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Chiral Phosphinooxathiane Ligands for Catalytic Asymmetric Diels−Alder Reaction

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Abstract: Chiral cationic palladium−phosphinooxathiane complexes have been found to be effective catalysts for enantioselective Diels−Alder (DA) reaction of cyclopentadiene with acyl-1,3-oxazolidin-2-ones to give the corresponding DA adducts in good yield and high enantioselectivity up to 93% ee.

The asymmetric Diels−Alder (DA) reaction is an important and versatile reaction in synthetic organic chemistry for preparation of an optically active compound,[1] for which many groups have reported[2] an enantioselective version of this reaction with a chiral catalyst formed from chiral ligands and Lewis acids. Of the successful ligands to give high enantioselectivity for the DA reaction, C_2-symmetrical bis-oxazolines,[3] phosphinooxazolines,[4] BINOL,[5] and BINAP[6] ligands have been so far reported. Most recently, we developed S−P type, chiral phosphinooxathiane (POT) ligands **1** and **5** and found that the Pd complex of ligand **1** works as an effective catalyst of Pd-catalyzed asymmetric allylic alkylation and amination.[8] These results prompted us to investigate the utility of POT ligands in the enantioselective DA reactions. In this paper, we report a detailed investigation of DA reactions of cyclopentadiene with acryloyl- and fumaroyl-1,3-oxazolidin-2-ones (**6a** and **6b**) using cationic Pd(II)− and Pt(II)−POT complexes **12a**−**g** and **14**. Especially, it is important that the more conformationally constrained cationic complexes **12e**−**g** (M = Pd, X = SbF_6) that were derived from newly modified ligands **2**−**4** gave fairly good results for enantioselectivity (Scheme 1).

Results and Discussion

Synthesis of Phosphinooxathiane Ligands. Three new chiral ligands **2**−**4** bearing 3-tolyl, 3,5-xylyl, and 1-naphthyl moieties were synthesized by the palladium-catalyzed cross-coupling type reaction as shown in Scheme 2. The reactions of 2-bromobenzaldehyde **8** with (3-$CH_3C_6H_4$)$_2$P(O)H, [3,5-$(CH_3)_2C_6H_4$]$_2$P(O)H, and (1-$C_{10}H_4$)$_2$P(O)H using $Pd(OAc)_2$, a catalytic amounts of dppp [1,3-bis(diphenylphosphino)propane], and *i*-Pr_2NEt in DMSO at 150 °C[9] gave the phosphine oxides **9a**−**c**, respectively. And then the condensations of commercially available (1*S*)-(−)-10-mercaptoisoborneol with **9a**−**c** in refluxing benzene afforded the products **10a**−**c** in 91, 85, and 87% yields. The products **10a**−**c** were reduced with $HSiCl_3$ and Et_3N[9] to give the desired chiral ligands **2**−**4** in 78, 83, and 65% yields.

Asymmetric Diels−Alder Reaction. The chiral $PdCl_2$−, $PtCl_2$−POT complexes **11a**−**e** and **13** were easily prepared by the reactions of Scheme 3 in good yields. For catalytic DA reactions, we first examined the reaction of cyclopentadiene and acryloyl-1,3-oxazolidin-2-one **6a** in the presence of 20 mol % of catalysts **11a** and **13** at −78 °C; however, these reactions provided the DA adduct **7a** in low chemical isolated yields (**11a**: 18%, **13**: 15%) and no enantioselectivity. To increase the reactivity of complexes, various counterion effects were tested using the complex **11a** (Scheme 3). The catalysts **12a**−**c** (X = OTf, ClO_4, SbF_6) were prepared by the reaction of **11a** (1 equiv) and the corresponding AgX (2 equiv) in dry CH_2Cl_2 at rt for 1 h under argon.

The DA reactions of cyclopentadiene (5 equiv) with dienophile **6a** (1 equiv) using the prepared catalysts **12a**−**c** (20 mol %) in dry CH_2Cl_2 at a low temperature gave the DA adduct. The absolute configuration of DA adduct **7a** (2*R*-configuration)[10] was determined on basis of comparison of the optical rotations with the literature. The results are summarized in Table 1. The reaction catalyzed by **12a** (X = OTf) gave the DA adduct **7a** in

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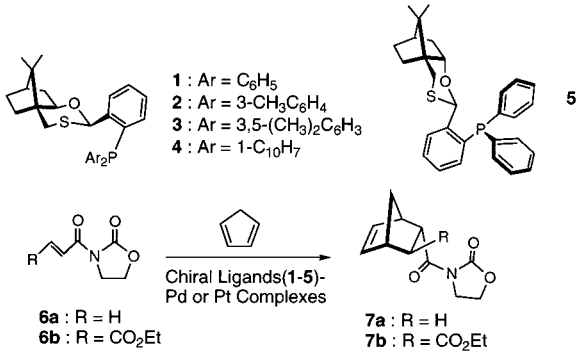
SCHEME 1



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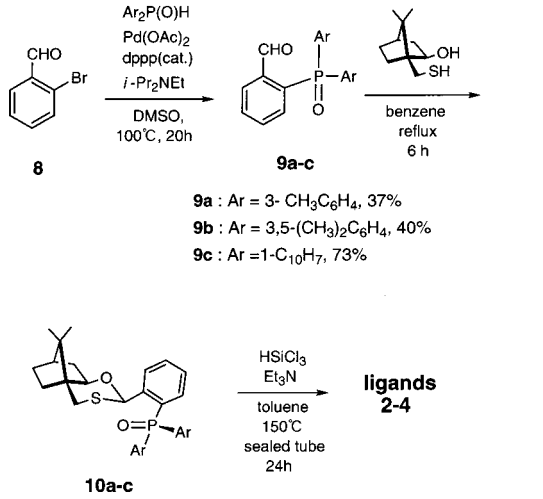

82% isolated yield and *endo* selectivity (36% ee) (entry 1), whereas the use of the catalyst **12b** (X = ClO_4) led to almost complete conversion, but the *endo* adduct was obtained in only 37% ee (entry 2). However, the reaction by Pd(II)−POT catalyst **12c** (X = SbF_6) gave the DA adduct **7a** in 90% isolated yield and *endo* enantioselectivity (69% ee) (entry 3). Furthermore, the reaction at the lower temperature of −78 °C afforded the *endo* adduct **7a** in the higher enantiomeric excess (85% ee) (entry 4). Even the use of 10 mol % of chiral complex **12c**, the reaction is no less effective than the use of 20 mol % (entry 5). These results indicated that the SbF_6 counterion was more effective than OTf and ClO_4. We also tested the catalytic ability of **14** (M = Pd, X = SbF_6) derived from the isomeric ligand **5** of **1**, but did not give satisfactory results (77%, 25% ee) (entry 6). To test the nature of the metal, we prepared the catalyst **12d** (M = Pt, X = SbF6), but did not afford good results in the chemical yield and enantioselectivity (30%, 16% ee) (entry 7). Continuously, we attempted to use the calatysts **12e**−**g** (M = Pd, X = SbF_6) that were derived from the modified ligands **2**−**4** of **1**. The DA reaction using chiral ligand **12e** under the similar reaction conditions to **12c** gave good results for both chemical yield and enantioselectivity (88%, 87%ee) (entry 8). The DA reaction using more conformationally constrained catalyst **12f** than **12e** also proceeded in good enantioselectivity (90% ee) when using 5 mol % and also 2.5 mol % (entry 9−10). Our attempt using the most conformationally constrained catalyst **12g** (10, 5 and 2.5 mol %) proved to give fairly good results (entry 11−13), in which gave the best results for the chemical yield (92%) and enantioselectivity (93% ee) when using 5 mol % of **12g**, and importantly the less molar use of **12g** (2.5 mol %) also gave the same result (93% ee). In addition, the DA reaction with fumaroyl-

SCHEME 3

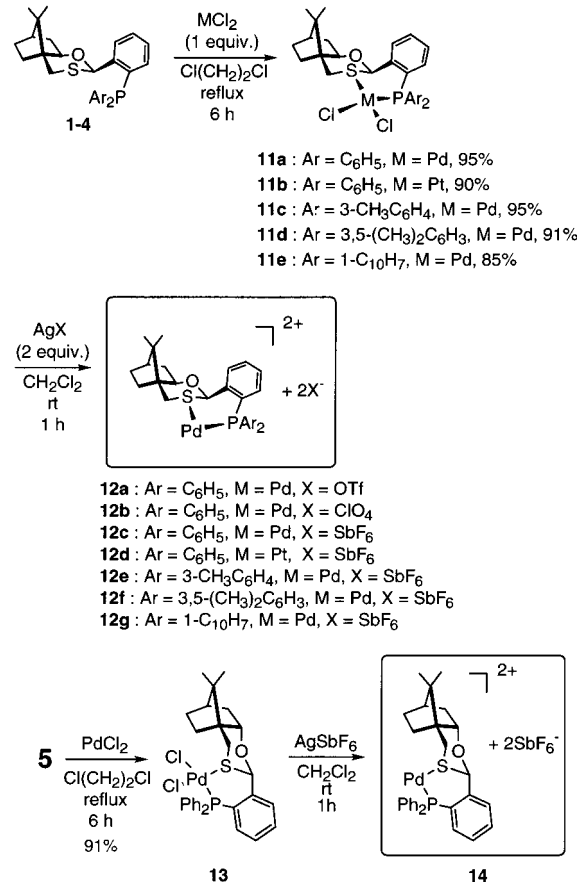

TABLE 1. Enantioselective Diels−Alder Reactions of Cyclopentadiene with Dienophiles 6a,b

entry	dienophile	catalyst (mol %)	temp (time, h)	% yield[a]	endo/exo[b]	% ee[c] (config)
1	**6a**	**12a**(20)	−45 °C(10)	82(**7a**)	91:9	36(2*R*)
2	**6a**	**12b**(20)	−45 °C(20)	95(**7a**)	89:11	37(2*R*)
3	**6a**	**12c**(20)	−45 °C(1)	90(**7a**)	89:11	69(2*R*)
4	**6a**	**12c**(20)	−78 °C(4)	74(**7a**)	93:7	85(2*R*)
5	**6a**	**12c**(10)	−78 °C(32)	61(**7a**)	91:9	81(2*R*)
6	**6a**	**14**(20)	−78 °C(3)	77(**7a**)	93:7	25(2*R*)
7	**6a**	**12d**(20)	−78 °C(24)	30(**7a**)	92:8	16(2*R*)
8	**6a**	**12e**(10)	−78 °C(15)	88(**7a**)	96:4	87(2*R*)
9	**6a**	**12f**(5)	−78 °C(15)	70(**7a**)	96:4	90(2*R*)
10	**6a**	**12f**(2.5)	−78 °C(15)	50(**7a**)	96:4	90(2*R*)
11	**6a**	**12g**(10)	−78 °C(3)	93(**7a**)	94:6	88(2*R*)
12	**6a**	**12g**(5)	−78 °C(5)	92(**7a**)	91:9	93(2*R*)
13	**6a**	**12g**(2.5)	−78 °C(24)	80(**7a**)	92:8	93(2*R*)
14	**6b**	**12g**(5)	−78 °C(92)	61(**7b**)	75:25	86(2*S*)[d]

[a] Isolated yields. [b] Endo/exo ratios were determined by HPLC or 1H NMR. [c] ee of endo isomers were determined by chiral HPLC using a Daicel OD-H column (**6c**: 0.5mL/min, hexane:2-propanol = 9:1). [d] After conversion to the corresponding iodolactone, the absolute configuration was determined by comparison with known optical rotation.[3e]

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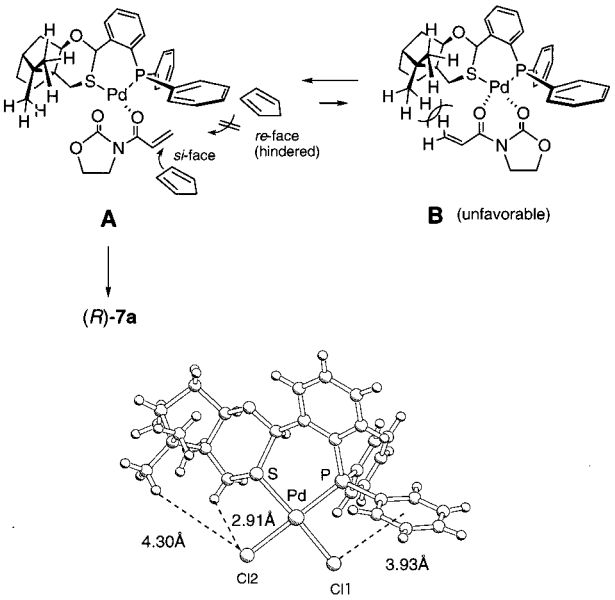
SCHEME 4



[a] X-ray structure of **11a**. Selected bond lengths and angles: Pd−Cl1: 2.305(3), Pd−Cl2: 2.349(4), Pd−S: 2.257(3), Pd−P: 2.234(3) Å, Cl1−Pd−Cl2: 91.9(1), Cl1−Pd−P: 89.1(1), Cl2−Pd−S: 85.5(1), S−Pd−P: 93.7(1), Cl1−Pd−S: 176.0(1), Cl2−Pd−P: 175.4(2)°. Short nonbonding distances of Cl atoms are drawn in the above structure. 3.93 Å is the distance between the Cl atom and the center of an equatorial phenyl ring.

1,3-oxazolidin-2-one **6b** using the catalysts **12g** also gave good enantioselectivity (86% ee),[3e] although the moderate chemical yield (61%).

To gain structural information about the palladium species coordinated with the POT ligand, the crystal structure of $PdCl_2$−POT **11a** was determined by X-ray study. As shown in Scheme 4, the complex **11a** has a square-planar geometry, being coordinated with S and P atoms of POT and one of the phenyl groups of $PdCl_2$−POT **11a** is oriented axially and the other equatorially with respect to the square-plane of the complex. In addition, there is also shown no space between the POT ligand and two Cl atoms since their nonbonding distances approach the sum of van der Waals radii. Based on the X-ray structure of **11a**, a model of the enantioselective reaction with dienophile **6a** and Pd(II)−POT complex was proposed (Scheme 4). It is thought that dienophile **6a** is L2-coordinated to the Pd(II)−POT complex via the two carbonyl oxygen atoms affording the square-planar complex in the intermediate **A**. Probably, intermediate **B**, having a different orientation of the dienophile, may be less favored to form due to the steric interaction of dimethyl groups on the norbornane ring and the olefin part on dienophile. Furthermore, the attack of diene at the *si*-face of the acryloyl group of **6a** is favored to afford the observed (2*R*)-cycloadduct, since the attack at the *re*-face would be hindered by the equatorial phenyl group of the ligand.

In conclusion, we have shown the first example using S−P type, phosphinooxathiane ligand for enantioselective DA reaction. The explored cationic Pd(II)−phosphinooxathiane complex **12g**, obtained from the reactions of chiral phosphinooxathiane ligand **4**, $PdCl_2$, and $AgSbF_6$, was an efficient chiral catalyst for the reaction. Further studies including modification to the dienes, dienophiles, ligands design, and mechanistic investigation are in progress.

Experimental Section

General Procedure for the Synthesis of Phosphine Oxides (10a−c). (1*S*)-(−)-10-mercaptoisoborneol (1.17 mmol), the corresponding (2-formylphenyl)(diaryl)phosphine oxides **9a−c** (1.17 mmol), *p*-toluenesulfonic acid monohydrate (0.12 mmol), and benzene (10 mL) were placed in a flask equipped with a Dean−Stark trap. The mixture was refluxed for 6 h. The solvent was evaporated under a reduced pressure, and the residue was purified by column chromatography on silica gel (elution with AcOEt: hexane = 1:2) to afford **10a−c**.

(1*R*,3*R*,5*R*,8*S*)-11,11-Dimethyl-4-oxa-5-[2-di(*m*-tolyl)phosphinyl]phenyl-6-thiatricyclo[6.2.1.0]undecane (10a): yield, 91% ; white solid; mp 70−74 °C. $[\alpha]^{23}_D = -106.2$ (*c* 2.1, $CHCl_3$). IR (KBr) cm^{-1}: 1181, 751, 712, 697. ^1H NMR ($CDCl_3$) δ: 0.72−0.82 (m, 1H), 0.88−0.99 (m, 4H), 1.34−1.53 (m, 4H), 1.59−1.68 (m, 2H), 1.77 (m, 1H), 1.89 (brs, 1H), 2.37 (d, J = 0.7, 6H), 2.63 (d, J = 14.2 Hz, 1H), 3.01 (d, J = 14.4 Hz, 1H), 3.19 (m, 1H), 6.35 (s, 1H), 7.13−7.41 (m, 8H), 7.52−7.59 (m, 3H), 7.84 (m, 1H). ^{13}C NMR ($CDCl_3$) δ: 20.44, 21.41, 21.46, 23.38, 27.23, 30.00, 34.18, 37.79, 41.68, 45.52, 46.66, 80.82, 85.50, 127.80, 127.98, 128.12, 128.14, 128.31, 128.33, 129.11, 129.27, 129.43, 129.69, 132.51, 132.58, 132.63, 132.67, 132.72, 138.22, 138.43, 143.79, 143.90. HRMS *m*/*z*: Calcd for $C_{31}H_{35}O_2PS$ (M^+): 502.2095. Found: 502.2051.

(1*R*,3*R*,5*R*,8*S*)-11,11-Dimethyl-4-oxa-5-[2-di(3,3-xylyl)-phosphinyl]phenyl-6-thiatricyclo[6.2.1.0]undecane (10b): yield, 85% ; white solid; mp 67−70 °C. $[\alpha]^{23}_D = -121.6$ (*c* 1.6, $CHCl_3$). IR (KBr) cm^{-1}: 1180, 851, 754, 692. 1H NMR ($CDCl_3$) δ: 0.75 (m, 1H), 0.89−0.99 (m, 4H), 1.33−1.53 (m, 5H), 1.59−1.64 (m, 2H), 1.78 (m, 1H), 2.31 (d, J = 0.50, 12H), 2.63 (d, J = 14.2 Hz, 1H), 2.97 (d, J = 14.2 Hz, 1H), 3.16 (m, 1H), 6.27 (s, H), 7.17 (m, 2H), 7.22−7.30 (m, 6H), 7.55 (m, 1H), 7.83 (m, 1H). ^{13}C NMR ($CDCl_3$) δ: 20.45, 21.30, 21.32, 23.38, 27.25, 29.97, 34.18, 37.85, 41.63, 45.52, 46.65, 80.97, 85.46, 127.81, 127.99, 129.60, 129.65, 129.74, 129.79, 129.88, 132.33, 132.37, 133.40, 133.44, 133.51, 137.93, 137.95, 138.12, 138.14, 143.63, 143.74. HRMS *m*/*z*: Calcd for $C_{33}H_{39}O_2PS$ (M^+): 530.2408. Found: 530.2425.

(1*R*,3*R*,5*R*,8*S*)-11,11-Dimethyl-4-oxa-5-[2-di(1-naphthyl)-phosphinyl]phenyl-6-thiatricyclo[6.2.1.0]undecane (10c): yield, 87%; white solid. mp 135−138 °C. $[\alpha]^{20}_D = -89.9$ (*c* 2.6, $CHCl_3$). IR (KBr) cm^{-1}: 1179, 802, 775, 753. ^1H NMR ($CDCl_3$) δ: 0.71 (m, 1H), 0.83−0.98 (m, 4H), 1.25−1.36 (m, 2H), 1.42−1.45 (m, 3H), 1.62−1.91 (m, 3H), 2.57 (d, J = 14.0, 1H), 2.95 (d, J = 13.9 Hz, 1H), 3.39 (brs, 1H), 6.75 (brs, 1H), 7.11−7.16 (m, 2H), 7.31−7.39 (m, 4H), 7.42−7.58 (m, 5H), 7.89−8.03 (m, 5H), 8.83 (d, J = 8.08 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ: 19.51, 20.37, 23.39, 27.11, 29.86, 33.92, 37.65, 41.69, 45.46, 46.67, 85.25, 124.04, 124.16, 124.26, 124.37, 126.44, 127.37, 127.92, 128.10, 128.19, 128.39, 128.64, 129.60, 129.74, 130.14, 132.51, 132.98, 133.12, 133.16, 133.47, 133.64, 133.83, 133.97, 134.09, 134.20. HRMS *m*/*z*: Calcd for $C_{37}H_{35}O_2PS$ (M^+): 574.2095. Found: 574.2087.

General Procedure for the Synthesis of Phosphinooxathiane Ligands (2−4). To a mixture of **10a−c** (0.82 mmol) and Et_3N (**10a,b**: 16.3 mmol, **10c**: 24.6 mmol) in toluene (**10a,b**: 20 mL, **10c**: 2 mL) was added trichlorosilane (**10a,b**: 8.16 mmol, **10c**: 16.4 mmol) at 0 °C. The reaction mixture was stirred at 150 °C for 24 h. After being cooled to room temperature, the reaction mixture was diluted with Et_2O and quenched with small amount of saturated $NaHCO_3$. The resulting suspension was filtered through Celite, and solid was washed with Et_2O. The combined organic layer was dried over anhydrous $MgSO_4$ and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel (elution with AcOEt: hexane = 1:4) to afford **2−4**.

(1*R*,3*R*,5*R*,8*S*)-11,11-Dimethyl-4-oxa-5-[2-di(*m*-tolyl)phosphino]phenyl-6-thiatricyclo[6.2.1.0]undecane (2): yield, 78% ; white solid. mp 38 °C. $[\alpha]^{24}_D = -89.3$ (*c* 2.2, $CHCl_3$). IR (KBr) cm^{-1}: 777, 747, 696. ^1H NMR ($CDCl_3$) δ: 0.86−1.06 (m, 5H), 1.41−1.51 (m, 4H), 1.58−1.74 (m, 3H), 1.90 (m, 1H), 2.29 (s, 6H), 2.71 (d, J = 14.2 Hz, 1H), 3.20 (d, J = 14.4 Hz, 1H), 3.59 (m, 1H), 6.39 (d, J = 7.8 Hz, 1H), 6.93 (m, 1H), 7.02−7.08 (m, 2H), 7.12−7.23 (m, 7H), 7.37 (m, 1H), 7.71 (m, 1H). ^{13}C NMR ($CDCl_3$) δ: 20.47, 21.43, 21.46, 23.41, 27.28, 29.98, 34.32, 37.92, 41.85, 45.58, 46.77, 81.16, 85.63, 127.28, 127.35, 128.20, 128.30,

128.48, 129.30, 129.43, 129.49, 130.45, 130.70, 131.05, 133.88, 134.10, 134.42, 137.82, 137.93, 143.97, 144.31. HRMS *m/z*: Calcd for $C_{31}H_{35}OPS$ (M^+): 486.2146. Found: 486.2063.

(1*R*,3*R*,5*R*,8*S*)-11,11-Dimethyl-4-oxa-5-[2-di(3,3-xylyl)-phosphino]phenyl-6-thiatricyclo[6.2.1.0]undecane (3): yield, 83% ; white solid. mp 38−42 °C. $[\alpha]^{23}_D = -84.8$ (*c* 2.1, $CHCl_3$). IR cm^{-1}: 847, 747, 693. ^1H NMR ($CDCl_3$) δ: 0.86−1.06 (m, 5H), 1.41−1.54 (m, 4H), 1.60−1.71 (m, 3H), 1.91 (m, 1H), 2.24 (s, 12H), 2.71 (d, J = 14.4 Hz, 1H), 3.20 (d, J = 14.4 Hz, 1H), 3.59 (m, 1H), 6.37 (d, J = 7.75 Hz, 1H), 6.89−6.98 (m, 7H), 7.18 (m, 1H), 7.37 (m, 1H), 7.71 (m, 1H). ^{13}C NMR ($CDCl_3$) δ: 20.22, 21.43, 21.48, 23.04, 27.13, 30.93, 33.71, 37.43, 39.98, 45.52, 45.75, 47.17, 81.95, 86.50, 127.21, 127.29, 128.42, 129.41, 130.26, 130.40, 131.06, 131.35, 131.39, 131.67, 133.91, 137.62, 137.72, 143.95, 144.29. HRMS *m/z*: Calcd for $C_{33}H_{39}OPS$ (M^+): 514.2459. Found: 514.2485.

(1*R*,3*R*,5*R*,8*S*)-11,11-Dimethyl-4-oxa-5-[2-di(1-naphthyl)-phosphino]phenyl-6-thiatricyclo[6.2.1.0]undecane (4): yield, 65%; white solid. mp 71−74 °C. $[\alpha]^{24}_D = -40.8$ (*c* 1.3, $CHCl_3$). IR (KBr) cm^{-1}: 798, 774, 746. ^1H NMR ($CDCl_3$) δ: 0.76−0.97(m, 5H), 1.33−1.46 (m, 4H), 1.54 (s, 1H), 1.65−1.68 (m, 2H), 1.81 (m, 1H), 2.67 (d, J =14.2 Hz, 1H), 3.08 (d, J = 14.2 Hz, 1H), 3.53 (brs, 1H), 6.49 (d, J = 7.42 Hz, 1H), 6.84 (m, 1H), 6.94−7.11 (m, 3H), 7.28−7.51 (m, 7H), 7.75−7.89 (m, 5H), 8.40−8.51 (m, 2H). ^{13}C NMR ($CDCl_3$) δ: 20.44, 23.41, 27.20, 29.95, 34.16, 37.81, 41.86, 45.53, 46.75, 81.33, 85.58, 125.66, 125.68, 125.78, 125.92, 126.24, 126.37, 126.46, 126.76, 126.85, 127.46, 127.53, 128.56, 128.59, 128.71, 129.47, 129.51, 129.82, 133.12, 133.17, 133.42, 133.43, 133.49, 134.63, 135.51, 144.06, 144.42. HRMS *m/z*: Calcd for $C_{37}H_{35}OPS$ (M^+): 558.2146. Found: 558.2196.

General Procedure for Preparation of $PdCl_2$− and $PtCl_2$−Phosphinooxathiane Complexes (11a−e, 13). $PdCl_2$ (0.035 mmol) or $PtCl_2$ (0.035 mmol) and phosphinooxathianes **1**−**5** (0.035 mmol) were suspended in 1,2-dichloroethane (2 mL) under Ar. The mixture was refluxed for 6h and the resulting yellow solution was cooled and filtered. The filtrate was condensed under a reduced pressure and the residue was recrystallized from hexane: CH_2Cl_2 to afford **11a**−**e** and **13**.

Dichloro[(1*R*,3*R*,5*R*,8*S*)-11,11-dimethyl-4-oxa-5-(2-diphenylphosphino)phenyl-6-thiatricyclo[6.2.1.0]undecane]palladium (11a): yield, 95%; yellow crystals. mp 238−241 °C. $[\alpha]^{23}_D$ = −159.2 (*c* 2.5, $CHCl_3$). IR (KBr) cm^{-1}: 747, 710, 692. ^1H NMR ($CDCl_3$) δ: 0.88−1.09 (m, 5H), 1.29 (s, 3H), 1.59−1.83 (m, 4H), 2.12 (m, 1H), 3.53 (m, 1H), 3.64 (d, J = 14.4, 1H), 4.13 (d, J = 14.2, 1H), 5.40 (s, 1H), 6.70 (m, 1H), 7.32−7.64 (m, 10H), 7.93 (m, 3H). ^{13}C NMR ($CDCl_3$) δ: 20.17, 22.99, 27.07, 33.65, 37.33, 40.02, 45.45, 45.73,47.11, 82.01, 86.59, 125.84, 125.97, 128.40, 128.59, 129.53, 129.62, 129.79, 131.79, 131.83, 132.43, 132.46, 132.95, 133.00, 134.34, 134.50, 134.80, 134.97, 139.02. Anal. Calcd for $C_{29}H_{31}Cl_2OPSPd$: C, 54.77; H, 4.91. Found: C, 54.65; H, 4.89. MS *m/z*: 634 (M^+).

Dichloro[(1*R*,3*R*,5*R*,8*S*)-11,11-dimethyl-4-oxa-5-(2-diphenylphosphino)phenyl-6-thiatricyclo[6.2.1.0]undecane]platinum (11b): yield, 90%; colorless crystals. mp 211−214 °C. $[\alpha]^{23}_D$ = −122.4 (*c* 2.0, $CHCl_3$). IR (KBr) cm^{-1}: 748, 713, 696. ^1H NMR ($CDCl_3$) δ: 0.86−1.09 (m, 5H), 1.29 (s, 3H), 1.62−1.82 (m, 4H), 2.13 (m, 1H), 3.57−3.62 (m, 2H), 4.11 (d, J = 14.0, 1H), 5.45 (s, 1H), 6.62−6.70 (m, 1H), 7.32−7.65 (m, 10H), 7.81−7.94 (m, 3H). ^{13}C NMR ($CDCl_3$) δ: 20.24, 22.91, 27.11, 33.51, 37.36, 39.99, 45.49, 45.86, 47.13, 81.29, 86.61, 125.62, 125.74, 128.23, 128.41, 129.19, 129.33, 129.49, 131.73, 131.77, 132.17, 132.20, 132.60, 132.64, 134.46, 134.49, 134.61, 134.66, 138.44. HRMS *m/z*: Calcd for $C_{29}H_{31}Cl_2OPSPt$: 723.0858. Found: 723.0629.

Dichloro[(1*R*,3*R*,5*R*,8*S*)-11,11-dimethyl-4-oxa-5-[2-di(*m*-tolyl)phosphino]phenyl-6-thiatricyclo[6.2.1.0]undecane]-palladium (11c): yield, 95%; yellow crystals. mp 203−205 °C. $[\alpha]^{20}_D = -127.1$ (*c* 2.2, $CHCl_3$). IR (KBr) cm^{-1}: 780, 706,691. ^1H NMR ($CDCl_3$) δ: 0.89−1.09(m, 5H), 1.29 (s, 3H), 1.61−1.83 (m, 4H), 2.11 (m, 1H), 2.38(d, J = 19.5 Hz, 6H), 3.54 (m, 1H), 3.65 (d, J = 14.4 Hz, 1H), 4.13 (d, J = 14.4 Hz, 1H), 5.42 (s, 1H), 6.69 (m, 1H), 7.17 (m, 1H), 7.29−7.47 (m, 6H), 7.50−7.65 (m, 2H), 7.85−7.92 (m, 2H). ^{13}C NMR ($CDCl_3$) δ: 20.22, 21.55, 21.63, 23.04, 27.12, 33.70, 37.40, 40.01, 45.50, 45.76, 47.16, 82.00, 86.56, 125.68, 125.81, 129.26, 129.44, 132.27, 132.31, 132.67, 133.77, 133.83, 133.85, 133.89, 134.88, 138.21, 138.40, 138.86, 138.99, 139.76, 139.94. Anal. Calcd for $C_{31}H_{35}Cl_2OPSPd$: C, 56.08; H, 5.31. Found: C, 56.09; H, 5.30. MS *m/z*: 662 (M^+).

Dichloro[(1*R*,3*R*,5*R*,8*S*)-11,11-dimethyl-4-oxa-5-[2-di(3,3-xylyl)phosphino]phenyl-6-thiatricyclo[6.2.1.0]undecane]-palladium (11d): yield, 91%; yellow crystals. mp 209−210 °C. $[\alpha]^{20}_D = -109.7$ (*c* 2.2, $CHCl_3$). IR (KBr) cm^{-1}: 847, 732, 688. ^1H NMR ($CDCl_3$) δ: 0.89−1.09 (m, 5H), 1.30 (s, 3H), 1.71−1.83 (m, 4H), 2.11 (m, 1H), 2.32(d, J = 16.0 Hz, 12H), 3.56 (m, 1H), 3.64 (d, J = 14.2 Hz, 1H), 4.12 (d, J = 14.2 Hz, 1H), 5.41 (s, 1H), 6.69 (m, 1H), 7.02 (d, J = 13.7 Hz, 2H), 7.12 (s, 1H), 7.25 (s, 1H), 7.34 (t, J = 7.7 Hz, 1H), 7.48 (d, J = 13.4 Hz, 2H), 7.61 (t, J = 7.7 Hz, 1H), 7.89 (m, 1H). ^{13}C NMR ($CDCl_3$) δ: 20.19, 21.39, 21.45, 23.01, 27.10, 33.68, 37.40, 39.94, 45.49, 45.72, 47.13, 81.91, 86.46, 125.49, 125.62, 129.22, 129.35, 131.98, 132.08, 132.11, 133.64, 133.68, 133.81, 133.87, 134.85, 137.86, 138.05, 138.79, 138.91, 139.25, 139.43. HRMS *m/z*: Calcd for $C_{33}H_{39}Cl_2OPSPd$ (M^+): 690.0871. Found: 690.0944.

Dichloro[(1*R*,3*R*,5*R*,8*S*)-11,11-dimethyl-4-oxa-5-[2-di(1-naphthyl)phosphino]phenyl-6-thiatricyclo[6.2.1.0]-undecane]palladium (11e): yield, 85%; yellow crystals. mp 204−208 °C. $[\alpha]^{22}_D = -97.5$ (*c* 2.4, $CHCl_3$). IR (KBr) cm^{-1}: 800, 772, 746. ^1H NMR ($CDCl_3$) δ: 0.83−1.06 (m, 5H), 1.25−1.47 (m, 3H), 1.58−1.78 (m, 4H), 1.99 (d, J = 13.4 Hz, 1H), 3.22 (m, 1H), 3.64 (d, J = 14.0 Hz, 1H), 4.18 (d, J = 14.0 Hz, 1H), 5.08 (s, 1H), 7.18−8.18 (m, 15H), 8.25 (d, J = 8.4 Hz, 1H), 8.69 (d, J = 7.8 Hz, 1H), 10.01 (dd, J = 6.9 Hz, 20.0 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ: 20.22, 22.99, 27.05, 33.94, 37.22, 40.38, 45.46, 45.84, 47.13, 82.09, 86.92, 124.41, 124.60, 124.52, 125.79, 125.90, 125.95, 126.80, 127.53, 127.62, 128.81, 128.94, 129.06, 129.36, 129.81, 130.89, 132.13, 132.46, 133.28, 133.62, 133.75, 134.25, 134.34, 134.91, 135.38, 138.75, 143.64.

Dichloro[(1*R*,3*S*,5*S*,8*S*)-11,11-dimethyl-4-oxa-5-(2-diphenylphosphino)phenyl-6-thiatricyclo[6.2.1.0]undecane]palladium (13): yield, 91%; yellow crystals. mp 204−207 °C. $[\alpha]^{20}_D = 74.8$ (*c* 2.5, $CHCl_3$). IR (KBr) cm^{-1}: 769, 750, 694. ^1H NMR ($CDCl_3$) δ: 0.95 (d, J = 13.4 Hz, 6H), 1.24 (m, 1H), 1.38 (m, 1H), 1.54 (m, 1H), 1.81−1.82 (m, 2H), 2.21−2.43 (m, 2H), 3.68−3.79 (m, 2H), 3.93 (d, J = 12.7 Hz, 1H), 5.66 (s, 1H), 6.68 (m, 1H), 7.35−7.57 (m, 8H), 7.63−7.70 (m, 2H), 7.90−8.05 (m, 3H). ^{13}C NMR ($CDCl_3$) δ: 18.62, 19.52, 24.83, 27.95, 33.94, 44.27, 45.31, 46.21, 48.73, 84.32, 85.75, 124.99, 125.95, 126.83, 128.44, 128.63, 129.54, 129.72, 129.81, 131.83, 132.58, 132.94, 133.65, 134.30, 134.46, 134.92, 135.09, 138.63, 138.75. HRMS *m/z*: Calcd for $C_{29}H_{31}Cl_2OPSPd$: 634.0245. Found: 634.0153.

General Procedure for Enantioselective Pd(II) and Pt(II)-Catalyzed Diels−Alder Reactions. $PdCl_2$−POT complexes **11a**, **11c**−**e**, **13** (1 equiv) or $PtCl_2$−POT complex **11b** (1 equiv) and 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-1,3-oxazolidin-2-one **6a** (50 mg, 0.36 mmol) or fumaroyl-1,3-oxazolidin-2-one **6b** (77 mg, 0.36 mmol) in CH_2Cl_2 (1 mL) followed by cyclopentadiene (117 mg, 1.77 mmol) was added. The reaction mixture was stirred for the specified amount of time and quenched with sat. aq $NaHCO_3$. The mixture was extracted with $CHCl_3$, and 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 **7a**,**b**. The ee of **7a** was determined by HPLC (Chiralcel OD-H, 1.0 mL/min, hexane:2-propanol = 90:10). The ee of **7b** was determined by comparison of the known optical rotation of iodolactonization product derived from **7b**.[3e]

X-ray Crystal Structure of $PdCl_2$−POT (11a). X-ray crystallographic data of $PdCl_2$−POT (**11a**) have been deposited at the Cambridge Crystallographic Data Center (CCDC 186659) in CIF format.

Supporting Information Available: Experimental information including structural data for compounds **9a**−**c**, and ^1H and ^{13}C NMR spectra data of compounds **2**−**4**, **9a**−**c**, **10a**−**c**, **11a**−**e**, and **13**. This material is available free of charge via the Internet at http://pubs.acs.org.

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