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P-Stereogenic PCP Pincer–Pd Complexes: Synthesis and Application in Asymmetric Addition of Diarylphosphines to Nitroalkenes

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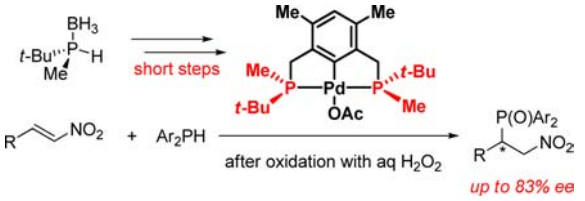
ABSTRACT



Novel P-stereogenic PCP pincer–Pd complexes were designed and prepared in short steps from optically pure *tert*-butylmethylphosphine-borane. These optically active Pd-complexes were successfully applied in asymmetric addition of diarylphosphines to nitroalkenes with high yields and good enantioselectivity.

Since the 1970s, tridentate pincer–metal complexes have attracted considerable attention due to their unique structural properties and reactivities.[1] The synthesis of chiral pincer–metal complexes and their applications in asymmetric catalysis have recently been reported.[2,3] Compared with N as the ligating atom,[2] the electron-rich P atom is not commonly found in chiral pincer–metal complexes due to their difficult synthesis and unsatisfactory stereocontrol.[3]

In contrast, over the past four decades, an enormous number of chiral bidentate phosphine ligands have been designed, synthesized, and applied in various transition-metal-catalyzed asymmetric reactions.[4] Among them, the P-stereogenic bisphosphine ligands possessing the smallest alkyl group (methyl group) and a bulky alkyl group (*tert*-butyl group) at each phosphorus atom have displayed excellent enantioselectivity and activity due to their efficient stereocontrol and electron-rich properties.[5] Furthermore, some of the above-mentioned ligands such as QuinoxP* and BenzP* can be synthesized via a simple route from optically pure *tert*-butylmethylphosphine–borane, which can be obtained on a kilogram scale.[5e,k,6] However, such a P-stereogenic phosphine group has not been used for the construction of chiral pincer ligands and their transition-metal complexes.[7]

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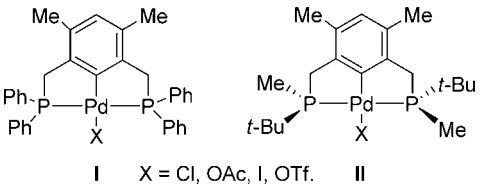
We previously developed a series of novel PCP pincer–Pd complexes **I** which were readily synthesized from diphenylphosphine oxide and successfully applied to chemoselective transfer hydrogenation.[8] We envisioned that the introduction of P-stereogenic *tert*-butylmethylphosphinyl group to such pincer scaffold would form highly strained two fused five-membered metallacycles. This conformational rigidity, in combination with the asymmetric environment and its electron-rich properties, might lead to high enantioselectivity and activity.

To extend our continuing research on PCP pincer–Pd complexes and P-stereogenic phosphine ligands, we have designed and synthesized novel P-stereogenic pincer–Pd complexes (**II** in Figure 1). On the other hand, Duan et al. extensively investigated PCP pincer–Pd-catalyzed asymmetric additions of diarylphosphines to electron-deficient alkenes or *N*-tosylimines, and they achieved very high to almost perfect enantioselectivities.[9] Among their reactions, we were especially interested in the addition reaction to nitroalkenes[9d] and employed it as the most suitable probing reaction to evaluate the catalytic efficiency and enantioinduction ability of **II**.



I X = Cl, OAc, I, OTf. II

Figure 1. Achiral pincer–Pd complexes and P-stereogenic pincer–Pd complexes.

The P-stereogenic pincer–Pd complex **4** was prepared from (*S*)-*tert*-butylmethylphosphine–borane **1**[6] in three high-yielding steps (Scheme 1). Deprotonation with *n*-butyllithium and subsequent nucleophilic substitution with 1,5-bis(chloromethyl)-2,4-dimethylbenzene afforded P-stereogenic phosphine–borane **2** as an air-stable white solid in 77% yield. The boranato groups were removed by the reaction with trifluoromethanesulfonic acid in toluene, followed by treatment with aqueous KOH in ethanol.[10] The resulting bisphosphine **3** was reacted with $PdCl_2(CH_3CN)_2$

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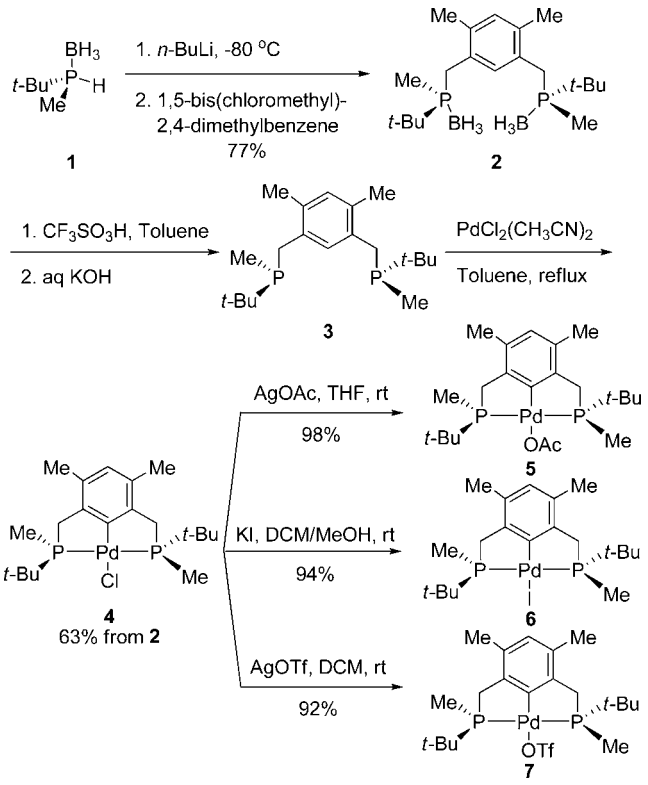
Scheme 1. Preparation of Pincer–Pd Complexes



via C–H bond activation to form the P-stereogenic pincer–Pd complex **4**. The total yield for the above two steps from **2** to **4** was 63%. The coordinating anion of **4** could be exchanged to give the corresponding P-stereogenic pincer–Pd complexes **5**, **6**, and **7** in yields of 98%, 94%, and 92%, respectively (Scheme 1).

The structure of pincer–Pd complex **4** was confirmed by single-crystal X-ray diffraction (Figure 2). The crystal structure indicates that there is a rigid and C_2-symmetric stereo environment around the Pd atom. The large difference between the small methyl group and bulky *tert*-butyl group would be expected to provide efficient stereocontrol for asymmetric catalysis.

The catalytic asymmetric 1,4-addition of diarylphosphines to α,β-unsaturated carbonyl compounds has been widely studied by using transition-metal complexes or organocatalysts.[11] However, nitroalkenes are rarely utilized as Michael acceptors of nucleophilic phosphines, though its asymmetric adducts are valuable precursors of pharmaceutically important compounds and potentially useful chiral P,N ligands or organocatalysts.[9d,11r] To evaluate the catalytic performance of our P-stereogenic

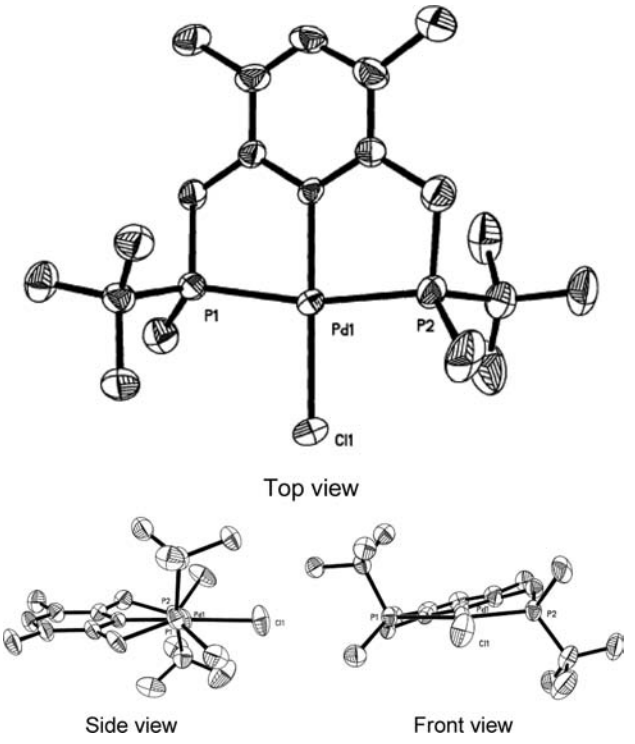


Figure 2. ORTEP drawing of P-stereogenic pincer–Pd complex **4**.

pincer–Pd complexes, we preliminarily applied them in asymmetric addition of diarylphosphines to nitroalkenes.

The P-stereogenic pincer–Pd complexes **4**–**7** were tested in a model reaction of *trans*-β-nitrostyrene with diphenylphosphine (Table 1). The reaction proceeded rapidly in various solvents at 25 °C when **5** was used as a catalyst (entries 1–7). DCM was found to be the optimal solvent to produce adduct **10a** in 96% yield and with 43% ee (entry 7). However, the other complexes **4**, **6**, and **7** provided the desired product with only 0–2% ee (entries 8–10), indicating the important role of the anionic ligand.

We next carried out the reaction to examine the effect of temperature on the reaction outcome using **5** as a catalyst

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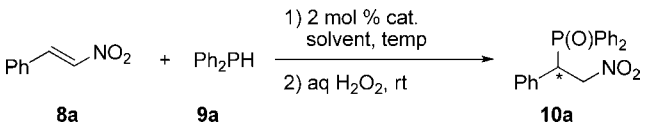
Table 1. Pd-Catalyzed Asymmetric Addition of Diphenylphosphine to *trans*-β-Nitrostyrene[a]



8a **9a** **10a**

entry	temp (°C)	solvent	time (min)	yield[b] (%)	ee[c] (%)
1	25	Et_2O	5	95	1
2	25	DCE	15	96	17
3	25	toluene	15	93	16
4	25	THF	15	94	10
5	25	CH_3CN	5	94	2
6	25	*s*-BuOH	5	92	15
7	25	DCM	15	96	43
8[d]	25	DCM	20	95	2
9[e]	25	DCM	10	95	0
10[f]	25	DCM	10	93	0
11	0	DCM	20	96	51
12	−20	DCM	30	96	60
13	−40	DCM	50	96	76
14	−50	DCM	60	96	73
15	−60	DCM	120	98	72

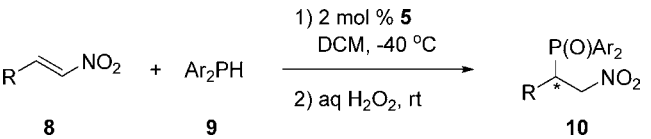
[a] Reaction conditions: **8a** (0.3 mmol), **9a** (1.05 equiv), **5** (2 mol %), solvent (3 mL). [b] Isolated yield. [c] Determined by HPLC Daicel ChiralPak IC-3 column with hexane/*i*-PrOH. [d] 2 mol % of **4** was used as the catalyst. [e] 2 mol % of **6** was used as the catalyst. [f] 2 mol % of **7** was used as the catalyst.

and DCM as solvent. The reaction was performed at different temperatures ranging from 0 to −60 °C (entries 11−15). Decreasing the temperature increased enantioselectivity, and running the reaction at −40 °C provided compound **10a** with the most promising results (96% yield and 76% ee) (entry 13).

With the optimized reaction conditions in hand, we next examined the reactions of various nitroalkenes (Table 2). Both electron-donating and electron-withdrawing aromatic substituted nitroalkenes reacted with diphenylphosphine to provide the desired products in high yields and with high enantioselectivities (entries 2−5, 92−96% yield, 72−83% ee). When substituents were moved from *para*- to *meta*- and *ortho*-positions, the enantioselectivities reduced from 83% to 23% and 43%, respectively (entries 6 and 7). For 2-naphthyl- and 2-thienyl-substituted nitroalkenes, the reactions also proceeded well to give products with ees of 76% and 69%, respectively (entries 8 and 9). Using the current system, an alkyl-substituted substrate gave the corresponding product in 93% yield with 34% ee (entry 10). In addition, it was found that bis(4-methoxyphenyl)-phosphine reacted smoothly with **8a**, providing the expected adduct in 90% yield but with low ee (entry 11). The use of bis(4-fluorophenyl)phosphine afforded the corresponding adduct in 88% yield and improved enantioselectivity (65%) (entry 12).

As a whole, the reactions proceeded smoothly to give the corresponding addition products in high yields, but the

Table 2. Pd-Catalyzed Asymmetric Addition of Diarylphosphines to Nitroalkenes[a]



8 **9** **10**

entry	**10**	R	Ar	time (h)	yield[b] (%)	ee[c] (%)
1	**10a**	Ph	Ph	0.8	96	76
2	**10b**	*p*-FC_6H_4	Ph	2	93	78
3	**10c**	*p*-ClC_6H_4	Ph	2	96	83
4	**10d**	*p*-BrC_6H_4	Ph	2	92	81
5	**10e**	*p*-$MeOC_6H_4$	Ph	2	92	72
6	**10f**	*m*-ClC_6H_4	Ph	2	95	23
7	**10g**	*o*-ClC_6H_4	Ph	6	93	43
8	**10h**	2-naphthyl	Ph	2.5	93	76
9	**10i**	2-thienyl	Ph	2	95	69
10	**10j**	cyclopropyl	Ph	40	93	34
11	**10k**	Ph	*p*-$MeOC_6H_4$	4	90	22
12	**10l**	Ph	*p*-FC_6H_4	3	88	65

[a] Reaction conditions: **8** (0.3 mmol), **9** (1.05 equiv), solvent (3 mL). [b] Isolated yield. [c] Determined by HPLC Daicel ChiralPak IC-3 or AD-H column with hexane/*i*-PrOH.

resulting enantioselectivities of up to 83% are less favorable compared with those (up to 94%) obtained by Duan and co-workers.[9d] The lower enantioselectivities are mainly ascribed to the different asymmetric environments formed by the respective PCP ligands (the ligand with *tert*-butylmethylphosphino groups vs the ligand with diphenylphosphino groups) and to the different reaction conditions such as the use of different solvents. Despite the observation of not very high enantioselectivities, these results indicate the potential utility of the new P-stereogenic PCP ligand in some other transition-metal-catalyzed asymmetric reactions.

In summary, we designed and readily synthesized novel P-stereogenic PCP pincer−Pd complexes. The potential utility of the complexes as chiral catalysts was demonstrated in the asymmetric addition of diarylphosphines to nitroalkenes.

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Supporting Information Available. General experimental procedures and characterization details. This material is available free of charge via the Internet at http://pubs.acs.org.

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