Journal of Organometallic Chemistry 696 (2012) 4309–4314

Contents lists available at SciVerse ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Preparation and application of air-stable *P,N*-bidentate ligands for the selective synthesis of δ-lactone via the palladium-catalyzed telomerization of 1,3-butadiene with carbon dioxide

Yao Dai, Xiujuan Feng*, Bin Wang, Ren He, Ming Bao**

State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian 116024, China

ARTICLE INFO

Article history:
Received 22 July 2011
Received in revised form
17 September 2011
Accepted 6 October 2011

Keywords:
Carbon dioxide
1,3-Butadiene
Palladium catalyst
P,N-Bidentate ligand
δ-Lactone

ABSTRACT

Air-stable *P,N*-bidentate ligands **L1**–**L7** with cyclic secondary amine moieties linked to the benzene rings of triphenylphosphine were designed and prepared. The chelating coordination mode of the *P,N*-bidentate ligands to the Pd(II) center was confirmed by determining the X-ray structures of the Pd(II) complexes **C1** and **C2** derived from ligands **L1** and **L2**, respectively. The ligands were used for the selective synthesis of δ-lactone through the palladium (Pd)-catalyzed telomerization of 1,3-butadiene with carbon dioxide. The highest yield (60% with 79% selectivity) was observed using the $Pd_2(dba)_3$/4-(2-(diphenylphosphino)phenyl)morpholine (**L2**) catalyst system.

1. Introduction

The selective synthesis of δ-lactone through the palladium (Pd)-catalyzed telomerization of 1,3-butadiene with carbon dioxide (CO_2) has attracted considerable attention (Scheme 1). Since its initial synthesis in 1978 by Musco's group [1], δ-lactone has gained interest because it could be transformed to various useful fine chemicals [2–7]. The Pd-catalyzed telomerization of 1,3-butadiene with CO_2 is the first successful example of the catalytic formation of a new C–C bond between CO_2 and an organic compound. Hence, this telomerization process has become an interesting and promising means of using CO_2 as a C1-builing block in synthetic organic chemistry. Electron-rich, sterically bulky phosphine ligands such as tricyclohexylphosphine (PCy_3), triisopropylphosphine (P^iPr_3), and the P,N-bidentate ligand $^iPr_2P–CH_2CH_2CH_2CH_2CH_2CH_2–CN$ favor the production of δ-lactone [8–12]. However, these bulky ligands are air-sensitive and too difficult to handle for use in laboratory research and industry production. Air-stable phosphine ligands are more desirable for large-scale δ-lactone synthesis.

Our group has continuously researched CO_2 chemistry [13–16]. In the present study, we designed and synthesized new types of *P,N*-bidentate ligands based on the air-stable triphenylphosphine (PPh_3) for the selective synthesis of δ-lactone (Scheme 2, **L1**–**L7**). The *ortho*-substituted cyclic secondary amino group on a benzene ring in triphenylphosphine is expected to increase the electron density of the phosphorus atom and the steric hindrance of the entire molecule. It is also expected that the newly formed sterically bulky *P,N*-bidentate ligands will hinder the formation of undesired product octadienyl ester **3** (Scheme 1) [8]. These ligands should accelerate the reductive elimination of intermediate **1** to produce δ-lactone **2** by their peculiar coordination properties [17,18]. The X-ray structures of the Pd(II) complexes **C1** and **C2** derived from ligands **L1** and **L2**, respectively, are also presented.

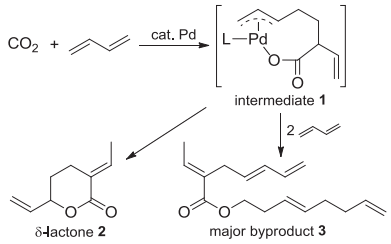
2. Results and discussion

2.1. Preparation and characterization of ligands *L1*–*L7*

The ligands **L1**–**L7** were prepared according to the synthetic routes schematically described in Scheme 3 and 4. The reaction of a Grignard reagent generated from 1-(2-bromophenyl)piperidine (BPPP) with diphenylphosphinous chloride (Ph_2PCl) proceeded smoothly to give ligand **L1** in satisfactory yield (66%), even although the Grignard reagent bore a relatively bulky substituent on *ortho* position (Scheme 3). When the Grignard reagent generated from 4-(2-bromophenyl)morpholine (BPMP) was treated with Ph_2PCl, dichlorophenylphosphine ($PhPCl_2$), and phosphorus tribromide

* Corresponding author. Tel.: +86 411 84986184; fax: +86 411 84986181.
** Corresponding author. Tel.: +86 411 84986180; fax: +86 411 84896181.
E-mail addresses: fengxiujuan@dlut.edu.cn (X. Feng), mingbao@dlut.edu.cn (M. Bao).

0022-328X/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2011.10.011



Scheme 1. Palladium-catalyzed telomerization of 1,3-butadiene with carbon dioxide.

(PBr_3), respectively, the desired ligands **L2**, **L6**, and **L7** were obtained in moderate yields (68%, 56%, and 51%, respectively; Scheme 3). Then the desired ligands **L3**–**L5** were synthesized through Pd-catalyzed C–N bond cross-coupling reaction (Buchwald–Hartwig cross-coupling reaction). The reaction of (2-bromophenyl)diphenylphosphine (BDPP) with piperazine was performed in the presence of catalytic amount of tris(dibenzylideneacetone)dipalladium [$Pd_2(dba)_3$] using **L7** as a ligand, which was prepared as described above. The ligand **L3** was obtained in 72% yield along with a debrominated product (PPh_3, 25%) (Scheme 4). However, the ligand **L4**, an analog of **L3**, was isolated in excellent yield (94%) from the reaction of BDPP with 1-methylpiperazine under the same reaction conditions (Scheme 4). The ligand **L5** was obtained in only 5% yield when the reaction of BDPP with 3,4-dihydro-2H-1,4-benzoxazine was carried out under the same reaction conditions as employed in the synthesis of ligands **L3** and **L4**. The yield of **L5** was increased to 44% by using (±)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl [(±)-BINAP] as a ligand (Scheme 4). All the new ligands **L1**–**L7** were identified through their NMR and HRMS data as well as IR spectra. Furthermore, the X-ray structure of ligand **L2** was determined as shown in Fig. 1 [19].

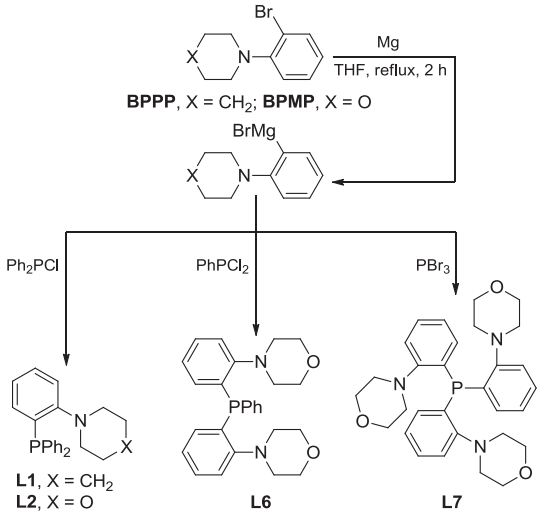
2.2. X-ray structures of Pd(II) complexes *C1* and *C2*

To confirm the chelating coordination manner of ligands **L1**–**L7**, the Pd complexes **C1** and **C2** were prepared by reacting of $PdCl_2(MeCN)_2$ with **L1** or **L2**. The X-ray structures of **C1** and **C2** are shown in Fig. 1 [20]. Clearly, the soft P and hard N atoms in **L1** or **L2** coordinated with the Pd(II) center to form a chelate complex. These results indicated that these ligands can be used as hemilabile ligands to promote the selective synthesis of δ-lactone **2**.

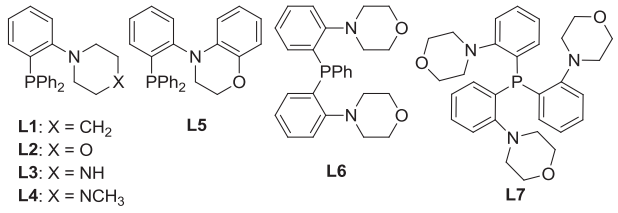
2.3. Pd-catalyzed telomerization of 1,3-butadiene with carbon dioxide

2.3.1. Ligand screening

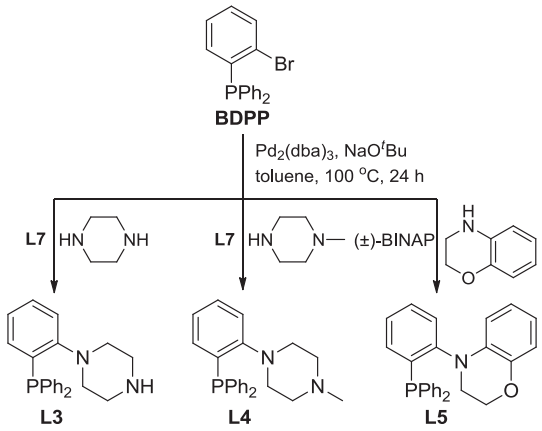
The effects of the newly formed *P,N*-bidentate ligands **L1**–**L7** on the selective synthesis of δ-lactone **2** were firstly examined. The selective synthesis involved the Pd-catalyzed telomerization of 1,3-butadiene with carbon dioxide using $Pd(acac)_2$ as the Pd source and acetonitrile (MeCN) as a solvent [8]. The results are shown in Table 1. Using **L1**, 72% conversion of 1,3-butadiene as well as 31% yield and 43% selectivity of δ-lactone **2** were achieved (entry 1). All these data were higher than those obtained using the parent ligand PPh_3 (entry 9). Using **L2**, increased yield and selectivity of **2** (43% and 66%, respectively) as well as slightly decreased conversion of 1,3-butadiene (65%) were achieved. With the exception of selectivity, these results were better than those obtained using PCy_3 (entry 10). Using **L3** and **L4** instead of **L2**, almost the same result for the conversion of 1,3-butadiene as **L2** was achieved (entries 3 and 4, 67%). However, the yield and selectivity of **2** decreased (**L3**: 34% yield with 51% selectivity; **L4**: 33% yield with 49% selectivity). Using **L5** led to poor results (22% yield of **2** with 37% selectivity, 60% conversion of 1,3-butadiene; entry 5). Using the more sterically bulky ligands **L6** and **L7** yielded only trace amounts of **2** (entries 6 and 7). In order to evaluate the effectiveness of cyclic amino groups in the P–N ligands, the ligand 2-(diphenylphosphino)-*N*,*N*-dimethylaniline [$(2\text{-}Me_2NC_6H_4)PPh_2$, **L8**] was synthesized [21] and used for the Pd-catalyzed telomerization of 1,3-butadiene with CO_2. The desired product δ-lactone **2** was obtained in only 11% yield with low selectivity, and the conversion of 1,3-butadiene was also not satisfactory (24% selectivity, 46% conversion; entry 8). These data were quite a bit lower than those obtained using **L1**–**L5** (entry 8 versus entries 1–5). Overall, **L2** was the most effective in promoting the selective synthesis of δ-lactone **2**. Therefore, **L2** was used in subsequent studies.



Scheme 3. Synthesis of the ligands **L1**, **L2**, **L6**, and **L7**.



Scheme 2. The structures of newly formed *P,N*-bidentate ligands.



Scheme 4. Synthesis of the ligands **L3**–**L5**.

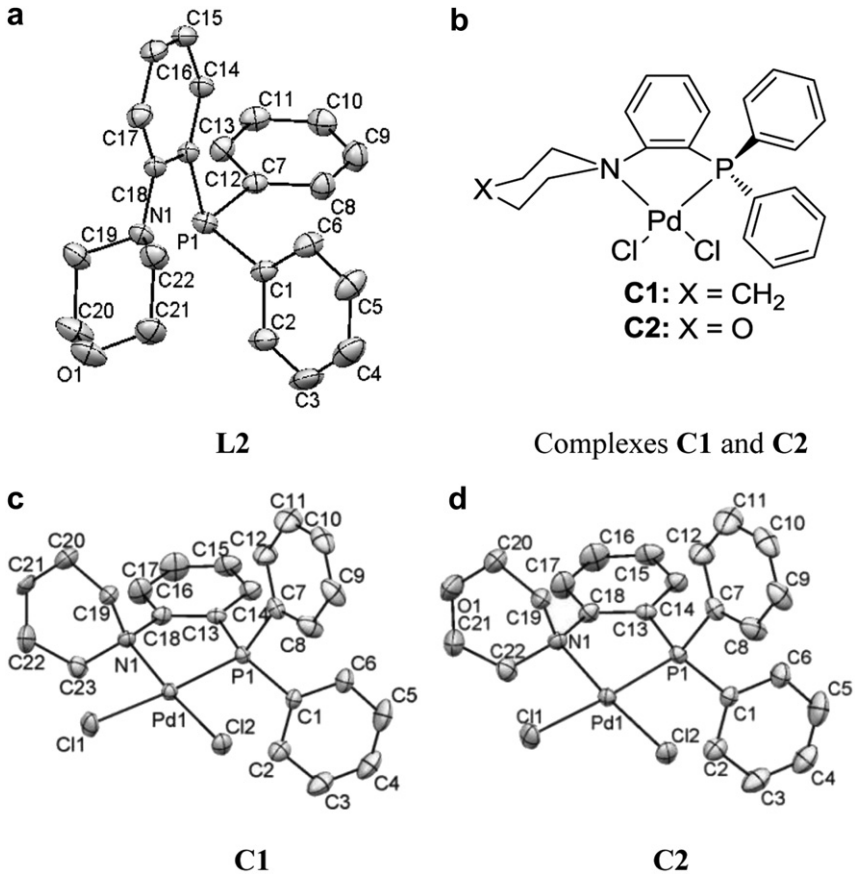
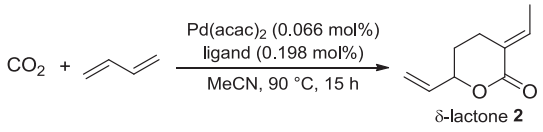


Fig. 1. Structures of ligand L2 (a), complexes C1 (c) and C2 (d) at 30% probability level. Hydrogen atoms are omitted for clarity.

2.3.2. Pd catalyst precursor screening for telomerization

Using **L2**, Pd catalyst precursors were screened for the selective synthesis of δ-lactone **2**. As shown in Table 2, Pd catalyst precursors significantly influenced the selective formation of **2**. Using $Pd(acac)_2$, which was also employed in section 2.3.1, yielded 43% of product **2** with 66% selectivity (entry 1). $Pd(OAc)_2$ showed inferior efficiency and yielded 30% of product **2** with 50% selectivity (entry 2). Using $Pd_2(dba)_3$ yielded 44% of product **2** with 68% selectivity (entry 3). These results were slightly higher than those observed using $Pd(acac)_2$. $Pd_2(dba)_3$ is a stable commercially available Pd^0 source, which could coordinate with **L2** to directly generate an active Pd species in situ.

Table 1
Ligands screening for the selective synthesis of **2**.[a]



Entry	Ligand	Conversion (%)	Yield (%)[b]	Selectivity (%)
1	**L1**	72	31	43
2	**L2**	65	43	66
3	**L3**	67	34	51
4	**L4**	67	33	49
5	**L5**	60	22	37
6	**L6**	50	trace	trace
7	**L7**	10	trace	trace
8	**L8**	46	11	24
9	PPh_3	64	14	23
10	PCy_3	45	37	82

[a] Reaction conditions: 0.066 mol% $Pd(acac)_2$ (10.0 mg), 0.198 mol% ligand (0.099 mmol), 2.70 g 1,3-butadiene (50 mmol), 2.45 g carbon dioxide (56 mmol), 5 mL MeCN, 90 °C, 15 h; all reactions were carried out in 25 mL autoclave.
[b] Isolated yield based on 1,3-butadiene.

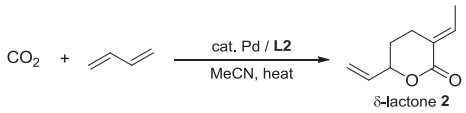
2.3.3. Effects of reaction temperature on telomerization

The catalyst system $Pd_2(dba)_3$/**L2** was chosen for reaction temperature optimization. Table 2 shows that the conversion of 1,3-butadiene increases with rising temperature (entries 3–8; temperature: from 50 °C to 100 °C; conversion: from 44% to 70%). This observation was consistent with the previous report [22]. The yield and selectivity of **2** were also increased with rising temperature within the range of 50–70 °C (entries 4–6; yield: from 29% to 50%; conversion: from 44% to 61%). When the reaction of CO_2 with 1,3-butadiene was performed at 80 °C, almost the same results were obtained as those obtained at 70 °C (entry 7). But the yield and selectivity of **2** decreased when the reaction temperature was higher than 80 °C (entries 3 and 8). The decreasing δ-lactone-formation was considered that due to its high temperature instability [22].

2.3.4. Effects of reaction time on telomerization

The next optimization step involved varying the reaction time, as detailed in Table 2. The conversion of 1,3-butadiene and the yield of **2** both increased with prolonging reaction time within the range of 10–25 h (entries 6, 9–11; yield: from 44% to 60%; conversion: from 56% to 76%). The selectivity is almost constant within the time range as mentioned above. With the exception of conversion,

Table 2
Optimization of reaction conditions for the selective synthesis of **2**.[a]



Entry	Pd source	T (°C)	Time (h)	Conversion (%)	Yield (%)[b]	Selectivity (%)
1	$Pd(acac)_2$	90	15	65	43	66
2	$Pd(OAc)_2$	90	15	60	30	50
3	$Pd_2(dba)_3$	90	15	65	44	68
4	$Pd_2(dba)_3$	50	15	44	29	66
5	$Pd_2(dba)_3$	60	15	57	44	77
6	$Pd_2(dba)_3$	70	15	61	50	82
7	$Pd_2(dba)_3$	80	15	63	51	81
8	$Pd_2(dba)_3$	100	15	70	33	47
9	$Pd_2(dba)_3$	70	10	56	44	79
10	$Pd_2(dba)_3$	70	20	70	54	77
11	$Pd_2(dba)_3$	70	25	76	60	79
12	$Pd_2(dba)_3$	70	30	82	59	72
13[c]	$Pd_2(dba)_3$	70	25	67	50	75
14[d]	$Pd_2(dba)_3$	70	25	55	37	67
15[e]	$Pd_2(dba)_3$	70	25	49	26	53

[a] Reaction conditions: 0.066 mol% $Pd(acac)_2$ (10.0 mg), 0.066 mol% $Pd(OAc)_2$ (7.4 mg), 0.033 mol% $Pd_2(dba)_3$ (15.1 mg), 0.198 mol% **L2** (34.4 mg), 2.70 g 1,3-butadiene (50 mmol), 2.45 g carbon dioxide (56 mmol), 5 mL MeCN; all reactions were carried out in 25 mL autoclave unless otherwise noted.
[b] Isolated yield based on 1,3-butadiene.
[c] 0.017 mol% $Pd_2(dba)_3$ (7.6 mg) and 0.099 mol% **L2** (17.4 mg) were used.
[d] A mixture of 0.008 mol% $Pd_2(dba)_3$ (11.4 mg), 0.048 mol% **L2** (25.0 mg), 8.10 g 1,3-butadiene (150 mmol), 7.40 g carbon dioxide (168 mmol), and 15 mL MeCN was treated in 75 mL autoclave.
[e] A mixture of 0.004 mol% $Pd_2(dba)_3$ (14.3 mg), 0.024 mol% **L2** (33.4 mg), 21.60 g 1,3-butadiene (400 mmol), 19.70 g carbon dioxide (448 mmol), and 40 mL MeCN was treated in 200 mL autoclave.

slightly decreased yield and selectivity were observed when the reaction of CO_2 with 1,3-butadiene was carried out under the same reaction conditions for a prolonged time (30 h, entry 12). Comparatively better results were obtained when the reaction time was 25 h (entry 11).

2.3.5. Effects of $Pd_2(dba)_3$ loading on telomerization

The effects of $Pd_2(dba)_3$ loading on the telomerization reaction of CO_2 with 1,3-butadiene was investigated using **L2**. The results are shown in Table 2. The $Pd_2(dba)_3$/**L2** catalyst system exhibited a high activity for the selective synthesis of δ-lactone **2**. Even when $Pd_2(dba)_3$ loading was decreased to 0.004 mol%, relatively better results were still obtained (entry 15; 26% yield of **2** with 53% selectivity; 49% conversion of 1,3-butadiene; turnover number, TON of 1560). The yield and selectivity of **2** as well as the conversion of 1,3-butadiene all decreased with decreased $Pd_2(dba)_3$ loading (entries 11, 13–15).

3. Conclusion

Air-stable hemilabile ligands **L1**–**L7** containing soft phosphorus and hard nitrogen atoms were prepared and were applied in the selective synthesis of δ-lactone **2**. Among these ligands, **L2** exhibited the best results (60% yield of **2** with 79% selectivity; 76% conversion of 1,3-butadiene). These results are comparable with those obtained using PCy_3 as a ligand. Our method is the first successful selective synthesis of δ-lactone **2** via the Pd-catalyzed telomerization of CO_2 with 1,3-butadiene using a triarylphosphine ligand. The X-ray structures of the Pd complexes **C1** and **C2** clearly showed the chelating coordination mode of the *P,N*-bidentate ligands to the Pd(II) center. Our group is now studying the grafting of **L2** onto an SBA-15 mesoporous membrane for a continuous process.

4. Experimental section

4.1. Reagents and materials

Acetonitrile (MeCN) was dried by refluxing with CaH_2 and was distilled under nitrogen (N_2) before use. 1-(2-Bromophenyl)piperidine (BPPP), 4-(2-bromophenyl)morpholine (BPMP), (2-bromophenyl)diphenylphosphine (BDPP), $PdCl_2(MeCN)_2$, $Pd(acac)_2$, and 3,4-dihydro-2H-1,4-benzoxazine were prepared according to previous reports [23–27]. Tris(dibenzylideneacetone) dipalladium ($Pd_2(dba)_3$; 98.5%) was purchased from the Shanghai Zealandchem Co., Ltd., China. Pd diacetate ($Pd(OAc)_2$; trimer, 99.5%) was purchased from the Tianjin Jinbolan Fine Chemical Co., Ltd., China. Tricyclohexylphosphine (PCy_3; 96%) was purchased from the Alfa Aesar China Co., Ltd. (Tianjin). Triphenylphosphine (PPh_3; 99.7%) was purchased from the Tianjin Kermel Chemical Reagent Co., Ltd., China. (±)-2,2′-Bis(diphenylphosphino)-1,1′-binaphthyl [(±)-BINAP; 98%] was purchased form J&K Chemical Ltd., China (Beijing). Phosphorus tribromide (PBr_3; 98.5%) was purchased from the Sinopharm Chemical Reagent Co., Ltd. (SCRC), China. Dichlorophenylphosphine ($PhPCl_2$; 98%) and diphenylphosphinous chloride (Ph_2PCl; 97%) were purchased from Aladdin Reagent Database Inc., China (Shanghai). Piperazine (99.5%), and 1-methylpiperazine (99.8%) were all purchased from the SCRC. Sodium tert-butoxide (NaO^tBu; 99%) was purchased from the Zibo Fuxi'er Chemical Co., Ltd., China. Silica gel (200–300 mesh) was purchased from the Qingdao Makall Group Co., Ltd., China. 1,3-Butadiene (99%) and CO_2 (99.99%) were purchased from the Dalian Date Gas Co. Ltd., China. N_2 (99.999%) was purchased from the Dalian Guangming Special Gas Products Co., Ltd., China. All other reagents were analytical grade and were used without further purification.

4.2. Characterization

^1H, ^{13}C, and ^{31}P nuclear magnetic resonance spectra were recorded in a $CDCl_3$ solution on a Bruker DPX-400 spectrometer (400 MHz for ^1H, 101 MHz for ^{13}C, and 162 MHz for ^{31}P). Chemical shifts (δ) were given relative to residual solvent signals for ^1H and ^{13}C. H_3PO_4 (85%) was used as the external standard for ^{31}P. Infrared (IR) spectra were recorded on a Perkin–Elmer FTIR 430 spectrometer. High-resolution mass spectra were recorded on a Micromass GC-TOF EI-MS spectrometer. Elemental analyses were recorded on an Elemental Vario EL-III elemental analyzer. Melting points were determined using an X-6 micro-melting point apparatus and were uncorrected.

4.3. Synthesis of ligands *L1*, *L2*, *L6*, and *L7*

4.3.1. 1-(2-(Diphenylphosphino)phenyl)piperidine (*L1*)

A solution of Grignard reagent was prepared from BPPP (2.64 g, 11 mmol) and magnesium powder (268 mg, 11 mmol) in THF (10 mL). A solution of Ph_2PCl (2.21 g, 10 mmol) in THF (5 mL) was then added dropwise at room temperature, and the mixture was stirred for 1 h. After the reaction mixture was further stirred at 80 °C for 2 h, excess saturated NH_4Cl aqueous solution was added at room temperature. The product was extracted with ether (20 mL × 3) and dried over Na_2SO_4. The solvent was then evaporated in vacuo and the remaining solid was recrystallized by ethanol to give **L1** as a white crystal (2.28 g, 66% yield).

^1H NMR (400 MHz, $CDCl_3$) δ 7.32–7.28 (m, 11H), 7.15–7.12 (m, 1H), 7.00 (t, J = 7.4 Hz, 1H), 6.71–6.68 (m, 1H), 2.76–2.75 (m, 4H), 1.36–1.34 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 157.4, 157.2, 138.5,

138.4, 136.8, 136.7, 134.1, 133.9, 133.0, 129.6, 128.33, 128.30, 128.2, 124.8, 121.6, 121.6, 54.1, 26.1, 24.2.; ^{31}P NMR (162 MHz, $CDCl_3$): δ −11.23; IR (KBr) 3051, 2938, 2850, 2797, 1579, 1466, 1433, 1224, 922, 765, 740, 696 cm^{-1}; HRMS (EI) calcd. for $C_{23}H_{24}NP$: 345.1646 $[M]^+$; found: 345.1652; m.p.: 96–98 °C.

4.3.2. 4-(2-(Diphenylphosphino)phenyl)morpholine (**L2**)

L2 was prepared similarly as **L1** using BPMP (2.66 g, 11 mmol) as a starting material (**L2**: 2.36 g, 68% yield, white crystal).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.30 (m, 11H), 7.17–7.14 (m, 1H), 7.03 (t, J = 7.5 Hz, 1H), 6.75–6.72 (m, 1H), 3.48 (t, J = 4.2 Hz, 4H), 2.80 (t, J = 4.5 Hz, 4H).; ^{13}C NMR (101 MHz, $CDCl_3$): δ 155.4, 155.3, 138.0, 137.9, 136.94, 136.86, 134.2, 134.0, 133.2, 129.8, 128.6, 128.4, 128.3, 125.5, 121.8, 121.7, 67.2, 52.8, 52.8.; ^{31}P NMR (162 MHz, $CDCl_3$) δ −3.97; IR (KBr) 3052, 2956, 2853, 2814, 1580, 1466, 1433, 1219, 1113, 932, 767, 742, 697 cm^{-1}; HRMS (EI) calcd. for $C_{22}H_{22}NOP$: 347.1439 $[M]^+$; found: 347.1440; m.p.: 116–118 °C.

4.3.3. 4,4′-((Phenylphosphinediyl)bis(2,1-phenylene))dimorpholine (**L6**)

L6 was prepared similarly as **L2** using BPMP (5.32 g, 22 mmol) as a starting material (**L6**: 2.42 g, 56% yield, white crystal).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.31 (m, 7H), 7.17–7.14 (m, 2H), 7.00 (t, J = 7.4 Hz, 2H), 6.70 (d, J = 7.4 Hz, 2H), 3.59–3.52 (m, 8H), 2.92–2.89 (m, 4H), 2.85–2.82 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 155.7, 155.5, 138.8, 138.7, 137.1, 137.0, 134.6, 134.4, 133.6, 129.5, 128.4, 128.3, 128.2, 125.0, 121.1, 67.3, 53.0, 52.9; ^{31}P NMR (162 MHz, $CDCl_3$): δ −19.69; IR (KBr) 3347, 3053, 2957, 2853, 2814, 1580, 1466, 1445, 1371, 1263, 1219, 1113, 932, 919, 847, 768, 735, 699 cm^{-1}; HRMS (EI) calcd. for $C_{26}H_{29}N_2O_2P$: 432.1967 $[M]^+$; found: 432.1973; m.p.: 153–154 °C.

4.3.4. Tris(2-morpholinophenyl)phosphine (**L7**)

L7 was prepared similarly as **L2** using BPMP (7.98 g, 33 mmol) as a starting material (**L7**: 2.64 g, 51% yield, white crystal).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.28 (m, 3H), 7.15–7.12 (m, 3H), 6.98–6.94 (m, 3H), 6.71–6.68 (m, 3H), 3.61 (s, 12H), 3.15 (s, 6H), 2.69 (s, 6H).; ^{13}C NMR (101 MHz, $CDCl_3$): δ 156.1, 155.9, 137.0, 136.9, 134.3, 129.4, 124.8, 120.43, 120.41, 67.4, 53.1.; ^{31}P NMR (162 MHz, $CDCl_3$): δ −19.69; IR (KBr) 3051, 2956, 2851, 2812, 1580, 1466, 1444, 1370, 1295, 1253, 1220, 1113, 932, 919, 846, 768, 735 cm^{-1}; HRMS (EI) calcd. for $C_{30}H_{36}N_3O_3P$: 517.2494 $[M]^+$; found: 517.2495; m.p.: 242–244 °C.

4.4. Synthesis of ligands **L3**–**L5**

4.4.1. 1-(2-(Diphenylphosphino)phenyl)piperazine (**L3**)

BDPP (341 mg, 1 mmol), NaO^{t}Bu (114 mg, 1.5 mmol), piperazine (129 mg, 1.5 mmol), $Pd_2(dba)_3$ (9 mg, 0.01 mmol), **L7** (31 mg, 0.06 mmol), and toluene (2.5 mL) were mixed in a Schlenk reactor. After the reaction mixture was placed in a pre-heated oil bath at 100 °C for 24 h, H_2O (20 mL) was added at room temperature. The product was extracted with ether (10 mL × 3) and was dried over Na_2SO_4. The solvent was evaporated in vacuo. The remaining solid was purified by chromatography (5:100 methanol/dichloromethane) to give **L3** (249 mg, 72% yield) as a yellow crystal along with a debrominated product (PPh_3, 25%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.28 (m, 11H), 7.18–7.15 (m, 1H), 7.04 (t, J = 7.5 Hz, 1H), 6.72–6.69 (m, 1H), 2.82 (t, J = 4.5 Hz, 4H), 2.69–2.68 (m, 4H).; ^{13}C NMR (101 MHz, $CDCl_3$): δ 156.0, 155.8, 138.1, 138.0, 136.84, 136.76, 134.1, 133.9, 133.0, 129.7, 128.5, 128.4, 128.3, 125.3, 121.8, 53.4, 45.9.; ^{31}P NMR (162 MHz, $CDCl_3$): δ −11.72; IR (KBr) 3281, 3052, 2942, 2817, 1580, 1466, 1434, 1371, 1219, 1316, 1220, 937, 909, 767, 739, 742, 697 cm^{-1}; HRMS (EI) calcd. for $C_{22}H_{23}N_2P$: 346.1599 $[M]^+$; found: 346.1610; m.p.: 98–100 °C.

4.4.2. 1-(2-(Diphenylphosphino)phenyl)-4-methylpiperazine (**L4**)

L4 was prepared similarly as **L3** using 1-methylpiperazine (150 mg, 1.5 mmol) as a starting material (**L4**: 339 mg, 94% yield, yellow crystal).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.28 (m, 11H), 7.20–7.17 (m, 1H), 7.03 (t, J = 7.4 Hz, 1H), 6.73–6.70 (m, 1H), 2.87 (t, J = 4.6 Hz, 4H), 2.46–2.01 (m, 7H).; ^{13}C NMR (101 MHz, $CDCl_3$): δ 155.8, 155.6, 138.2, 138.1, 136.8, 136.7, 134.2, 134.0, 133.2, 129.8, 128.5, 128.43, 128.35, 125.4, 121.9, 55.2, 52.3, 46.1.; ^{31}P NMR (162 MHz, $CDCl_3$): δ −12.01; IR (KBr) 3052, 2936, 2795, 1579, 1466, 1434, 1369, 1287, 1226, 1146, 1009, 927, 909, 768, 740, 742, 697 cm^{-1}; HRMS (EI) calcd. for $C_{23}H_{25}N_2P$: 360.1755 $[M]^+$; found: 360.1750, m.p.: 106–107 °C.

4.4.3. 4-(2-(Diphenylphosphino)phenyl)-3,4-dihydro-2H-benzo[b][1,4]oxazine (**L5**)

L5 was prepared similarly as **L3** using 3,4-dihydro-2H-1,4-benzoxazine (203 mg, 1.5 mmol) as a starting material and (±)-BINAP (37 mg, 0.06 mmol) as a ligand. The crude product was purified by chromatography (5:100 ethyl acetate/petroleum ether) to give **L5** (172 mg, 44% yield) as a white crystal, and 36% of starting material BDPP was recovered.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.21 (m, 13H), 6.98–6.96 (m, 1H), 6.78–6.76 (m, 1H), 6.65–6.56 (m, 2H), 6.14–6.13 (m, 1H), 4.07 (d, J = 10.7 Hz, 1H), 3.97 (t, J = 9.7 Hz, 1H), 3.53–3.48 (m, 1H), 3.06 (d, J = 11.1 Hz, 1H).; ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.2, 150.0, 144.3, 139.4, 139.3, 137.1, 137.0, 136.7, 136.5, 134.6, 134.3, 134.0, 130.7, 128.9, 128.7, 128.6, 128.5, 128.4, 128.0, 127.4, 120.9, 119.0, 116.3, 115.7, 64.5, 49.0.; ^{31}P NMR (162 MHz, $CDCl_3$): δ −13.95; IR (KBr) 3053, 2977, 2841, 1604, 1582, 1497, 1463, 1434, 1314, 1242, 1057, 909, 795, 767, 740, 697 cm^{-1}; HRMS (EI) calcd. for $C_{26}H_{22}NOP$: 395.1439 $[M]^+$; found: 395.1449; m.p.: 130–131 °C.

4.5. Synthesis of the Pd(II) complexes **C1** and **C2**

4.5.1. 1-(2-(Diphenylphosphino)phenyl)piperidine Pd(II) dichloride (**C1**)

L1 (173 mg, 0.5 mmol), $PdCl_2(MeCN)_2$ (130 mg, 0.5 mmol), and $CHCl_3$ (5 mL) were mixed in a Schlenk reactor at room temperature. The reaction mixture was stirred for 1 h, filtered, and evaporated in vacuo. The residue obtained was washed with ethanol to give **C1** (237 mg, 91% yield) as a yellow powder.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19–8.15 (m, 1H), 7.82–7.77 (m, 4H), 7.65–7.56 (m, 3H), 7.49–7.35 (m, 6H), 5.52–5.45 (m, 2H), 3.34 (d, J = 13.2 Hz, 2H), 2.17–2.01 (m, 4H),1.70 (d, J = 13.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 160.4, 160.3, 134.7, 133.9, 133.8, 133.6, 132.3, 130.1, 129.6, 129.4, 129.2, 129.1, 128.2, 127.6, 126.2, 126.1, 60.7, 22.7, 21.1.; ^{31}P NMR (162 MHz, $CDCl_3$): δ 39.82; IR (KBr) 3447, 3056, 2940, 2877, 2797, 1579, 1477, 1464, 1435, 1101, 911, 729, 690 cm^{-1}; Anal. calcd. for $C_{23}H_{24}Cl_2NPPd$: C, 52.85; H, 4.63; N, 2.68. Found: C, 51.95; H, 4.68; N, 2.40; m.p.: 204 °C, decomposed.

4.5.2. 4-(2-(Diphenylphosphino)phenyl)morpholine Pd(II) dichloride (**C2**)

C2 was prepared similarly as **C1** using **L2** (174 mg, 0.5 mmol) as a ligand instead of **L1** (**C2**: 245 mg, 94% yield, yellow powder).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21–8.18 (m, 1H), 7.82–7.76 (m, 4H), 7.71–7.69 (m, 1H), 7.61–7.57 (m, 2H), 7.50–7.46 (m, 4H), 7.44–7.37 (m, 2H), 5.36–5.31 (m, 2H), 4.30–4.26 (m, 2H), 4.02–3.97 (m, 2H), 3.40–3.37 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 160.1, 156.0, 134.4, 133.8, 133.7, 132.5, 129.5, 129.4, 129.3, 129.2, 129.0, 127.8, 127.1, 126.6, 126.5, 61.9, 59.5.; ^{31}P NMR (162 MHz, $CDCl_3$): δ 38.65; IR (KBr) 3056, 2956, 2883, 1579, 1480, 1436, 1102, 910, 727, 690 cm^{-1}; Anal. calcd. for $C_{22}H_{22}Cl_2NOPPd$: C, 50.36; H,

4.23; N, 2.67. Found: C, 50.47; H, 4.30; N, 2.47; m.p.: 224 °C, decomposed.

4.6. Crystal structure determination

Crystal data were collected using a Bruker Smart APEX CCD area detector diffractometer (graphite-monochromated Mo Kα radiation, $\lambda = 0.71073$ Å) at 273 K. The frame data were integrated with the program SAINT. The structure was determined by direct methods using the program SHELXS-97 [28]. Structure refinement by full-matrix least-squares on F^2 was carried out using the program SHELXL-97 [28]. Anisotropic displacement parameters were assigned to all the non-hydrogen atoms of the complex. Hydrogen atoms were inserted into idealized positions and were refined by riding with the atoms to which they were bonded.

4.7. Typical procedure for synthesis of **2** using Pd-catalyzed telomerization of 1,3-butadiene with CO_2

$Pd_2(dba)_3$ (15.1 mg, 0.016 mmol, 0.033 mol%) and **L2** (34.4 mg, 0.099 mmol, 0.198 mol%) were placed in a 25 mL autoclave. The sealed autoclave was purged with N_2 three times. MeCN (5 mL), 1,3-butadiene (2.70 g, 50 mmol), and CO_2 (2.45 g, 56 mmol) were then charged into the autoclave at −20 °C. The autoclave was placed in a 70 °C oil bath and was maintained constant for 25 h. Upon completion of the desired reaction time, the autoclave was half-submerged in a mixed ice/water bath. When the autoclave was cooled to room temperature, the remaining gas was vented into a measuring equipment to determine the conversion of 1,3-butadiene. The remaining liquid in the autoclave was then evaporated in vacuo to give the crude product. The crude product was purified by silica gel chromatography (20:100 ethyl acetate/petroleum ether) to give **2** (2.27 g, 60%) as a light yellow oil. The yields of **2** as well as the amounts of Pd precursors and phosphine ligands were all calculated based on 1,3-butadiene.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18–7.13 (m, 1H), 5.99–5.72 (m, 1H), 5.37 (d, $J = 17.2$ Hz, 1H), 5.25 (d, $J = 10.6$ Hz, 1H), 4.79 (s, 1H), 2.63–2.45 (m, 2H), 2.14–1.99 (m, 1H), 1.83–1.76 (m, 4H); ^{13}C NMR (101 MHz,) δ 166.3, 141.3, 135.8, 125.9, 117.0, 79.0, 27.7, 22.0, 14.2; IR (KBr) 2924, 2854, 1713, 1636, 1379, 1257, 1209, 1147, 1066, 988, 723 cm^{-1}; HRMS (EI) calcd. for $C_9H_{12}O_2$: 152.0837 $[M]^+$; found: 152.0840 [9].

Acknowledgments

We are grateful to the National Natural Science Foundation of China (21073025) for financial support. This work was partly supported by China Postdoctoral Science Foundation (20100471433) and the Fundamental Research Funds for the Central Universities (DUT10LK06).

Appendix A. Supplementary material

X-ray crystal data for ligand **L2** as well as complexes **C1**and **C2**, and ^{1}H, ^{13}C as well as ^{31}P NMR spectra for all new products. This material can be found in the online version, at doi:10.1016/j.jorganchem.

Appendix. Supplementary material

Supplementary material related to this article can be found online at doi:10.1016/j.jorganchem.2011.10.011. These data include MOL files and InChiKeys of the most important compounds described in this article.

References

[1] A. Musco, C. Perego, V. Tartiari, Inorg. Chim. Acta 28 (1978) L147–L148.
[2] V. Haack, E. Dinjus, S. Pitter, Angew. Makromol. Chem. 257 (1998) 19–22.
[3] A. Behr, V.A. Brehme, J. Mol. Catal. A: Chem. 187 (2002) 69–80.
[4] A. Behr, V.A. Brehme, Adv. Synth. Catal. 344 (2002) 525–532.
[5] A. Behr, M. Urschey, V.A. Brehme, Green Chem. 5 (2003) 198–204.
[6] A. Behr, G. Henze, L. Johnen, S. Reyer, J. Mol. Catal. A: Chem. 287 (2008) 95–101.
[7] A. Behr, G. Henze, Green Chem. 13 (2011) 25–39.
[8] A. Behr, K.D. Juszak, J. Organometall. Chem. 255 (1983) 263–268.
[9] A. Behr, K.D. Juszak, W. Keim, Synthesis (1983) 574.
[10] A. Behr, R. He, K.D. Juszak, C. Krüger, Y.H. Tsay, Chem. Ber. 119 (1986) 991–1015.
[11] S. Pitter, E. Dinjus, J. Mol. Catal. A: Chem. 125 (1997) 39–45.
[12] K. Buchmüller, N. Dahmen, E. Dinjus, D. Neumann, B. Powietzka, S. Pitter, J. Schön, Green Chem. 5 (2003) 218–223.
[13] X.J. Feng, X.B. Lu, R. He, Appl. Catal. A 272 (2004) 347–352.
[14] X.J. Feng, X.G. Li, R. He, H. Zhou, Chin. Chem. Lett. 16 (2005) 767–770.
[15] X.J. Feng, M. Yan, T. Zhang, Y. Liu, M. Bao, Green Chem. 12 (2010) 1758–1766.
[16] X.J. Feng, M. Yan, X. Zhang, M. Bao, Chin. Chem. Lett. 22 (2011) 643–646.
[17] C.S. Slone, D.A. Weinberger, C.A. Mirkin, Prog. Inorg. Chem. 48 (1999) 233–350.
[18] P. Braunstein, F. Naud, Angew. Chem. Int. Ed. 40 (2001) 680–699.
[19] The crystal data of **L2** has been deposited at Cambridge Crystallographic Data Center on Mar. 11, 2010 (CCDC No. 769048), which can be obtained free of charge from the Cambridge Crystallographic Data Centre through www.ccdc.cam.ac.uk/data_request/cif. While the present paper was in preparation, K.D. Hesp et al. reported the same structure of ligand **L2** for the palladium-catalyzed α-arylation of acetone with electron-deficient 4-bromobenzonitrile K.D. Hesp, R.J. Lundgren, M. Stradiotto, J. Am. Chem. Soc. 133 (2011) 5194–5197.
[20] The crystal data of **C1** and **C2** has been deposited at Cambridge Crystallographic Data Center on Sep. 28, 2010 (CCDC No. 794754, 794753), which can be obtained free of charge from the Cambridge Crystallographic Data Centre through www.ccdc.cam.ac.uk/data_request/cif.
[21] H.P. Fritz, I.R. Gordon, K.E. Schwarzhans, L.M. Venanzi, J. Chem. Soc. (1965) 5210–5216.
[22] A. Behr, P. Bahke, B. Klinger, M. Becker, J. Mol. Catal. A: Chem. 267 (2007) 149–156.
[23] W. Verboom, D.N. Reinhoudt, R. Visser, S. Harkema, J. Org. Chem. 49 (1984) 269–276.
[24] M.T. Whited, E. Rivard, J.C. Peters, Chem. Commun. (2006) 1613–1615.
[25] C.J. Mathews, P.J. Smith, T. Welton, J. Mol. Catal. A: Chem. 206 (2003) 77–82.
[26] G. Künstle, H. Siegel, Verfahren zur Herstellung von palladium(II)acetylacetonat DE2402383 (1975).
[27] P. Mizar, B. Myrboh, Tetrahedron Lett. 47 (2006) 7823–7826.
[28] G.M. Sheldrick, SHELX97: Program System for Crystal Structure Determination. University of Göttingen, Germany, 1997.