally, the low molar ratios of catalyst **13c** are sufficient for efficient reactions, and enantioselectivities of up to 98% ee were achieved for the DA reactions of cyclopentadiene with the dienophiles **20a**−**c**. This is a superlative result for a DA reaction with Pd- and Pt-complex catalysts. The Pd and Pt complexes with POZ ligands that we explored have a characteristic structure; therefore, they should prove useful not only for other DA reactions but also for other asymmetric processes.

Finally, semiempirical PM5 calculations for $PdCl_2$ complexes indicate that the stabilities of the complexes are closely related to the enantioselectivities of the catalysts.

Experimental Section

X-ray Crystallography. X-ray data were collected on a Rigaku/MSC Mercury CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). Low-temperature equipment was used to maintain the stability of crystals (173 K). The data were corrected for Lorenz and polarization effects. The structures were solved by direct method and refined by the full-matrix least-squares method. Crystal data of compound **14b**: MF = $C_{36}H_{32}NOPPtCl_2$−

(15) Semiempirical PM5 (transition metal) calculations were performed with the WinMOPAC version 3.9 program [MOPAC2002, version 1.5, J. J. Stewart, Fujitsu, Tokyo, Japan, 2003]. First, we examined PM3 calculations of **12** and **14a**; however, the results disagreed with the experimental results.

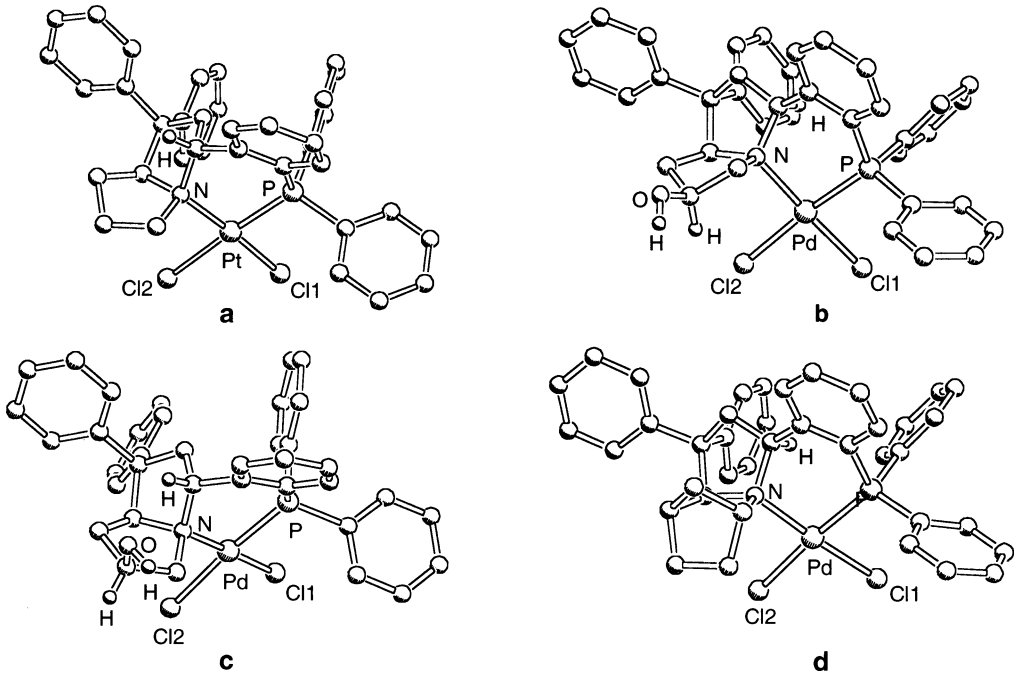


FIGURE 2. (a) X-ray structure of **14b**. Hydrogen atoms except for one hydrogen atom of the POZ ligand were omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Pt−Cl1 = 2.302(1), Pt−Cl2 = 2.382(1), Pt−P = 2.203(1), Pt−N = 2.107(4), Cl1−Pt−Cl2 = 88.34(4), Cl1−Pt−N = 175.7(1), Cl2−Pt−N = 87.6(1), Cl1−Pt−P = 88.51(4), Cl2−Pt−P = 176.33(4), P−Pt−N = 95.6(1). Maximum deviation from the least-squares plane of five atoms in Pd coordination is 0.044 and the dihedral angle between the two planes N−Pt−Cl2 and P−Pt−Cl1 is 2.37°. (b) X-ray structure of **16b**. Hydrogen atoms except for three hydrogen atoms of the POZ ligand were omitted for clarity. Selected bond lengths (Å) and bond angles (deg) averaging over two independent molecules: Pd−Cl1 = 2.289(0), Pd−Cl2 = 2.356(0), Pd−P = 2.246(0), Pd−N = 2.109(2), Cl1−Pd−Cl2 = 89.23(3), Cl1−Pd−N = 177.39(7), Cl2−Pd−N = 92.96(7), Cl1−Pd−P = 85.46(3), Cl2−Pd−P = 174.33(3), P−Pd−N = 92.38(7). Maximum deviation from the least-squares plane of five atoms in Pd coordination is 0.052 and the dihedral angle between the two planes N−Pd−Cl2 and P−Pd−Cl1 is 2.35°. (c) X-ray structure of **16c**. Hydrogen atoms except for three hydrogen atoms of the POZ ligand were omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Pd−Cl1 = 2.298(0), Pd−Cl2 = 2.372(0), Pd−P = 2.232(0), Pd−N = 2.112(2), Cl1−Pd−Cl2 = 89.32(3), Cl1−Pd−N = 178.24(6), Cl2−Pd−N = 89.05(5), Cl1−Pd−P = 86.99(2), Cl2−Pd−P = 175.18(3), P−Pd−N = 94.68(6). Maximum deviation from the least-squares plane of five atoms in Pd coordination is 0.049 and the dihedral angle between the two planes N−Pt−Cl2 and P−Pt−Cl1 is 3.12°. (d) X-ray structure of **18**. Hydrogen atoms except for one hydrogen atom of the POZ ligand were omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Pd−Cl1 = 2.295(2), Pd−Cl2 = 2.374(2), Pd−P = 2.249(2), Pd−N = 2.128(6), Cl1−Pd−Cl2 = 89.28(7), Cl1−Pd−N = 176.9(2), Cl2−Pd−N = 93.4(2), Cl1−Pd−P = 84.42(7), Cl2−Pd−P = 173.29(8), P−Pd−N = 92.8(2). Maximum deviation from the least-squares plane of five atoms in Pd coordination is 0.047 and the dihedral angle between the two planes N−Pt−Cl2 and P−Pt−Cl1 is 2.75°.

12 : ━H
14a : ┈H

16a : ┈H : R^1 = OH, R^2 = H
16b : ┈H : R^1 = H, R^2 = OH

16c : ━H : R^1 = H, R^2 = OH
16d : ━H : R^1 = OH, R^2 = H

12 : HF = 79.53 kcal/mol
14a : HF = 73.32 kcal/mol

ΔHF(**12**-**14a**) = 6.21 kcal/mol

16a : HF = 26.31 kcal/mol
16b : HF = 33.64 kcal/mol

ΔHF(**16b**-**16a**) = 7.33 kcal/mol
ΔHF(**16d**-**16a**) = 6.22 kcal/mol

16c : HF = 38.18 kcal/mol
16d : HF = 32.53 kcal/mol

ΔHF(**16c**-**16d**) = 5.65 kcal/mol
ΔHF(**16c**-**16b**) = 4.54 kcal/mol

FIGURE 3. PM5 geometry optimation for Cl_2 complexes.

$CHCl_3$, colorless prism, sizes = 0.20 × 0.20 × 0.20 mm, orthorhombic, a = 11.253(2) Å, b = 14.021(2) Å, c = 22.776(3) Å, V = 3593.8(9) Å^3, space group = $P2_12_12_1$ (no. 19), Z = 4, D_{calcd} = 1.684 g/cm^3, μ(Mo Kα) = 43.36 cm^{-1}. Of the 28435 reflections measured, 7936 were unique (R_{int} = 0.051). The final R factor was 0.020 (R_w = 0.024) for 6481 reflections with $I > 5\sigma(I)$. Crystal data of compound **16b**: MF = $C_{36}H_{32}NO_2PPdCl_2 \cdot C_4H_8O_2$, colorless prism, sizes = 0.20 × 0.20 × 0.10 mm, orthorhombic, a = 30.160(1) Å, b = 14.1000(4) Å, c = 17.3200(5) Å, V = 7365.4(4) Å^3, space group = $P2_12_12_1$ (no. 19),

$Z = 8$, $D_{calcd} = 1.455$ g/cm^3, μ(Mo Kα) = 7.34 cm^{-1}. Two independent Pd complexes and two CH_3COOEt solvents are present in asymmetric unit of the crystal structure. Of the 56264 reflections were measured, 16743 were unique (R_{int} = 0.032). The final R_1 factor was 0.034 for reflections with $I > 2\sigma(I)$ and wR_2 was 0.094 for all reflections. Crystal data of compound **16**:, MF = $C_{36}H_{32}NO_2PPdCl_2$, colorless prism, sizes = 0.20 × 0.25 × 0.15 mm, monoclinic, a = 12.259(3) Å, b = 10.597(2) Å, c = 12.465(3) Å, β = 93.697(1), V = 1615.9(6) Å^3, space group = $P2_1$ (no. 4), $Z = 2$, D_{calcd} = 1.477 g/cm^3, μ(Mo Kα) = 8.22 cm^{-1}. Of the 24969 reflections measured, 7248 were unique (R_{int} = 0.037). The final R_1 factor was 0.022 for reflections with $I > 2\sigma(I)$ and wR_2 was 0.047 for all reflections. Crystal data of compound **18**: MF = $C_{38}H_{34}NOPPdCl_2$·$CHCl_3$, colorless prism, sizes = 0.20 × 0.20 × 0.20 mm, orthorhombic, a = 12.785(3) Å, b = 14.625(4) Å, c = 19.215(5)Å, V = 3593(1) Å^3, space group = $P2_12_12_1$ (no. 19), $Z = 4$, D_{calcd} = 1.568 g/cm^3, μ(Mo Kα) = 9.66 cm^{-1}. Of the 33784 reflections measured, 8125 were unique (R_{int} = 0.037). The final R factor was 0.046 (R_w = 0.054) for 5256 reflections with $I > 5\sigma(I)$.

All calculations were made with TeXsan software (TEXRAY Structure Analysis Package, Molecular Structure Corp., 1985) and Crystal Structure software [Crystal Structure Analysis Package, Rigaku and RigakuMSC (2000−2004). 9009 New Tails Dr., The Woodlands, TX 77381].

(2*S*,4*R*)-4-Hydroxy-α,α-diphenyl-2-pyrrolidinemethanol (7). To a solution of **5**[12] (500 mg, 2.30 mmol) in dry THF (10 mL) was added PhMgBr (1 M in THF, 23 mL, 23.02 mmol) at 0 °C under Ar. After being stirred for 5 h, the reaction solution was diluted with ether and washed with saturated aqueous NH_4Cl. The organic layer was dried over anhydrous $MgSO_4$ and filtered. The filtrate was concentrated under reduced pressure to give a residue, which was chromatographed on silica gel (1:1 hexane/EtOAc as eluent) to give the crude product **6**, which was used for the next step without further purification. A suspension of the crude product **6** (440 mg) and KOH (258 mg, 4.60 mmol) in H_2O (5 mL)−methanol (10 mL) was heated at 100 °C for 24 h. After the solution was cooled, water was added and the precipitate was removed by filtration and dried under high vacuum to give the amino alcohol (**7**) (343 mg, 55%) as a colorless powder: mp 176 °C; $[\alpha]^{20}_D$ −32.03 (*c* 1.28, DMSO); IR (KBr) 707, 1420, 1454, 1612 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.26 (s, 1H), 1.47 (dd, J = 6.4, 13.6 Hz, 1H), 1.63 (br s, 2H), 1.80−1.90 (m, 1H), 2.99 (d, J = 11.5, 1H), 3.19 (dd, J = 4.2, 11.5 Hz, 1H), 4.39 (m, 1H), 4.65 (dd, J = 6.2, 9.7 Hz, 1H), 7.13−7.33 (m, 6H), 7.47 (d, J = 7.3 Hz, 2H), 7.58 (d, J = 7.4 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 36.4, 55.6, 63.4, 69.7, 71.2, 125.3, 125.7, 126.4, 126.5, 126.8, 126.9, 127.3, 127.9, 128.1, 135.6, 144.9, 146.8; MS *m*/*z* 269 (M$^+$); HRMS calcd for $C_{17}H_{19}NO_2$ (M$^+$) 269.1416, found 269.1400.

(2*S*,5*S*,7*R*)-1-Aza-4-hydroxy-2-(diphenylphosphino)-phenyl-3-oxa-4,4-diphenylbicyclo[3.3.0]octane (2a). Compound **7** (30 mg, 0.11 mmol), 2-(diphenylphosphino)benzaldehyde **8** (36 mg 0.12 mmol), *p*-TsOH (4 mg, 0.02 mmol) or DL-camphor-10-sulfonic acid (CSA)(5 mg, 0.02 mmol) and benzene (10 mL) were placed in a flask equipped with a Dean−Stark trap and the mixture was refluxed for 24 h. The solvent was removed under reduced pressure and the residue was purified by preparative TLC (1:1 hexane/EtOAc) to give the product **2a** (*p*-TsOH: 33 mg, 55%; CSA: 46 mg, 77%) as colorless prisms; mp 92 °C; $[\alpha]^{20}_D$ −43.20 (*c* 0.81, $CHCl_3$); IR (KBr) 697, 745, 1434 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.99 (d, J = 18.7 Hz, 1H), 1.42−1.51 (m, 1H), 1.62 (d, J = 10.1 Hz, 1H), 18.54 (dd, J = 8.4, 13.9 Hz, 1H), 2.51 (dd, J = 3.4, 10.0 Hz, 1H), 3.71−3.76 (m, 1H), 4.63 (dd, J = 6.1, 8.2 Hz, 1H), 6.19 (d, J = 5.4 Hz, 1H), 7.04−7.16 (m, 4H), 7.18−7.26 (m, 5H), 7.28−7.53 (m, 12H), 7.56−7.59 (m, 2H), 8.17 (q, J = 3.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 39.7, 66.4, 71.8, 73.3, 90.7, 92.6, 124.0, 124.8, 126.2, 126.5, 126.6, 127.2, 127.2, 127.5, 127.7, 128.3, 128.3, 128.4, 128.6, 128.7, 128.8, 128.8, 129.9, 131.5, 131.5, 131.7, 131.7, 132.0, 132.0, 133.4, 133.5, 133.7, 134.8, 135.0, 136.6, 140.9; MS *m*/*z* 541 (M$^+$); HRMS calcd for $C_{36}H_{32}NO_2P$ (M$^+$) 541.2171, found 541.2186.

(2*S*,4*S*)-4-Benzoyloxy-2-methoxycarbonyl-*N*-ethoxycarbonylpyrrolidine (9). To a solution of **5**[12] (1.0 g, 2.91 mmol), PPh_3 (1.3 g, 5.06 mmol), and benzoic acid (618 mg, 5.06 mmol) in THF (15 mL) was added azodicarboxylic acid diethylester (40% in toluene, 2.2 mL, 5.06 mmol) at 0 °C and the reaction mixture was stirred for 5 h. The solution was diluted with ether and washed with saturated aqueous NH_4Cl and brine. The organic layer was dried over anhydrous $MgSO_4$ and filtered. The filtrate was concentrated under reduced pressure to give a residue, which was chromatographed on silica gel (1:1 hexane/EtOAc as eluent) to give the pure product **9** as a colorless oil: $[\alpha]^{23}_D$ +33.33 (*c* 0.54, $CHCl_3$); IR (NaCl) 716, 1712, 1758 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.21−1.31 (m, 3H), 2.49−2.58 (m, 2H), 3.67 (d, J = 6.8 Hz, 3H), 3.73−3.91 (m, 2H), 4.07−4.25 (m, 2H), 4.60 (ddd, J = 3.1, 7.9, 23.3 Hz, 1H), 5.55 (s, 1H), 7.40−7.45 (m, 2H), 7.52−7.59 (m, 1H), 7.96 (d, J = 8.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.7, 35.8, 52.4, 57.7, 61.5, 72.3, 73.3, 128.3, 129.5, 133.2, 154.7, 165.6, 171.7; MS *m*/*z* 321 (M$^+$); HRMS calcd for $C_{16}H_{19}NO_6$ (M$^+$) 321.1212, found 321.1185.

(2*S*,4*S*)-4-Hydroxy-α,α-diphenyl-2-pyrrolidinemethanol (11). To a solution of **9** (206 mg, 0.64 mmol) in dry THF (10 mL) was added PhMgBr (1 M in THF, 13 mL, 12.82 mmol) under Ar. After being stirred for 5 h, the reaction solution was diluted with ether and washed with saturated aqueous NH_4-Cl. The organic layer was dried over anhydrous $MgSO_4$ and filtered. The filtrate was concentrated under reduced pressure to give a residue, which was chromatographed on silica gel (1:1 hexane/EtOAc as eluent) to give the crude product **10**, which was used for the next step without further purification. A suspension of the crude product **10** (157 mg) and KOH (72 mg, 1.28 mmol) in H_2O (5 mL)−methanol (10 mL) was heated at 100 °C for 24 h. After the solution was cooled, water was added and the precipitate was removed by filtration and dried under high vacuum to give the amino alcohol (**37**) (112 mg, 65%) as a colorless powder: mp 174 °C; $[\alpha]^{23}_D$ −18.00 (*c* 2.00, DMSO); IR (KBr) 696, 750, 1448, 3332 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.60−1.68 (m, 1H), 1.92−2.10 (m, 2H), 2.99−3.10 (m, 1H), 4.25−4.29 (m, 1H), 4.38 (dd, J = 5.1, 9.4 Hz, 1H), 7.14−7.48 (m, 6H), 7.55 (d, J = 0.7 Hz, 2H), 7.58 (d, J = 1.3 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 36.4, 55.6, 63.4, 71.2, 125.3, 125.7, 126.4, 126.5, 126.8, 127.3, 127.7, 128.0, 128.1,144.9, 146.8; MS *m*/*z* 269 (M$^+$); HRMS calcd for $C_{17}H_{19}NO_2$ (M$^+$) 269.1416, found 269.1398.

(2*S*,5*S*,7*S*)-1-Aza-4-hydroxy-2-(diphenylphosphino)phenyl-3-oxa-4,4-diphenylbicyclo[3.3.0]octane (2b). Compound **11** (50 mg, 0.19 mmol), 2-(diphenylphosphino)benzaldehyde **8** (54 mg 0.19 mmol), *p*-TsOH (7 mg, 0.04 mmol) or CSA (9 mg, 0.04 mmol) and benzene (10 mL) were placed in a flask equipped with a Dean−Stark trap and the mixture was refluxed for 24 h. The solvent was removed under reduced pressure and the residue was purified by preparative TLC (1:1 hexane/EtOAc) to give the products [*p*-TsOH: **2b** + **2c** (59 mg), 59%; CSA: **2b** (58 mg), 58%]. **2b**: colorless prisms, mp 93 °C; $[\alpha]^{20}_D$ −44.30 (*c* 1.58, $CHCl_3$); IR (KBr) 696, 745, 1434 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.20−1.29 (m, 2H), 2.09−2.16 (m, 2H), 2.39 (t, J = 8.7 Hz, 1H), 3.89−4.00 (m, 1H), 4.56 (t, J = 7.5 Hz, 1H), 5.91 (d, J = 4.0 Hz, 1H), 7.03−7.37 (m, 17H), 7.46−7.97 (m, 6H), 8.17 (dd, J = 3.6, 7.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 38.8, 63.8, 71.1, 72.0, 87.4, 89.7, 113.1, 118.6, 126.1, 126.6, 126.8, 126.8, 127.0, 128.1, 128.2, 128.4, 128.6, 128.7, 129.0, 132.9, 133.2, 134.0, 134.1, 134.2, 134.5, 135.9, 136.0, 144.1, 145.4, 147.0; MS *m*/*z* 541 (M$^+$); HRMS calcd for $C_{36}H_{32}NO_2P$ (M$^+$) 541.2171, found 541.2153.

Dichloro[(2*R*,5*S*)-1-aza-2-(diphenylphosphino)phenyl-3-oxa-4,4-diphenylbicyclo[3.3.0]octane]palladium (12). A mixture of POZ **1** (52.6 mg, 0.1 mmol) and $PdCl_2$ (17.7 mg, 0.1 mmol) in dichloromethane was stirred for 72 h at room temperature under Ar. The resulting suspension was filtered, and the filtrate was condensed under a reduced pressure. The residue was recrystallized from hexane−$CHCl_3$ to afford yellow crystals **12** (66.8 mg, 95%): mp 198 °C; $[\alpha]^{20}_D$ −395.96 (*c* 1.24,

$CHCl_3$); IR (KBr) 590, 747, 1584 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.44 (m, 1H), 1.88 (m, 1H), 2.08 (m, 1H), 2.62 (m, 1H), 2.92 (m, 1H), 4.41 (m, 1H), 4.95 (s, 1H), 6.84−6.90 (m, 2H), 7.00 (t, J = 7.6 Hz, 2H), 7.07−7.19 (m, 6H), 7.22−7.39 (m, 12H), 7.51 (t, J = 7.6 Hz, 1H), 7.59 (dd, J = 4.4, 6.6 Hz, 1H), 7.68 (t, J = 7.4 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 27.0, 28.9, 54.9, 77.4, 89.2, 94.4, 124.9, 126.2, 126.6, 126.7, 127.1, 127.3, 128.0, 128.2, 128.5, 128.5, 128.6, 130.7, 130.7, 130.8, 130.8, 132.1, 132.2, 132.2, 132.8, 133.3, 133.4, 133.7, 133.9, 134.0, 136.0, 136.0, 137.3, 137.4, 142.2, 143.5. Anal. Calcd for $C_{36}H_{32}Cl_2NOPPd$: C, 61.51; H, 4.59; N, 1.99. Found: C, 61.21; H, 4.76; N, 1.71.

Dichloro[(2*R*,5*S*)-1-aza-2-(diphenylphosphino)phenyl-3-oxa-4,4-diphenylbicyclo[3.3.0]octane]palladium (14a) and Dichloro[(2*R*,5*S*)-1-aza-2-(diphenylphosphino)phenyl-3-oxa-4,4-diphenylbicyclo[3.3.0]octane]platinum (14b). A mixture of POZ **1** (52.6 mg, 0.1 mmol) and $PdCl_2$ (17.7 mg, 0.1 mmol) or $PtCl_2$ (26.5 mg, 0.1 mmol) in 1,2-dichloroethane was refluxed for 24 h under Ar. The resulting suspension was filtered, and the filtrate was condensed under reduced pressure. The residue was recrystallized from hexane−$CHCl_3$ to afford yellow crystals of **14a** (63.3 mg, 90%) or **14b** (53.7 mg, 68%). **14a**: mp 229−231 °C; $[\alpha]^{20}_D$ −231.29 (*c* 1.31, $CHCl_3$); IR (KBr) 692, 755, 1584 cm^{-1}; ^1H NMR ($CHCl_3$) δ 1.24 (m, 1H), 1.62 (m, 1H), 2.02 (m, 1H), 2.44 (m, 1H), 2.87 (m, 1H), 3.56 (m, 1H), 5.71 (s, 1H), 6.35 (t, J = 7.6 Hz, 1H), 6.96 (t, J = 8.8 Hz, 1H), 7.17−7.53 (m, 18H), 7.67−7.73 (m, 4H), 7.98 (dd, J = 3.9, 7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 25.6, 31.5, 43.5, 58.8, 74.2, 90.5, 92.4, 124.6, 126.5, 126.5, 127.5, 127.7, 128.2, 128.3, 128.4, 128.5, 128.6, 128.8, 128.9, 129.0, 130.0, 130.1, 131.5, 131.5, 131.8, 131.8, 132.0, 132.0, 133.7, 133.8, 135.0, 135.1, 136.9, 137.0, 141.6, 141.7. Anal. Calcd for $C_{36}H_{32}Cl_2NOPPd$: C, 61.51; H, 4.59; N, 1.99. Found: C, 61.32; H, 4.61; N, 1.71. **14b**: mp 222 °C; $[\alpha]^{20}_D$ −243.60 (*c* 2.11, $CHCl_3$); IR (KBr) 690, 747 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.41−1.52 (m, 2H), 1.58 (br s, 1H), 1.90 (m, 1H), 2.13 (m, 1H), 2.63 (m, 1H), 3.04 (m, 1H), 4.55 (m, 1H), 4.93 (s, 1H), 6.89−7.34 (m, 21H), 7.53−7.57 (m, 2H), 7.65 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 27.6, 29.5, 57.4, 78.6, 88.8, 94.7, 124.6, 126.3, 126.7, 126.8, 127.6, 127.7, 128.2, 128.2, 128.4, 130.0, 130.1, 130.5, 130.5, 130.6, 131.4, 131.4, 131.8, 131.9, 132.7, 132.8, 133.3, 133.5, 133.7, 133.9, 135.1, 135.1, 136.4, 136.6, 141.8, 143.2; HRMS calcd for $C_{36}H_{32}Cl_2NOPPt$ requires *m/z* 790.1246, found *m/z* 720.1741 $[M - Cl_2]^+$ (FAB with *p*-nitrobenzyl alcohol added).

Dichloro[(2*S*,5*S*,7*R*)-1-aza-4-hydroxy-2-(diphenylphosphino)phenyl-3-oxa-4,4-diphenylbicyclo[3.3.0]octane]-palladium (16a) and Dichloro[(2*S*,5*S*,7*S*)-1-aza-4-hydroxy-2-(diphenylphosphino)phenyl-3-oxa-4,4-diphenylbicyclo[3.3.0]octane]palladium (16b). $PdCl_2$ (15 mg, 0.085 mmol) and **2a** or **2b** (46 mg, 0.085 mmol) were suspended in anhydrous toluene (5 mL) under Ar. The mixture was stirred at 100 °C for 5 h and the resulting yellow solution was cooled and filtered. The filtrate was concentrated under reduced pressure to give a residue, which was chromatographed on silica gel (1:1 $CHCl_3$/EtOAc as eluent) to give the products **16a** or **16b** (**16a**: 50 mg, 82%; **16b**: 48 mg, 79%). **16a**: yellow prisms; mp 247 °C, $[\alpha]^{22}_D$ +114.45 (*c* 0.90, DMSO); IR (KBr) 687, 749, 1095, 1224, 1435 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.53−1.64 (m, 2H), 2.00 (dd, J = 8.6, 14.8 Hz, 1H), 2.97 (dd, J = 2.5, 12.2 Hz, 1H), 3.55 (d, J = 11.9 Hz, 1H), 4.21 (br s, 1H), 5.38 (d, J = 11.1 Hz, 1H), 5.93 (s, 1H), 6.61 (t, J = 8.7 Hz, 1H), 7.04 (t, J = 8.7 Hz, 1H), 7.19−7.56 (m, 17H), 7.66−7.73 (m, 4H), 7.95 (dd, J = 4.2, 7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 39.6, 66.4, 71.8, 73.3, 90.7, 92.6, 123.9, 124.8, 126.1, 126.5, 126.6, 127.2, 127.2, 127.5, 127.6, 128.3, 128.3, 128.4, 128.6, 128.7, 128.8, 128.8, 130.0, 131.5, 131.5, 131.7, 131.8, 132.0, 132.0, 133.4, 133.5, 133.7, 134.8, 135.0, 136.5, 140.9; calcd for $C_{36}H_{31}NO_2PPd$ requires *m/z* 646.11280, found *m/z* 646.0972 $([M - HCl_2]^+)$ (FAB with *p*-nitrobenzyl alcohol added). **16b**: yellow prisms; mp 229 °C; $[\alpha]^{22}_D$ +110.69 (*c* 0.73, DMSO); IR (KBr) 692, 748, 1097, 1435 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.29−1.36 (m, 1H), 1.64 (br s, 1H), 2.15−2.24 (m, 1H), 2.33 (br s, 1H), 2.76 (t, J = 10.0 Hz, 1H), 3.57 (dd, J = 5.6, 10.2 Hz, 1H), 5.27 (br s, 1H), 5.68 (s, 1H), 6.33 (t, J = 8.7 Hz, 1H), 6.95 (dd, J = 7.8, 10.0 Hz, 1H), 7.15−7.52 (m, 16H), 7.63−7.73 (m, 5H), 8,01 (dd, J = 4.1, 7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 39.0, 62.5, 69.3, 73.0, 90.2, 91.7, 123.8, 124.6, 126.3, 126.6, 126.8, 127.1, 127.3, 127.4, 127.7, 128.1, 128.3, 128.3, 128.5, 128.6, 128.7, 128.8, 129.9, 131.3, 131.3, 131.7, 131.7, 132.0, 132.0, 133.4, 133.5, 133.6, 134.7, 134.9, 136.2, 141.0; calcd for $C_{36}H_{32}NO_2PPd$ requires *m/z* 647.1205, found *m/z* 647.1051 $([M - Cl_2]^+)$ (FAB with *p*-nitrobenzyl alcohol added).

Dichloro[(2*R*,5*S*,7*S*)-1-aza-4-hydroxy-2-(diphenylphosphino)phenyl-3-oxa-4,4-diphenylbicyclo[3.3.0]octane]-palladium (16c). $PdCl_2$ (39 mg, 0.22 mmol) and the mixture of **2b** and **2c** (118 mg, 0.22 mmol) were suspended in anhydrous toluene (5 mL) under Ar. The mixture was stirred at 100 °C for 24 h and the resulting yellow solution was cooled and filtered. The filtrate was concentrated under reduced pressure to give a residue, which was chromatographed on silica gel (1:1 $CHCl_3$/EtOAc as eluent) to give the products **16b** and **16c** (**16b**: 72 mg, 46%; **16c**: 48 mg, 47%), respectively. **16c**: yellow prisms; mp 232 °C; $[\alpha]^{23}_D$ −291.37 (*c* 2.32, DMSO); IR (KBr) 691, 1435, 1670, 3058, 3472 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.56−1.64 (m, 1H), 1.68 (br s, 1H), 2.33 (b t, J = 8.1, 13.9 Hz, 1H), 2.89 (dd, J = 4.2, 12.9 Hz, 1H), 4.66 (dd, J = 7.6, 12.9 Hz, 1H), 5.03−5.10 (m, 1H), 5.51 (d, J = 1.2 Hz, 1H), 6.81−6.88 (m, 2H), 6.97−7.01 (m, 2H), 7.07−7.10 (m, 3H), 7,-12−7.20 (m, 2H), 7.23−7.41 (m, 13H), 7.47−7.51 (m, 1H), 7.63−7.68 (m, 1H), 7.70−7.73 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 38.2, 62.0, 73.1, 77.1, 89.4, 94.2, 122.5, 123.1, 124.7, 125.8, 126.3, 126.6, 126.9, 127.1, 127.8, 128.0, 128.1, 128.4, 128.5, 130.5, 130.6, 131.7, 131.8, 132.0, 132.7, 133.1, 133.3, 133.6, 133.8, 134.1, 134.2, 135.5, 136.9, 137.1, 141.9; calcd for $C_{36}H_{32}NO_2PPd$ requires *m/z* 647.1205, found *m/z* 647.1232 $([M\text{-}Cl_2]^+)$ (FAB with *p*-nitrobenzyl alcohol added).

Dichloro[(1*R*,3*S*,6*S*,7*S*)-2-aza-3-(2-diphenylphosphino)-phenyl-4-oxa-5,5-diphenyltricyclo[5.2.1.$0^{2,6}$]decane]-palladium (18). A mixture of POZ **3** (118 mg, 0.12 mmol) and $PdCl_2$ (38 mg, 0.12 mmol) in CH_2Cl_2 (4 mL) was refluxed for 24 h under Ar. The resulting suspension was filtered, and the filtrate was condensed under reduced pressure. The residue was recrystallized from hexane−$CHCl_3$ to afford yellow crystals of **18** (153 mg, 98%): mp 224 °C; $[\alpha]^{20}_D$ −172.72 (*c* 1.43, $CHCl_3$); IR (KBr) 691, 748, 1586 cm^{-1}; ^1H NMR ($CHCl_3$) δ 0.84 (d, J = 10.6 Hz, 1H), 1.34 (m, 1H), 1.64 (m, 1H), 1.83 (d, J = 4.0 Hz, 1H), 2.08 (d, J = 10.6 Hz, 1H), 2.31 (m, 1H), 3.27 (s, 1H), 3.35 (m, 1H), 6.07 (s, 1H), 6.10 (s, 1H), 7.12 (t, J = 8.6 Hz, 1H), 7.20 (td, J = 2.6, 7.9 Hz, 2H), 7.24−7.60 (m, 12H), 7.68 (t, J = 7.7 Hz, 1H), 7.76 (dd, J = 7.3, 12.1 Hz, 2H), 7.98 (dd, J = 4.0, 7.7 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 25.8, 31.2, 36.4, 38.3, 66.5, 73.5, 91.0, 94.3, 125.1, 125.5, 126.4, 126.4, 127.4, 127.8, 128.0, 128.3, 128.4, 128.6, 128.7, 128.7, 128.7, 128.9, 130.1, 130.1, 131.4, 131.5, 131.6, 131.7, 131.9, 131.9, 133.2, 133.5, 135.6, 135.6, 136.2, 136.2, 141.2, 141.8; HRMS calcd for $C_{38}H_{34}Cl_2NOPPd$ requires *m/z* 727.0790, found *m/z* 657.1339 $[M - Cl_2]^+$ (FAB with *p*-nitrobenzyl alcohol added).

General Procedure for Enantioselective Pd- and Pt-Catalyzed Diels−Alder Reactions. $PdCl_2$−POZ complexes **12**, **14a**, **16a**−**c**, **18** (1 equiv) or $PtCl_2$−POZ complex **14b** (1 equiv) and the appropriate silver salt (2 equiv) in CH_2Cl_2 (1 mL) were stirred at room temperature under Ar for 1 h. The catalyst complex was then cooled to the temperature as shown in Table 1 and acryloyl−**20a** (50 mg, 0.36 mmol), crotonyl−**20b** (56 mg, 0.36 mmol), or fumaroyl-1,3-oxazolidin-2-one−**20c** (77 mg, 0.36 mmol) in CH_2Cl_2 (1 mL) followed by cyclopentadiene (150 mg, 1.80 mmol), cyclohexadiene (144 mg, 1.80 mmol), 2,3-dimethyl-1,3-butadiene (148 mg, 1.80 mmol), or isoprene (148 mg, 1.80 mmol) were added, respectively. The reaction mixture was stirred for the specified amount of time and quenched with saturated $NaHCO_3$ aq. The mixture was extracted with $CHCl_3$. The organic layer was washed with brine and dried over $MgSO_4$. Evaporation of the solvent under a reduced pressure afforded a crude residue that was purified by column chromatograpy on silica gel (elution with AcOEt:

hexane = 1:4) to give the cycloadducts **21**−**27**. The ee values of **21**, **22**, **24**, **25**, and **27** were determined by HPLC (**21**: Chiralcel OD-H, 1.0 mL/min, hexane:2-propanol = 90:10; **22**: Chiralcel OD, 1.0 mL/min, hexane:2-propanol = 96:4; **24**: Chiralpak AD, 1.0 mL/min, hexane:2-propanol = 95:5; **25**: Chiralpak AS, 1.0 mL/min, hexane:2-propanol = 97:3; **27**: Chiralpak AD, 1.0 mL/min, hexane:2-propanol = 90:10).[4d,6] The ee of **23** was determined by comparison of the known optical rotation of iodolactonization product derived from **23**.[3c] The ee of **26** was determined by comparison of the known optical rotation of product **26**.[4c]

Diels−**Alder Reaction of Furan with *N*-Acryloyloxazolidinone (20a) Catalyzed by Cationic Pd**−**POZ (13c).** A suspension of $PdCl_2$−POZ complex (20 mg, 0.071 mmol) and $AgSbF_6$ (25 mg, 0.177 mmmol) in CH_2Cl_2 (1 mL) was stirred at room temperature for 1 h under Ar. The catalyst complex was then cooled to the temperature shown in Table 3 and acryloyl−**20a** (40 mg, 0.283 mmol) in CH_2Cl_2 (1 mL) followed by furan (0.2 mL, 2.83 mmol) in CH_2Cl_2 (1 mL) were added. The reaction mixture was stirred for the specified amount of time and quenched with saturated NH_4Cl. The mixture was extracted with ether. The organic layer was washed with brine and dried over $MgSO_4$. Evaporation of the solvent under a reduced pressure afforded a crude residue that was purified by preparative TLC (AcOEt:hexane = 2:1) to give the mixture of DA adducts, *endo*-**28**[4c,14] and *exo*-**28**. The endo/exo rate and enantioselectivity were determined by HPLC (Chiralcel OD-H, 0.65 mL/min, hexane:AcOEt = 70:30, t_R[*2S-endo*-**28**] = 15.1 min, t_R[*2R-endo*-**28**] = 17.6 min, t_R[*2S* or *2R-exo*-**28**] = 20.0 min, t_R[*2S* or *2R-exo*-**28**] = 28.9 min. The mixture of DA adducts (45 mg of *endo*-**28**/*exo*-**28** = 28:72) was allowed to stand at room temperature for 48 h, and was purified by preparative TLC (AcOEt:hexane = 2:1) to give *exo*-**28** (22 mg, 68%). ***exo*-28**: colorless oil; $[\alpha]^{20}_D$ −85.23 (*c* 1.50, $CHCl_3$); IR (film) 759, 1216, 1388, 1700, 1779, 3020 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.59 (1H, dd, J = 8.3, 11.5 Hz), 2.30 (1H, dt, J = 4.3, 11.5 Hz), 3.41 (1H, dd, J = 4.0, 8.3 Hz), 4.02−4.13 (2H, m), 4.14−4.51 (2H, m), 5.09 (1H, d, J = 4.6 Hz), 5.13 (1H, s), 6.39−6.48 (2H, m); ^{13}C NMR ($CDCl_3$) δ 28.8, 42.9, 43.6, 62.3, 78.3, 81.3, 135.1, 137.3, 153.8, 173.1; MS *m*/*z* 209 (M^+); HRMS calcd for $C_{10}H_{11}NO_4$ (M^+) 209.0688, found 209.0695.

Diels−**Alder Reaction of Cyclopentadiene with Methylacrylate (29) Catalyzed by Cationic Pd**−**POZ (13c).** A suspension of $PdCl_2$−POZ complex (80 mg, 0.11 mmol) and $AgSbF_6$ (0.78 mg, 0.177 mmmol) in CH_2Cl_2 (1 mL) was stirred at room temperature for 1 h under Ar. Methylacrylate (**29**) (100 mg, 1.16 mmol) in CH_2Cl_2 (1 mL) followed by cyclopentadiene (380 mL, 5.8 mmol) in CH_2Cl_2 (1 mL) were added at 0 °C and the solution was stirred for 72 h. The reaction was chromatographed on silica gel (8:1 hexane/EtOAc as eluent) to give **30** (60 mg, 25%). The ee and absolute configration of **30** were determined by comparison of the known optical rotation of **30**.[4c]

Supporting Information Available: General methods, ^1H and ^{13}C NMR spectra for compounds **2a**, **2b**, **7**, **9**, **11**, **12**, **14a**, **14b**, **16a**, **16b**, **16c** and **18**, and X-ray data for **12**, **14a**, **14b**, **16b**, **16c** and **18** in CIF format and ORTEP drawings. This material is available free of charge via the Internet at http://pubs.acs.org.

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