Phosphido Pincer Complexes of Palladium as New Efficient Catalysts for Allylation of Aldehydes

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*Summary: Palladium complexes supported by tridentate phosphido diphosphine ligands ($P(o\text{-}C_6H_4PR_2)_2$: **1**, $R = {}^iPr$; **2**, $R =$ Ph) have been synthesized, characterized, and tested as catalysts for the electrophilic allylation of aldehydes. The palladium complex **2** resulted in an interesting catalyst for electrophilic allylation in the presence of allyltributyltin, giving good yields under very mild reaction conditions and even in the absence of the solvent.*

Palladium-catalyzed allylation is a reliable and widely used method for the selective formation of new C−C, C−N, and C−O bonds.[1−4] In particular, it offers a versatile tool for the introduction of an allylic moiety into both nucleophilic[5] and electrophilic[6] substrates. Although allylic alkylation of nuclophiles is a very useful and well-established method, application of electrophiles[6,7] still receives considerable current attention.

Yamamoto and co-workers[6a,8] first reported allylation of aldehydes and imines with allyltributyltin catalyzed by a (η^3-allyl)(η^1-allyl)palladium intermediate which serves as the nucleophilic allyl transfer species. A considerable synthetic limitation to the employment of this system is the difficult control of the regioselectivity when the two allyl moieties bear different substituents. A further problem is that the bis(allyl)palladium complexes may undergo allyl−allyl coupling prior to the reaction with electrophiles.

In 2003, Szabò[9] and co-workers achieved an interesting goal demonstrating that pincer-based palladium complexes can be highly active and robust catalysts for the catalytic allylation of electrophiles with allylstannanes, showing several benefits compared to generally used bis(allyl)palladium intermediates.

First of all, tridentate pincer ligands, occupying three of the four coordination sites of a square-planar Pd^{II} complex, impose an η^1 coordination mode of the allyl fragment; therefore, the catalytic activities are largely restricted to this single free site on palladium. Moreover, the direct aryl−metal bonding, providing an electron-rich palladium atom, assures a nucleophilic character to the allyl group. The fact that this electron-supplying part is forced to a trans position with respect to the allyl ligand prevents Stille coupling between the pincer ligand and the allyl moiety. Finally, a firm palladium−ligand bonding avoids undesired dynamic processes and ligand exchange, ensuring a high stability of the catalyst.[10]

Subsequent to the Szabò finding, several pincer-based palladium complexes were tested in the catalytic allylation of electrophiles with allylstannanes. In particular, while palladium NCN-pincer complexes exhibited low catalytic activity, PCP-pincer (with phosphine,[10] phosphinite,[10] and phosphite[11] ancillary ligands), SeCSe-pincer,[12] and SCS-pincer[13] complexes proved to be much more efficient.

Although the electronic nature of the central ligand (trans to the allyl moiety) plays a crucial role in the reactivity of these (η^1-allyl)palladium complexes, studies concerning the effects of the presence of a different anionic central donor in the ligand framework are definitively less numerous.[13−15]

Recently the Peters group developed new diarylphosphido phosphine (PPP) ligands[16] that represent good candidates as ligands for palladium-catalyzed electrophilic allylation of aldehydes in order to investigate the effects of the presence of a different anionic donor atom on the catalytic behavior of the metallic center. The incorporation of a strongly electron donating

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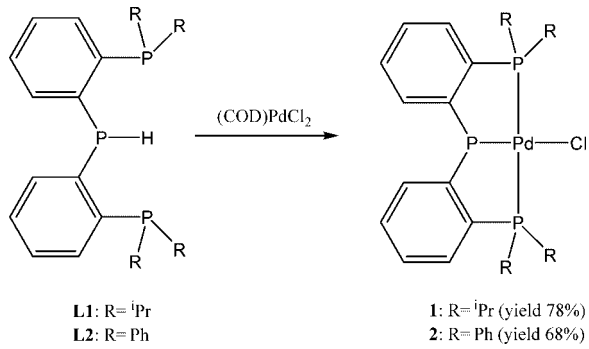
Scheme 1. Synthesis of Complexes 1 and 2



and trans-labilizing donor group as the phosphido phosphorus atom may promote the formation of coordinatively unsaturated complexes that may exhibit different reactivity properties.

In this paper we report the synthesis and characterization of two new PPP-based palladium complexes, bearing ligands with different substituent groups on the side arms, and their use as catalysts for the electrophilic allylation of aldehydes in the presence of allyltributyltin.

Synthesis and Characterization of Palladium Complexes. The (R-PPP)H ligands (**L1** and **L2**; see Scheme 1) were synthesized according to a procedure previously reported in the literature.[16,17]

The reactions between the ligands **L1** and **L2** and (COD)-$PdCl_2$ in THF in the presence of NEt^iPr_2 at 50 °C produce orange solutions of desired complexes in high yield (see scheme 1). Solution NMR studies on the reaction performed in C_6D_6 indicate that the cyclooctadiene (COD) ligand is easily displaced from (COD)$PdCl_2$ by the ligands **L1** and **L2** at room temperature upon mixing to form a solution of each complex. ^{31}P and ^1H NMR spectra show that no intermediate species containing the P−H functionality are initially formed, also in the absence of the amine base, in agreement with the strong tendency of the ligand to bind to the metal as an anionic (upon less of proton) meridional PPP ligand. The NMR data are consistent with a square-planar geometry for complex **1**, where **L1** is in a meridional coordination mode, as evidenced by the multiplicity of the resonances observed for the *o*-phenylene carbons in the ^{13}C NMR spectrum.[18]

In the ^{13}C NMR spectrum four resonances are observed for four nonequivalent CH carbons of the isopropyl groups, suggesting a low symmetry of the complex in solution and a scarce flexibility of the chelate backbone.

In the ^{31}P NMR spectrum, the two resonances corresponding to the neutral and anionic phosphorus donors are strongly shifted downfield from those of the corresponding ligand precursor. The chemical shift (58.41 ppm) related to the neutral phosphorus atoms is typical of square-planar Pd(II) complexes with *trans*-phosphine; comparable values are reported for analogous (^{i}Pr-PNP)−[19] and (^{i}Pr-PCP)−palladium[20] complexes.

Complex **1** is stable in solution; no decomposition was detected by NMR after heating in C_6D_6 (80 °C, 24 h).

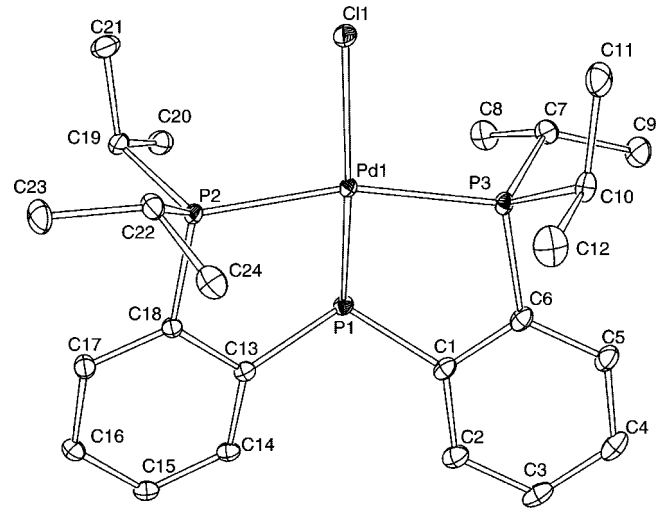


Figure 1. ORTEP representation of the structure of complex **1**. Hydrogens have been omitted for clarity. Selected bond distances (Å) and angles (deg): Pd(1)−P(1), 2.2533(9); Pd(1)−P(2), 2.2894(8); Pd(1)−P(3), 2.3146(8); Pd(1)−Cl(1), 2.4122(10); P(1)−Pd(1)−P(2), 85.06(3); P(1)−Pd(1)−P(3), 84.17(3); P(2)−Pd(1)−P(3), 164.429(19); P(1)−Pd(1)−Cl(1), 170.842(19); P(2)−Pd(1)−Cl(1), 93.84(3); P(3)−Pd(1)−Cl(1), 98.55(3).

Also for complex **2**, the solution NMR data confirm the square-planar geometry reminiscent of the analogous (Ph-PCP)−[21] and (Ph-PNP)−palladium[22] complexes.

The solid-state structure of **1** was determined by an X-ray diffraction study. The molecular structure of complex **1** and relevant structural data are given in Figure 1.

The geometry of the palladium center is approximately square planar, with the two neutral phosphorus atoms in a distorted trans configuration with a P2−Pd−P3 angle of 164.4° (see Figure 1). The environment about the phosphido phosphorus atom is pyramidal with a stereochemically active lone pair. The Pd−Cl distance (2.4122(9) Å) is slightly longer than that observed in the (^{i}Pr-PNP)PdCl complex (2.3157(11) Å)[23] and similar to that observed in (^{t}Bu-PCP)PdCl (2.3969(6) Å),[24] suggesting that the trans influence of the phosphido donor is somewhat higher than that of the amido ligand and comparable to that of an anionic aryl carbon.

To test the activity of complexes **1** and **2**, the allylation of a number of representative aldehydes with allyltributyltin were examined in DMF and in the absence of solvent under different reaction conditions (Table 1, Scheme 2). Complex **2** showed higher activity and gave higher yields in the presence of benzaldehyde (entries 1−5). As expected, electron-poor aldehydes reacted more quickly with higher yields with both **1** and **2** under milder conditions at room temperature and with lower catalyst loading (entries 7−9). In the case of *o*-NO_2-benzaldehyde (entry 9), the presence of the nitro group in an ortho position on the aromatic ring did not affect the reactivity of the aldehyde. In contrast, the electronically deactivated anisaldehyde was poorly reactive in the presence of **2** (entries 10 and 11) and it was completely unreactive in the presence of **1** (entry 12). It is very interesting to note that, in the absence of solvent,

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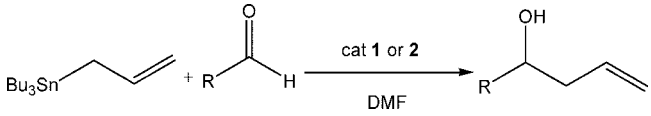
Table 1. Allylation of Aldehydes Catalyzed by Complexes 1 and 2

entry no.	aldehyde (R)	aldehyde concn (M)	cat.	amt of cat. (%)	*T* (°C)/*t* (h)	yield (%)[a]
1	benzaldehyde	0.17	**2**	5	50/23	75
2	benzaldehyde	0.17	**1**	5	50/23	50
3	benzaldehyde	neat	**2**	2.5	RT[b]/23	72
4	benzaldehyde	neat	**1**	2.5	RT/23	20
5	benzaldehyde	0.43	**2**	2.5	RT/23	41
6	benzaldehyde	neat	no cat.		RT/23	
7	*p*-$NO_2C_6H_4$	0.43	**2**	2.5	RT/18	99
8	*p*-$NO_2C_6H_4$	0.43	**1**	2.5	RT/18	93
9	*o*-$NO_2C_6H_4$	0.43	**2**	2.5	RT/18	99
10	*p*-$OMeC_6H_4$	neat	**2**	2.5	RT/23	43
11	*p*-$OMeC_6H_4$	0.43	**2**	2.5	50/23	39
12	*p*-$OMeC_6H_4$	neat	**1**	2.5	RT/23	no reacn
13	$PhCH_2CH_2$	neat	**2**	2.5	RT/23	61
14	citronellal	0.43	**2**	2.5	RT/23	59(60/40)[c]

[a] All of the yields refer to isolated chromatographically pure compounds. [b] RT: room temperature. [c] Values in parentheses refer to syn/anti diastereoisomeric ratios that were determined by ^{1}H NMR analysis performed on the crude products.

Scheme 2. Catalytic Allylation Reaction of Aldehydes



2.5 mol % of **2** was able to achieve comparable yield with benzaldehyde even at room temperature (entry 3), while the control experiment without catalyst gave no product (entry 6). The absence of solvent allowed us to omit the isolation procedure, and the reaction mixture was directly purified by column chromatography.

Interestingly, under these mild reaction conditions, complex **2** was also able to catalyze the allylation of aliphatic aldehydes in good yields (entries 13 and 14). However, in the case of citronellal (entry 14), an aliphatic aldehyde with a chiral center on the β-carbon, the diastereoselectivity was low. In all cases complex **2** showed a higher catalytic activity than complex **1**. This could be attributable to the fact that the transmetalation reactions with allylstannane are faster for less bulky and more electron poor palladium systems.[25]

In summary, we have shown that the new (R-PPP)−Pd chloride complexes **1** and **2** are efficient catalysts for the allylation of aldehydes with allybutyltin. The activity of complex **2** is higher than those reported in the literature for palladium pincer complexes that feature a chloride ligand. It is worth noting that catalyst **2** requires very mild reaction conditions to achieve good yields and, interestingly, it can be also used in the absence of solvent.

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Supporting Information Available: Text, figures, and tables giving experimental procedures for the synthesis and characterization data of compounds **1** and **2** and X-ray structural solution and crystal data for **1**; X-ray data for **1** are also given as a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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