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Bis(NHC)–Pd(II) complexes as highly efficient catalysts for allylation of aldehydes with allyltributyltin

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Abstract

Novel cis-chelated bidentate bis(NHC)–Pd(II) complexes derived from 1,1′-binaphthyl-2,2′-diamine (BINAM) bearing weakly coordinating acetate or trifluoroacetate counterions have been synthesized and their structures have been characterized by X-ray diffraction of single crystals. We found that these bis(NHC)–Pd(II) complexes were highly effective in the allylation of aldehydes with allyltributyltin to give the corresponding products in good to excellent yields in most cases at room temperature.

Keywords: cis-Chelated bidentate bis(NHC)–Pd(II) complex; Weakly coordinating counterions; 1,1′-Binaphthyl-2,2′-diamine; Electrophilic attack; Allylation; Allyltributyltin

1. Introduction

Since the isolation and characterization of the stable free *N*-heterocyclic carbene (NHC) by Arduengo and co-workers in 1991,[1] much attention has been paid toward their properties and applications. During the past 12 years, numerous publications related to their metal complexes and catalytic reactions have been reported in a broad range of reactions.[2] NHC ligands can generally replace phosphine ligands in transition metal catalysis to provide more effective metal complexes due to their stability to air and moisture and their strong σ-donor and poor π-acceptor properties.[2i,3a] Significantly, a number of NHC–Pd complexes have emerged as effective catalysts for a variety of coupling reactions.[4] Previously, we reported the synthesis of a cis-chelated bidentate bis(NHC)–Pd(II) complex **1** derived from 1,1′-binaphthyl-2,2′-diamine (BINAM) and a new dimeric bidentate NHC–Pd(II) complex from *trans*-cyclohexane-1,2-diamine and their applications in the Suzuki reaction and Heck reaction.[5] Recently, it has been reported that replacing phosphine ligands with NHC ligands decreases the electrophilicity of the allylpalladium complex, and slows down the rate of attack by nucleophiles. However, the electrophilic attack to the active allylpalladium species can be facilitated.[6] In this paper, we wish to report the synthesis of cis-chelated bidentate bis(NHC)–Pd(II) complexes **2** and **3**, which bear weakly coordinating counterions such as acetate and trifluoroacetate, and their applications in the allylation of aldehydes with allyltributyltin under mild conditions (Fig. 1).[7,8]

2. Results and discussion

2.1. Synthesis and characterization

Complexes **2** and **3** were synthesized by treatment of complex **1**[5a] with silver acetate and silver trifluoroacetate in the mixed solvent of CH_2Cl_2/CH_3CN (3:1) at room temperature and isolated as white solids in 88 and 90% yields, respectively.

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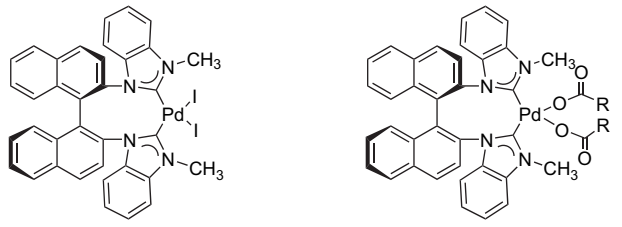


Figure 1. Bis(NHC)–Pd(II) complexes **1**–**3**.

They are fairly stable toward air in solution and as solids. In addition, these solid materials can be stored at room temperature for months without decomposition. Crystals suitable for X-ray diffraction study were grown from hexane/CH_2Cl_2 mixtures. Figure 2 shows the X-ray crystal structure of complex **2**.[9] The bis(NHC) ligand chelates the palladium center through two carbon atoms, and the two acetate anions acting as monodentate ligand coordinate to the metal center through oxygen atoms, stabilizing a 16-electron configuration around the metal center (Fig. 2).

2.2. Catalytic allylation of aldehydes with allyltributyltin

Allylation of 4-bromobenzaldehyde with allyltributyltin was first examined in tetrahydrofuran (THF) in the presence of bis(NHC)–Pd(II) complexes **1**, **2** or **3** (1 mol %) to find out the optimal conditions. The results are summarized in Table 1.

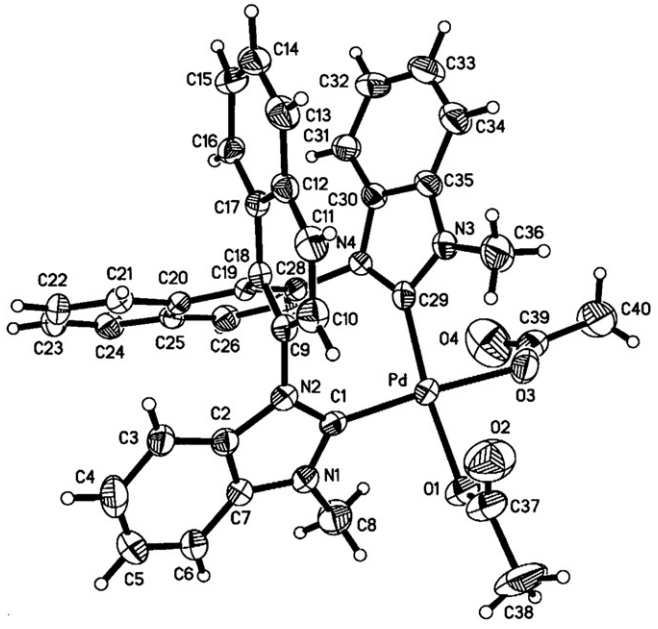
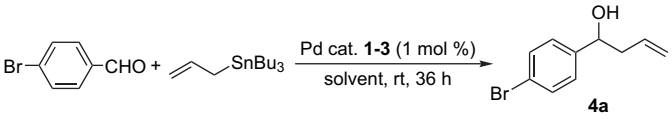


Figure 2. ORTEP drawing of bis(NHC)–Pd(II) complex **2** with thermal ellipsoids at the 30% probability level. Selected bond distances (Å) and angles (°): Pd–C1=1.955(5), Pd–C29=1.953(5), Pd–O1=2.060(4), Pd–O3=2.053(4), O1–C37=1.243(10), O2–C37=1.254(10), O3–C39=1.192(10), O4–C39=1.232(10); O1–Pd–O3=86.61(19), C1–Pd–O1=89.8(2), C1–Pd–C29=96.0(2), C29–Pd–O3=87.8(2), C1–Pd–O3=175.3(3), C29–Pd–O1=172.8(2).

Table 1
Allylation of 4-bromobenzaldehyde with allyltributyltin using bis(NHC)–Pd(II) complexes **1**, **2** or **3** as the catalyst[a]



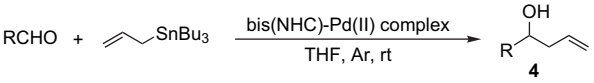
Entry	Catalyst	Solvent	Yield[b] of **4a** (%)
1	**1**	THF	26
2	**2**	THF	92
3	**3**	THF	91
4	**2**	DMF	87
5	**2**	DCE	84
6	**2**	CH_3CN	90
7	**2**	Toluene	62

[a] Reaction conditions: 0.5 mmol of aldehyde, 0.6 mmol of allyltributyltin, 0.005 mmol of Pd cat. and 1.0 mL of solvent.
[b] Isolated yields.

After several trials and errors, we were pleased to observe that bis(NHC)–Pd(II) complexes **2** and **3** were highly efficient catalysts for the allylation of 4-bromobenzaldehyde with allyltributyltin under mild conditions, while the original bis(NHC)–Pd(II) complex **1** is not effective in this reaction under identical conditions (Table 1, entries 1–3). Solvent effects were examined using bis(NHC)–Pd(II) complex **2** as a catalyst in a variety of solvents. We found that THF is the best one for this reaction (Table 1, entries 4–7).

With these optimal conditions in hand, we next carried out the reactions of various aldehydes with allyltributyltin under catalysis of complex **2** or **3**. All reactions proceeded smoothly to give the expected products **4** in good to high yields (Table 2). As can be seen from Table 2, as for arylaldehydes bearing electron-withdrawing groups or moderately electron-donating groups such as methyl or hydroxy group, the corresponding

Table 2
Allylation of aldehydes with allyltributyltin using bis(NHC)–Pd(II) complexes **2** or **3** as the catalyst in THF[a]

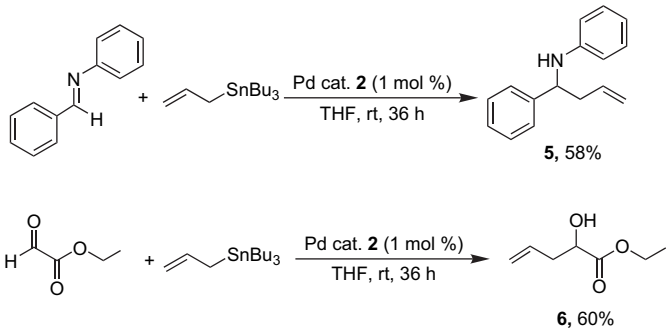


Entry	R, Aldehyde	Catalyst	Yield[b] of **4** (%)
1	C_6H_5	**2**	**4b** (89)
2	4-$NO_2C_6H_4$	**2**	**4c** (99)
3	4-MeC_6H_4	**2**	**4d** (88)
4	4-MeC_6H_4	**3**	**4d** (90)
5	3-$NO_2C_6H_4$	**2**	**4e** (95)
6	2-$NO_2C_6H_4$	**2**	**4f** (99)
7	4-$MeOC_6H_4$	**2**	**4g** (67)
8	$C_6H_5CH_2CH_2$	**2**	**4h** (46)
9[c]	$C_6H_5CH_2CH_2$	**3**	**4h** (80)
10	*E*-C_6H_5CH=CH	**2**	**4i** (68)
11	4-ClC_6H_4	**2**	**4j** (97)
12	2-OHC_6H_4	**2**	**4k** (92)

[a] Reaction conditions: 0.5 mmol of aldehydes, 0.6 mmol of allyltributyltin, 0.005 mmol of bis(NHC)–Pd(II) complex and 1.0 mL of THF.
[b] Isolated yields.
[c] Reaction was performed at 50 °C.

allylated products **4** were obtained in high yields in the presence of **2** or **3** (Table 2, entries 1–6, 11 and 12). Aliphatic aldehydes or arylaldehyde bearing a strongly electron-donating group such as methoxy group afforded the corresponding products **4** in moderate yields under identical conditions (Table 2, entries 7–10). To our disappointment, although chiral complexes **2** and **3** were used for this transformation, no or very lower ee was found for products **4**.

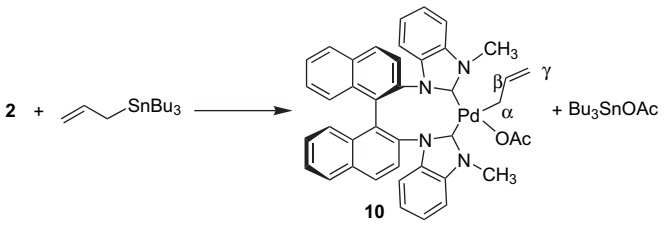
Bis(NHC)–Pd(II) complex **2** can also be used for the allylation of imine and ethyl glyoxalate to give the corresponding allylated products **5** and **6** in 58 and 60% yields under identical conditions, respectively (Scheme 1).



Scheme 1. Allylation of imine and ethyl glyoxalate with allyltributyltin.

We also investigated the use of bis(NHC)–Pd(II) complex **2** as catalyst in the allylic alkylation of acetic acid 1,3-diphenylallyl ester **7**.[10] A THF solution of **7** was added into to a THF suspension of bis(NHC)–Pd(II) complex **2** and Cs_2CO_3, followed by addition of a solution of sodium dimethylmalonate **8** at 0 °C. The reaction mixture was heated at 50 °C and stirred for 24 h. As a result, we found that complex **2** was not effective in this reaction since the transformation was sluggish and the desired substitution product **9** was formed only in 13% yield with 7% ee under the standard reaction conditions (Scheme 2).

A plausible explanation for why bis(NHC)–Pd(II) complexes **2** and **3** are so effective in this reaction is proposed as below: (1) the powerful σ-donating and weak π-accepting character of carbene ligand increase the electron density at the metal center and consequently increase the electron density at the allylic group as well, thereby drastically retarding attack by nucleophiles while significantly promoting the electrophilic attack process. (2) Weakly coordinating counterions (such as acetate and trifluoroacetate) on the palladium center facilitate the transmetalation step, and therefore increase the catalytic activity of the applied bis(NHC)–Pd(II) complex via η^1-allylpalladium intermediate **10** (Scheme 3).[11] A plausible catalytic cycle of the allylation reaction is outlined in Scheme 4 via intermediate **11**.

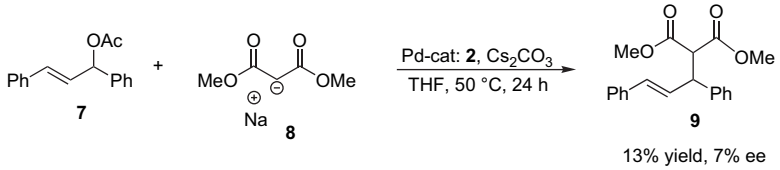


Scheme 3. Formation of η^1-allylpalladium complex **10** by transmetalation of allyltributyltin with bis(NHC)–Pd(II) complex **2**.

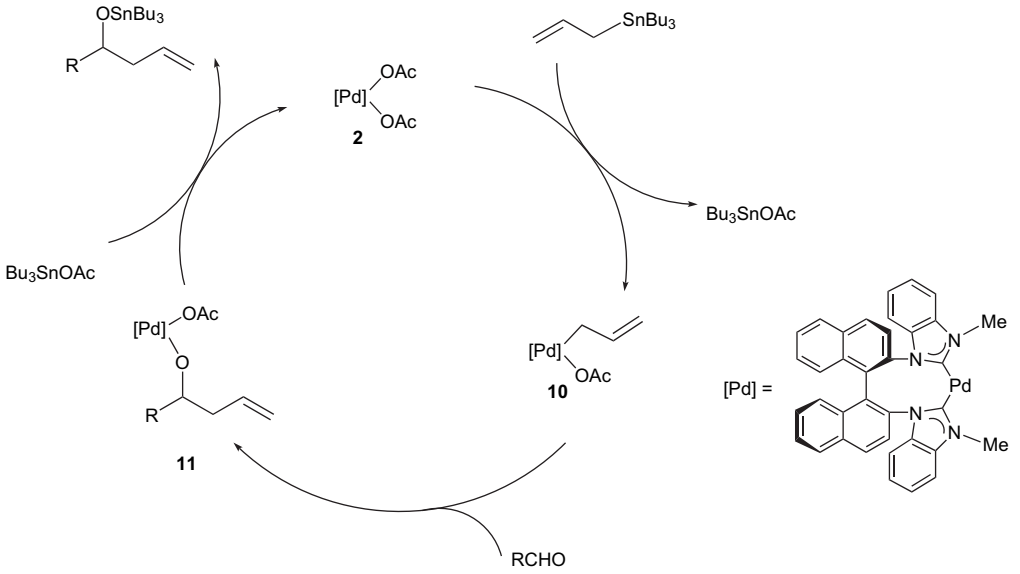
To probe the key step in the the proposed mechanism, ^{1}H NMR spectroscopic trace experiment was performed with bis(NHC)–Pd(II) complex **2** or **3** and allyltributyltin in $CDCl_3$. A number of relevant peaks between 2.0 and 6.0 ppm could be observed in the ^{1}H NMR spectroscopic charts (Scheme 3 and Fig. 3). In the reaction of bis(NHC)–Pd(II) complex **2** (1 equiv) with allyltributyltin (100 equiv), the α-methylene protons (CH_2) and γ-olefinic protons in η^1-allylpalladium complex **10** were observed with downfield shift to 2.90 ppm, 4.92 and 5.02 ppm relative to those of allyltributyltin (1.78, 4.63 and 4.78 ppm), respectively (Fig. 3a and b). Whereas the β-olefinic protons (5.58 ppm) of complex **10** shifted upfield relative to that of allyltributyltin (5.95 ppm) (Fig. 3a and b). Furthermore, the characteristic singlet (two methyl groups) of the NHCs groups in complex **2** at 3.87 ppm partially changed to two singlets at 3.48 and 3.63 ppm, respectively, indicating that the two methyl groups at the bis(NHC) ligand located in different environment. The formation of a π-allylpalladium complex was not found on the basis of ^{1}H NMR spectrum and η^1-allylpalladium complex **10** is the only species in this reaction, although a dynamic equilibration between the η^1-allylpalladium complex and the π-allylpalladium complex may conceivably exist. The similar results were also observed when bis(NHC)–Pd(II) complex **3** was used for this reaction (Fig. 3c).

3. Conclusions

In conclusion, novel cis-chelated bidentate bis(NHC)–Pd(II) complexes derived from 1,1′-binaphthyl-2,2′-diamine (BINAM) bearing weakly coordinating acetate or trifluoroacetate counterions have been synthesized and their structures have been characterized by X-ray diffraction of single crystals. We have also identified an efficient bis(NHC)–Pd(II) complex system in the allylation of a variety of electrophiles as aldehydes and imine to furnish the corresponding allylated products in



Scheme 2. Allylic alkylation catalyzed by bis(NHC)–Pd(II) complex **2**.



Scheme 4. Catalytic cycle of bis(NHC)–Pd(II) complex **2**-catalyzed allylation of aldehydes, imine, and ethyl glyoxalate with allyltributyltin.

good to high yields under mild conditions, although they are not so effective in the allylic alkylation of acetic acid 1,3-diphenylallyl ester **7**.[12] The bis(NHC) ligand decreases the electrophilicity of the allylpalladium complex, therefore, slows down the rate of attack by nucleophiles while promotes the attack by the electrophiles. Moreover, the employed weekly coordinating counterions also play key role in this transformation. Efforts are underway to further elucidate the reaction mechanism and to understand the scope and limitations of this process.

4. Experimental section

4.1. General remarks

^{1}H NMR spectra were recorded on a Varian Mercury vx 300 MHz spectrometer for solution in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard; *J*-values are in Hz. Mass spectra were recorded with a HP-5989 instrument. Organic solvents used were dried by standard methods when necessary. The solid compounds reported in this paper gave satisfactory CHN microanalyses with a Carlo-Erba 1106 analyzer. X-ray diffraction analysis was performed on a Rigaku AFC7R X-ray diffraction meter. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Huanghai GF_{254} silica gel coated plates. Flash column chromatography was carried out using 300–400 mesh silica gel at increased pressure.

*4.2. Synthesis of bis(NHC)–Pd(II) complex **2***

The bis(NHC)–Pd(II) complex **1**[5a] (174 mg, 0.20 mmol) was suspended in a mixed solution of CH_2Cl_2 (15 mL) and CH_3CN (5 mL). AgOAc (70 mg, 0.42 mmol) was added and the mixture was stirred at room temperature for 3 h. The resulting suspension was filtered from the precipitated AgI over Celite and the solvent was removed under reduced pressure to give the product bis(NHC)–Pd(II) complex **2** (131 mg, 88%) as a white solid. Crystals suitable for X-ray diffraction study were grown from CH_2Cl_2/hexane solutions. Mp 268 °C (dec); IR (CH_2Cl_2) ν 3408, 3053, 2924, 2847, 1580, 1510, 1385, 751 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 1.88 (br, 6H, CH_3), 3.90 (s, 6H, CH_3), 6.70–6.73 (m, 2H, ArH), 6.83–6.92 (m, 10H, ArH), 7.20–7.26 (m, 2H, ArH), 7.71 (d, J=8.4 Hz, 2H, ArH), 8.05 (d, J=8.4 Hz, 2H, ArH), 8.15 (d, J=8.4 Hz, 2H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 23.7, 35.0, 109.1, 112.4, 123.1, 123.4, 124.9, 126.4, 126.9, 127.5, 130.1, 131.2, 132.5, 132.7, 133.1, 135.1, 135.8, 171.6, 177.3; MS (MALDI) *m/e* 620.2.0 ($M^+-2O_2CCH_3$); Anal. Calcd for $C_{40}H_{32}N_4O_4Pd\cdot1.5H_2O$ requires: C, 62.71; H, 4.60; N, 7.31%. Found: C, 62.75; H, 4.62; N, 7.30%.

*4.3. Synthesis of bis(NHC)–Pd(II) complex **3***

The bis(NHC)–Pd(II) complex **1**[5a] (174 mg, 0.20 mmol) was suspended in a mixed solution of CH_2Cl_2 (15 mL) and CH_3CN (5 mL). $AgOCOCF_3$ (93 mg, 0.42 mmol) was added and the reaction mixture was stirred at room temperature for 3 h. The resulting suspension was filtered from the precipitated AgI over Celite and the solvent was removed under reduced pressure to give the product bis(NHC)–Pd(II) complex **3** (153 mg, 90%) as a white solid. Crystals suitable for diffraction study were grown from CH_2Cl_2/hexane solutions. Mp 248 °C (dec); IR (CH_2Cl_2) ν 3558, 2924, 1680, 1510, 1393, 745 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 3.88 (s, 6H, CH_3), 6.75–6.78 (m, 2H, ArH), 6.83–6.97 (m, 10H, ArH), 7.22–7.27 (m, 2H, ArH), 7.73 (d, J=8.1 Hz, 2H, ArH), 8.09 (s, 4H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 34.9, 109.4, 112.6, 115.9 (q, J_{C-F}=287.9 Hz, CF_3), 123.8, 124.0, 124.4, 126.8, 127.3, 127.7, 130.5, 131.1, 132.5, 132.8, 133.0, 134.6, 135.7, 161.7 (q, J_{C-F}=36.7 Hz, CO), 166.7; ^{19}F NMR (282 MHz, $CDCl_3$, $CFCl_3$) δ −74.9; MS (MALDI) *m/e* 515.2 ($M^+-2OCOCF_3-Pd$); Anal. Calcd for $C_{40}H_{26}F_6N_4O_4Pd\cdot H_2O$

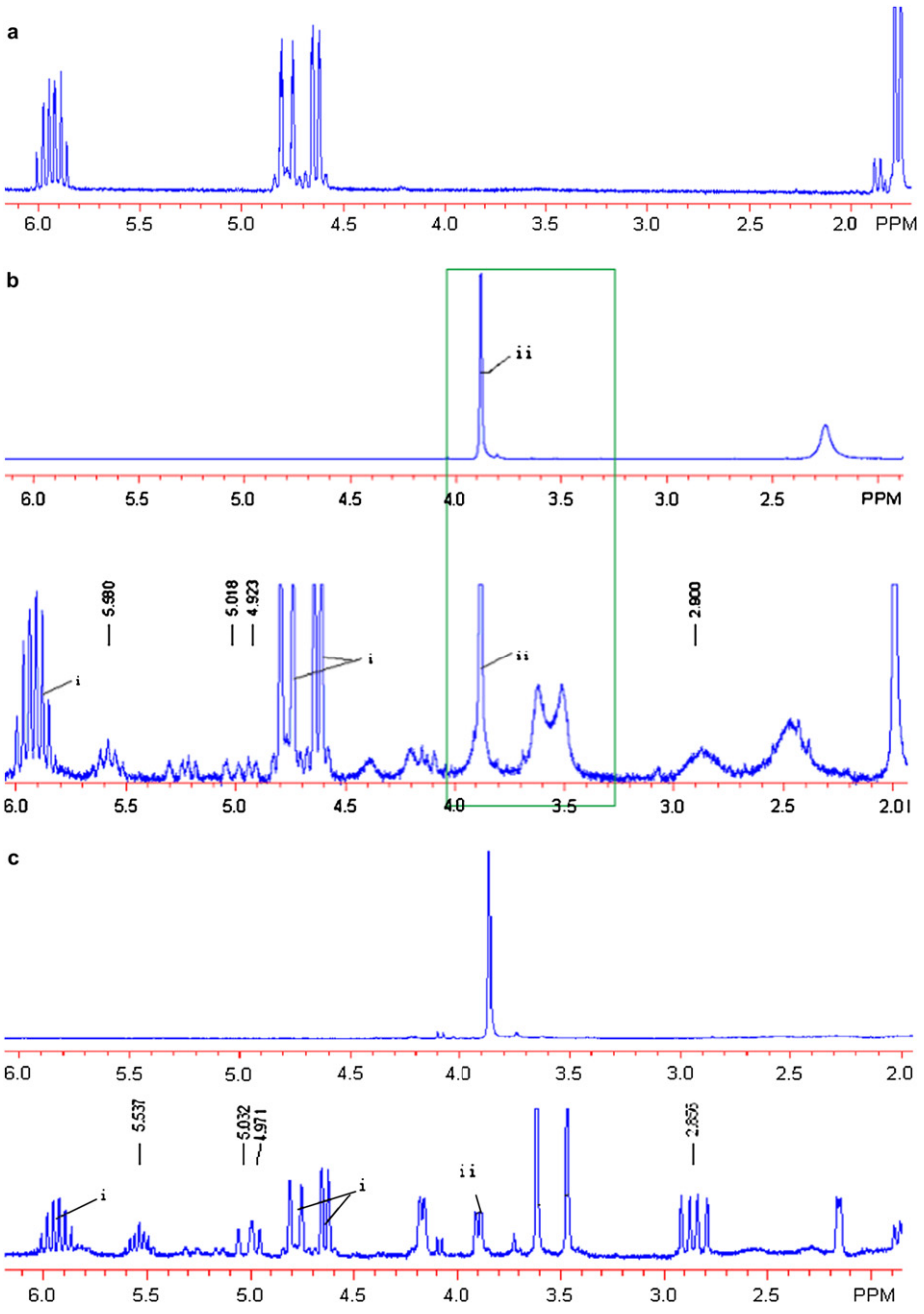


Figure 3. (a) ^{1}H NMR spectrum of allyltributyltin in $CDCl_3$. (b) ^{1}H NMR spectrum of the reaction of bis(NHC)–Pd(II) complex **2** with allyltributyltin in $CDCl_3$ ((i) allyltributyltin; (ii) complex **2**). (c) ^{1}H NMR spectrum of the reaction of bis(NHC)–Pd(II) complex **3** with allyltributyltin in $CDCl_3$ ((i) allyltributyltin; (ii) complex **3**).

requires: C, 55.54; H, 3.26; N, 6.48%. Found: C, 55.64; H, 3.11; N, 6.27%.

4.4. Allylation of aldehydes catalyzed by bis(NHC)–Pd(II) complex

4.4.1. General procedure for bis(NHC)–Pd(II) catalyzed allylation of aldehydes

A mixture of the appropriate catalyst (0.005 mmol, 1.0 mol %) and aldehyde (0.5 mmol) was dissolved in 1.0 mL of THF under argon atmosphere. Subsequently, allylstannane (0.6 mmol) was added to this mixture at room temperature. Then the reaction mixture was stirred at room temperature for 36 h. To the mixture ether and aqueous KF (10%, w/v) were added and stirred for further 3 h. Then the mixture was extracted with ether. The organic layer was dried over Na_2SO_4 and concentrated. The crude product was purified by flash column chromatography (eluent: hexanes/EtOAc=8:1) to give the corresponding alcohol **4**.

4.4.2. Analytical data of the products

4.4.2.1. 1-(p-Bromophenyl)-3-buten-1-ol ***4a***[13a]. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 2.13 (br, 1H, OH), 2.44–2.51

(m, 2H, CH_2), 4.70 (t, J=6.3 Hz, 1H, CH), 5.13–5.19 (m, 2H, vinyls), 5.73–5.82 (m, 1H, vinyl), 7.23 (d, 2H, J=8.4 Hz, ArH), 7.47 (d, 2H, J=8.4 Hz, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 43.8, 72.5, 118.9, 121.2, 127.5, 131.4, 133.9, 142.7.

4.4.2.2. 1-Phenyl-3-buten-1-ol ***4b***[13a]. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 2.01 (br, 1H, OH), 2.48–2.54 (m, 2H, CH_2), 4.73 (t, 1H, J=6.9 Hz, CH), 5.12–5.20 (m, 2H, vinyls), 5.76–5.82 (m, 1H, vinyl), 7.26–7.36 (m, 5H, ArH).

4.4.2.3. 1-(p-Nitrophenyl)-3-buten-1-ol ***4c***[13b]. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 2.36 (br, 1H, OH), 2.40–2.61 (m, 2H, CH_2), 4.85–4.89 (m, 1H, CH), 5.16–5.22 (m, 2H, vinyls), 5.72–5.86 (m, 1H, vinyl), 7.52–7.55 (m, 2H, ArH), 8.18–8.23 (m, 2H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 43.9, 72.1, 119.6, 123.59, 123.61, 126.5, 133.2, 151.1.

4.4.2.4. 1-(p-Methylphenyl)-3-buten-1-ol ***4d***[13b]. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 2.33 (s, 3H, CH_3), 2.37 (br, 1H, OH), 2.46 (t, 2H, J=6.6 Hz, CH_2), 4.63 (t, 1H, J=6.6 Hz, CH), 5.01–5.15 (m, 2H, vinyls), 5.73–5.82 (m, 1H, vinyl), 7.05–7.24 (m, 4H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 21.3, 43.6, 73.2, 118.0, 122.8, 126.4, 128.1, 128.2, 134.5, 137.9, 143.8.

4.4.2.5. 1-(o-Nitrophenyl)-3-buten-1-ol ***4e***[13b]. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 2.45–2.58 (m, 2H, CH), 2.89 (s, 1H, OH), 4.83–4.87 (m, 1H, CH), 5.13–5.19 (m, 2H, vinyls), 5.72–5.83 (m, 1H, vinyl), 7.51 (t, 1H, J=7.8 Hz, ArH), 7.69 (d, 1H, J=7.8 Hz, ArH), 8.09 (d, 1H, J=7.8 Hz, ArH), 2.89 (s, 1H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 43.7, 72.0, 119.3, 120.7, 122.3, 129.2, 132.0, 133.2, 145.9, 148.1.

4.4.2.6. 1-(m-Nitrophenyl)-3-buten-1-ol ***4f***[13c]. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 2.43–2.59 (m, 2H, CH_2), 2.89 (s, 1H, OH), 4.85 (t, 1H, J=6.0 Hz, CH), 5.12–5.18 (m, 2H, vinyls), 5.71–5.85 (m, 1H, vinyl), 7.51 (t, 1H, J=8.1 Hz, ArH), 7.69 (d, 1H, J=7.5 Hz, ArH), 8.08–8.11 (m, 1H, ArH), 8.21 (t, 1H, J=2.1 Hz, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 43.6, 72.0, 119.2, 120.7, 122.2, 129.2, 131.9, 133.2, 145.9, 148.1.

4.4.2.7. 1-(p-Methoxyphenyl)-3-buten-1-ol ***4g***[13a]. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 2.32 (br, 1H, OH), 2.48 (t, 2H, J=6.6 Hz, CH_2), 3.78 (s, 3H, CH_3), 4.65 (t, 1H, J=6.6 Hz, CH), 5.08–5.19 (m, 2H, vinyls), 5.73–5.79 (m, 1H, vinyl), 6.86 (d, 2H, J=8.4 Hz, ArH), 7.25 (d, 2H, J=8.4 Hz, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 43.6, 55.1, 72.9, 113.7, 118.0, 127.0, 134.6, 136.0, 158.9.

4.4.2.8. 1-Pheny-5-hexen-3-ol ***4h***[13a]. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 1.65 (d, 1H, J=3.9 Hz, OH), 1.76–1.83 (m, 2H, CH_2), 2.16–2.36 (m, 2H, CH_2), 2.67–2.84 (m, 2H, CH_2), 3.68 (m, 1H, CH), 5.14 (d, 2H, J=12.9 Hz, vinyls), 5.78–5.84 (m, 1H, vinyl), 7.16–7.32 (m, 5H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 32.0, 38.4, 42.0, 69.9, 118.3, 125.8, 128.37, 128.41, 134.6, 142.0.

4.4.2.9. 1-Phenyl-1,5-hexadien-3-ol ***4i***[13b]. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 2.10 (br, 1H, OH), 2.36–2.43 (m, 2H, CH_2), 4.33 (dd, 1H, J=6.6 Hz, CH), 5.12–5.20 (m, 2H, vinyls), 5.77–5.89 (m, 1H, vinyl), 6.22 (dd, 1H, J_1=16.2 Hz, J_2=6.6 Hz, vinyl), 6.58 (d, 1H, J=16.2 Hz, vinyl), 7.20–7.38 (m, 5H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 41.9, 71.6, 118.3, 126.4, 127.6, 128.5, 130.2, 131.5, 134.0, 136.6.

4.4.2.10. 1-(p-Chlorophenyl)-3-buten-1-ol ***4j***[13b]. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 2.37–2.47 (m, 3H), 4.66 (t, 1H, J=6.9 Hz, CH), 5.10–5.16 (m, 2H, vinyls), 5.68–5.82 (m, 1H, vinyl), 7.23–7.31 (m, 4H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 43.7, 72.5, 118.6, 127.1, 128.4, 133.0, 133.9, 142.2.

4.4.2.11. 2-(1-Hydroxy-but-3-enyl)-phenol ***4k***[13a]. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 2.56–2.66 (m, 2H, CH_2), 2.85 (br, 1H, OH), 4.85–4.90 (m, 1H, CH), 5.20–5.25 (m, 2H, vinyls), 5.78–6.00 (m, 1H, vinyl), 6.81–6.89 (m, 2H, ArH), 6.97 (d, 1H, J=10.8 Hz, ArH), 7.22 (t, 1H, J=17.1 Hz, ArH), 8.04 (br, 1H, OH).

4.4.2.12. Phenyl-(1-phenyl-3-butenyl)-amine[13d]. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 2.45–2.62 (m, 2H, CH_2), 4.14 (br, 1H, NH), 4.35–4.39 (m, 1H, CH), 5.11–5.20 (m, 2H, vinyls), 5.70–5.80 (m, 1H, vinyl), 6.48 (d, 2H, J=8.4 Hz, ArH), 6.63 (t, 1H, J=7.2 Hz, ArH), 7.06 (t, 2H, J=10.5 Hz, ArH), 7.22 (t, 1H, J=7.2 Hz, ArH), 7.28–7.36 (m, 4H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 43.3, 57.1, 113.4, 117.3, 118.3, 126.2, 126.9, 128.5, 129.0, 134.6, 143.5, 147.3.

4.4.2.13. 2-Hydroxy-pent-4-enoic acid ethyl ester[13e]. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 1.30 (t, 3H, J=6.6 Hz, CH_3), 2.42–2.49 (m, 1H, CH_2), 2.54–2.61 (m, 1H, CH_2), 2.88 (d, 1H, J=6.0 Hz, OH), 4.21–4.29 (m, 3H), 5.13 (s, 1H, vinyl), 5.17 (d, 1H, J=8.1 Hz, vinyl), 5.77–5.86 (m, 1H, vinyl); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 14.2, 38.6, 61.7, 69.9, 118.7, 132.5, 174.4.

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Supplementary data

Supplementary data and representative spectra associated with this article can be found in the online version, at doi:10.1016/j.tet.2008.01.017.

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