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Counterions of BINAP–Pt(II) and –Pd(II) Complexes: Novel Catalysts for Highly Enantioselective Diels–Alder Reaction

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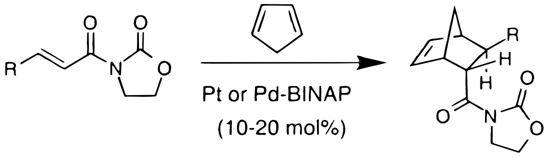
ABSTRACT



Platinum and palladium chiral bisphosphine complexes and their counterion effects in asymmetric Diels–Alder reactions have been investigated. The reaction of cyclopentadiene and various bidentate dienophiles in the presence of a catalytic amount of Pt(II)– or Pd(II)–BINAP complex proceeds with excellent *endo/exo* selectivity as well as *endo* enantioselectivity (up to 99% ee).

Asymmetric Diels−Alder reaction is one of the most powerful and versatile reactions in organic synthesis.[1] Catalytic enantioselective processes with chiral Lewis acid derived catalysts significantly extended the scope and utility of this reaction.[2,3] In the design of chiral Lewis acids, the choice of the chiral ligand and the metal and its counterion is critical to superior *endo/exo* selectivity as well as *endo* enantioselectivity. Among the metals, transition metal−ligand complexes have particularly shown exceptional promise as chiral Lewis acids for enantioselective Diels−Alder reactions.[4] Interestingly, the potential of late transition metals such as platinum- and palladium-based chiral Lewis acids has not been explored in detail for enantioselective Diels−Alder reactions.[5] Prompted by the report of Furukawa and co-workers on the Pd−bisphosphine complex catalyzed asymmetric 1,3-dipolar cycloaddition reactions, we have elected to investigate Pt(II)− and Pd(II)−BINAP complexes for our preliminary studies.[6] Herein, we report that cationic Pt(II) and Pd(II) chiral bisphosphine complexes are highly effective catalysts for the enantioselective Diels−Alder reaction of cyclopentadiene and various bidentate dienophiles. With appropriate counterions, the reaction proceeds with excellent *endo/exo* selectivity, *endo* enantioselectivity (up to 99% ee), and isolated yields.

Chiral Pt(II)−bisphosphine was conveniently prepared by reaction of commercial $PtCl_2$ (1 equiv) with (*R*)-BINAP (1 equiv) in chloroform at reflux for 24 h to provide $PtCl_2$[(*R*)-BINAP] complex **3** in 91% yield.[7] Initial attempts at a catalytic Diels−Alder reaction of acryloyl-*N*-oxazolidinone **1a** and cyclopentadiene in the presence of 20 mol % of catalyst **3** at −78 to −40 °C for 48 h resulted in a very sluggish reaction (yield <5%) with practically no enantioselectivity (<5% ee). To increase the reactivity of the Pt(II)−bisphosphine complex, we have investigated various counterion effects. Thus, a Pt(II)−BINAP complex with triflate

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[1] Oppolzer, W. *Comprehensive Organic Syntheses: Selectivity, Strategy and Efficiency in Modern Organic Chemistry*; Trost, B. M., Ed.; Pergamon Press: Oxford, 1991; Vol. 5, p 315 and references therein.

[2] (a) Corey, E. J.; Sarshar, S.; Lee, D.-H. *J. Am. Chem. Soc.* **1994**, *116*, 12089. (b) Kagan, H. B.; Riant, O. *Chem. Rev.* **1992**, *92*, 1007. (c) Pindur, U.; Lutz, G.; Otto, C. *Chem. Rev.* **1993**, *93*, 741. (d) Deloux, L.; Srebnik, M. *Chem. Rev.* **1993**, *93*, 763. (e) Oh, T.; Reilly, M. *Org. Prep. Proceed. Int.* **1994**, *26*, 129 and references therein.

[3] For a recent review on metal−bis(oxazoline) catalyzed reactions, see: Ghosh, A. K.; Mathivanan, P.; Cappiello, J. *Tetrahedron: Asymmetry* **1998**, *9*, 1 and references therein.

[4] Diaz, L. C. *J. Braz. Chem. Soc.* **1997**, *8*, 289 and references therein.

[5] Oi, S.; Kashiwagi, K.; Inoue, Y. *Tetrahedron Lett.* **1998**, *39*, 6253.

[6] Hori, K.; Kodama, H.; Ohta, T.; Furukawa, I. *J. Org. Chem.* **1999**, *64*, 5017.

[7] Strukul, G.; Varagnolo, A.; Pinna, F. *J. Mol. Catal.* **1997**, 413.

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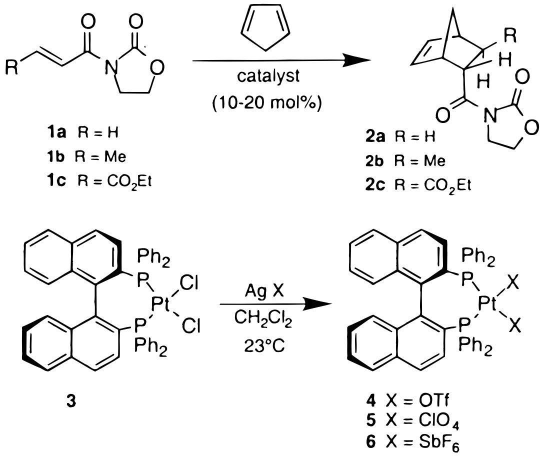
counterions (complex **4**) was prepared by reaction of $PtCl_2$-[(*R*)-BINAP] complex **3** (1 equiv) and AgOTf (2 equiv) in dry CH_2Cl_2 at 23 °C for 1 h under nitrogen (Scheme 1).

Scheme 1



The resulting catalyst (20 mol %) suspension was cooled to −40 °C, and acryloyl-*N*-oxazolidinone **1a** (1 equiv) followed by freshly cracked cyclopentadiene (4−6 equiv) was added. The mixture was stirred at this temperature for 96 h to provide the Diels−Alder cycloadducts in 81% yield after silica gel chromatography. As shown in Table 1, analysis of the resulting cycloadducts by ^{1}H NMR (400 MHz) and chiral HPLC analysis (Daicel Chiracel OD column, 10% 2-propanol/hexane as the eluent) revealed that the reaction proceeded with high *endo* selectivity (*endo/exo* ratio 95:5) as well as *endo* enantioselectivity (89% ee). The absolute configuration of the cycloadduct **2a** (2*S*-configuration) was determined on the basis of a comparison of optical rotations with the literature values.[8]

Table 1. Enantioselective Diels−Alder Reaction

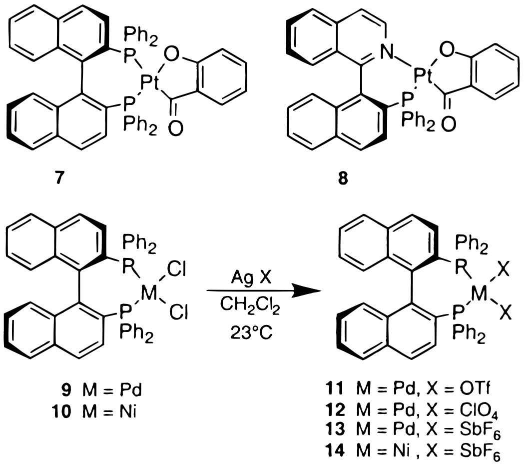
Entry	Dieno-phile	Catalyst (mol %)	Temp (time, h)	% Yield[a]	*endo/exo*[b]	*endo* ee[c,d] (config.)
1.	**1a**	**4** (20)	-40°C (96)	81	95 : 5	89 (2*S*)
2.	**1a**	**5** (20)	-78°C (18)	93	98 : 2	97 (2*S*)
3.	**1a**	**6** (20)	-78°C (21)	99	97 : 3	98 (2*S*)
4.	**1a**	**7** (20)	-40°C (20)	80	94 : 6	96 (2*S*)
5.	**1a**	**7** (20)[e]	-40°C (1)	80	96 : 4	98 (2*S*)
6.	**1a**	**12** (10)	-78°C (24)	75	97 : 3	99 (2*S*)
7.	**1a**	**13** (10)	-78°C (10)	87	97 : 3	96 (2*S*)
8.	**1a**	**14** (10)	-40°C (96)	55	94 : 6	15 (2*S*)
9.	**1b**	**5** (40)	0°C (48)	51	91 : 9	90 (2*S*)
10.	**1b**	**6** (20)	0°C (40)	74	92 : 8	93 (2*S*)
11.	**1c**	**5** (20)	-40°C (8)	75	90 : 10	90 (2*R*)
12.	**1c**	**6** (20)	-40°C (4)	84	89 : 11	90 (2*R*)
13.	**1c**	**12** (10)	-40°C (4)	91	77 : 23	57 (2*R*)
14.	**1c**	**13** (10)	-40°C (4)	96	75 : 25	67 (2*R*)

[a] Isolated yield after silica gel chromatography. [b] *Endo/exo* ratios were determined by ^{1}H-NMR and HPLC. [c] Enantiomeric excess (ee) was determined by chiral HPLC and comparison of reported optical rotation [d] Average of two determinations. [e] Cationic aqua complex was prepared with 2 equiv of water.

Pt(II)−BINAP complex **5** with perchlorate counterion was prepared by reaction of chloro complex **3** and $AgClO_4$ by following a procedure similar to that described above for triflate complex **4**. The catalyst complex **5** exhibited a stronger counterion effect than the corresponding triflate complex **4**. The results of various counterion effects in the Diels−Alder reactions are summarized in Table 1. The reaction of cyclopentadiene with dienophile **1a** in the presence of catalyst **5** (20 mol %) proceeded at −78 °C, and the reaction was completed within 18 h (entry 2), providing cycloadduct **2a** in 93% isolated yield and excellent *endo/exo* selectivity (98:2) and *endo* enantioselectivity (97% ee, 2*S*-isomer). Complex **6** with antimonate counterion has also shown results comparable with those of dienophile **1a**, affording cycloadduct **2a** with superior *endo* enantioselectivity (98% ee) and a nearly quantitative isolated yield.

Catalytic properties of chiral Pt(II) complexes with triflate counterions generated from Pt−(*R*)-BINAP−Sal complex **7** and Pt−(*R*)-QUINAP−Sal complex **8** have also been investigated in enantioselective Diels−Alder reactions (Scheme 2). Platinum complex **7** was prepared as reported previously by Fujimura.[9] Activation of complex **7** with 2 equiv of anhydrous triflic acid in CH_2Cl_2 at 23 °C for 15 min provided the cationic Pt(II) species. Diels−Alder reaction with dienophile **1a** in the presence of the above cationic Pt complex (20 mol %) at −40 °C for 20 h provided cycloadduct **2a** in comparable yield (80%) but with improved reaction time and *endo* enantioselectivity (96% ee, 2*S*-isomer, 94:6 *endo/exo*

Scheme 2



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(8) Narasaka, K.; Inoue, M.; Okada, N. *Chem. Lett.* **1986**, 1109.
(9) Fujimura, O. *J. Am. Chem. Soc.* **1998**, *120*, 10032.

ratio) compared to those of cationic complex **4** (entry 1). Further generation of the cationic aqua complex derived from **7** with 2 equiv of triflic acid and 2 equiv of water at 23 °C for 15 min and subsequent reaction with **1a** exhibited dramatic improvement in reactivity.[10] The reaction proceeded at −40 °C within 1 h to provide cycloadduct **2a** (entry 5) with excellent *endo* enantioselectivity (98% ee, 96:4 *endo/exo* ratio) and isolated yield (80%). Interestingly, the addition of water (2 equiv) to cationic complexes **4**−**6** did not have any appreciable effect except for complex **5** with perchlorate counterion which has shown nearly complete *endo* enantioselectivity (99% ee) in 86% yield (−78 °C, 24 h, *endo/exo* ratio 98:2). We have also investigated the catalytic properties of triflic acid activated Pt−(*R*)-QUINAP−Sal complex **8** in Diels−Alder reaction with **1a**.[11] While the reaction is sluggish at −40 °C, the reaction at 0 °C proceeded to completion within 21 h (87% yield). However, cycloadduct **2a** has shown no enantioselectivity (<5% ee). Thus, the importance of BINAP is critical to the observed enantioselectivity in the present Diels−Alder reactions.

Beside the counterions and the ligands, we have also investigated other late transition state metals. Among the metals surveyed, Pd(II)−BINAP complexes have shown counterion effects similar to those of the platinum complexes in the Diels−Alder reaction with acryloyl-*N*-oxazolidinone **1a** (entries 6 and 7).[5] The Pd(II)−(*R*)-BINAP complexes with various counterions were prepared by reaction of commercial $PdCl_2$[(*R*)-BINAP] complex **9** with the appropriate silver salt as described above for the platinum complexes. As shown in Table 1, Pd−BINAP complex **12** with perchlorate counterions (entry 6) has provided near complete *endo* enantioselectivity (99% ee) with 2*S*-absolute configuration for cycloadduct **2a**. With dienophile **1a**, nickel−BINAP complex **14** with antimonate counterions (entry 8) has exhibited poor *endo* enantioselectivity (15% ee), reactivity (96 h at −40 °C), and isolated yield (55%).[12] Diels−Alder reactions with crotonoyl (**1b**) and fumaroyl oxazolidinones (**1c**) in the presence of platinum complexes **5** and **6** (20−40 mol %) also provided excellent *endo/exo* selectivities and *endo* enantioselectivities (90−93% ee). In comparison, Pd complexes have shown significantly lower enantioselectivities with fumaroyl oxazolidinone **1c** (entries 13 and 14; 57−67% ee) and the reaction with oxazolidinone **1b** was very sluggish even at 23 °C.

The high degree of enantiofacial selection associated with the present Pt(II)− or Pd(II)−BINAP complex catalyzed Diels−Alder reaction can be rationalized by the postulated transition state assembly shown in Figure 1. The model is derived on the basis of the hypothesis that both Pt(II) and Pd(II) adopt a square planar geometry with the BINAP ligand and the bidentate acyl oxazolidinone.[13] Also, the dienophile assumes an *s-cis* conformation.[14] In this model, the *Si*-face attack of cyclopentadiene is not favored because of the developing nonbonded interaction between the phenyl ring on the phosphine ligand and the incoming diene. Thus, the *endo*-*Re*-face attack is more favorable and this leads to the observed enantioselectivity with 2*S*-absolute configuration for cycloadduct **2a**. The observed 2*R*-enantioselectivity for cycloadduct **2c** is consistent with this model.

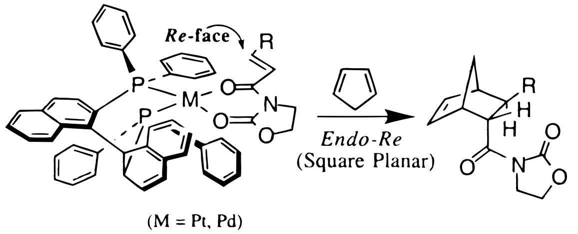

Figure 1.

In summary, the utility of chiral Pt− and Pd−bisphosphine complexes and their counterion effects in enantioselective Diels−Alder reactions are now reported. The counterions of perchlorates and antimonates represent a highly effective catalytic system for enantioselective Diels−Alder reactions. Since optically active BINAP ligands are commercially available, the current catalytic Diels−Alder technology provides convenient access to either enantiomer of the cycloadduct with high optical purity and isolated yield. Further design of novel catalytic systems is the subject of ongoing research in our laboratory.

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Supporting Information Available: Experimental procedures and spectral data for the preparation of BINAP−metal complexes and Diels−Alder reaction protocols and ^1H NMR spectra for cycloadducts **2a**−**c**. This material is available free of charge via the Internet at http://pubs.acs.org..

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[10] The reactive species is presumably the cationic complex as proposed by Strukul, see: Baccin, C.; Gusso, A.; Pinna, F.; Strukul, G. *Organometallics* **1995**, *14*, 1161 and references therein.

[11] Pt−(*R*)-QUINAP−Sal complex (mp 219−221 °C; $[\alpha]^{23}_D$ +150.9, *c* 0.52, $CHCl_3$) was prepared by following the procedure of Pt−(*R*)-BINAP−Sal as described previously. See ref 9.

[12] $NiCl_2$[(*R*)-BINAP] complex (mp 243 − 247 °C; $[\alpha]^{23}_D$ +254.5, *c* 0.22, $CHCl_3$) was prepared by heating anhydrous $NiCl_2$ and (*R*)-BINAP in DMSO at 100 °C for 96 h.

[13] The $PdCl_2$−BINAP complex crystal structure has a distorted-square-planar geometry, see: Ozawa, F.; Kubo, A.; Matsumoto, Y.; Hayashi, T.; Nishioka, E.; Yanagi, K.; Moriguchi, K.-I. *Organometallics* **1993**, *12*, 4188.

[14] Loncharich, R. J.; Schwarz, T. R.; Houk, K. N. *J. Am. Chem. Soc.* **1987**, *109*, 14.