

## Co-Immobilization of a Palladium–Bisphosphine Complex and Strong Organic Base on a Silica Surface for Heterogeneous Synergistic Catalysis

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Co-immobilization of a palladium–bisphosphine complex and a strong organic base, 1,4-diazabicyclo[2.2.2]octane (DABCO), on a silica support was successfully achieved. The new catalyst structure was characterized by X-ray photoelectron spectroscopy, solid-state NMR spectroscopy, X-ray absorption fine structure spectroscopy, and elemental analysis. Although the local structure of the Pd–bisphosphine complex was unaffected by the presence of DABCO on the same silica surface, its catalytic activity in allylation reactions of nucleophiles was significantly enhanced, achieving turnover numbers (TON) up to > 10000, owing to dual-activation of substrate molecules by the Pd complex and DABCO.

Synergies between immobilization methods for well-defined molecules, such as metal complexes and organocatalysts, on solid surfaces and atomic-level characterization techniques for these functionalized surfaces provide new opportunities for the creation of highly efficient heterogeneous catalysts.<sup>[1]</sup> Heterogeneous synergistic catalysis by immobilized molecules is a new concept in catalysis. Since Kubota and co-workers reported acid–base catalysis by silica-supported amines,<sup>[2]</sup> various types of heterogeneous synergistic catalysis by acidic inorganic material-supported basic amines have been developed.<sup>[3,4]</sup>

The next targets for heterogeneous synergistic catalysis are combinations of metal complexes or nanoparticles with organic functional molecules, which would enable a wide range of catalytic transformations. Tada and co-workers have demonstrated synergistic catalysis between metal nanoparticles and surface-immobilized functionalities by immobilizing ethynylpyr-

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idine functionalities in proximity to Pt nanoparticles to increase the catalytic activity for sugar oxidation.<sup>[5]</sup> For metal complexes, we have already reported palladium and rhodium complexes with diamine ligands coexisting with tertiary amine groups on silica surfaces.<sup>[6,7]</sup> These bifunctional surfaces significantly accelerated the Tsuji-Trost allylations and the 1,4-addition of organoboronic acids through the synergistic effect of metal complexes and tertiary amines. To expand the variation of metal complexes and organic functional groups on the same surface, we aimed to prepare and characterize a SiO<sub>2</sub> surface with two specifically controlled molecules: a palladiumbisphosphine complex<sup>[8]</sup> and a strong organic base, 1,4-diazabicyclo[2.2.2]octane (DABCO).<sup>[9]</sup> Oxidation of phosphine ligands on the silica surface<sup>[10]</sup> was effectively avoided by pre-complexation of the Pd species before immobilization. Spectroscopic techniques, namely, X-ray photoelectron spectroscopy (XPS), Xray absorption fine structure spectroscopy (XAFS), and solidstate NMR spectroscopy enabled atomic-level characterization of the immobilized Pd complexes and DABCO functionality. The prepared catalysts were applied in the Tsuji-Trost allylations of a ketoester and nitroalkane.

Scheme 1 shows the synthetic procedure for preparation of the SiO<sub>2</sub>-supported Pd-bisphosphine complex and DABCO skeleton (SiO<sub>2</sub>/DABCO/PP-Pd). A silane-coupling reaction successfully attached a chloropropyl group to the SiO<sub>2</sub> surface (SiO<sub>2</sub>/Cl), which was subsequently used to quaternarize DABCO, affording SiO<sub>2</sub>-supported DABCO (SiO<sub>2</sub>/DABCO). Before immobilizing the palladium complex on SiO<sub>2</sub>, a palladium-bisphosphine complex containing a silane-coupling moiety (PP-Pd) was prepared from the appropriate bisphosphine ligand and [PdCl( $\eta^3$ -allyl)]<sub>2</sub>.<sup>(11]</sup> The reaction between PP-Pd and SiO<sub>2</sub>/DABCO gave the dual SiO<sub>2</sub>-supported DABCO and Pd-bisphosphine complex (SiO<sub>2</sub>/DABCO/PP-Pd). A SiO<sub>2</sub>-supported palladium complex (SiO<sub>2</sub>/PP-Pd) was prepared by using a similar procedure.

The elemental analysis results for the prepared samples are summarized in Table S1 (in the Supporting Information). Chlorine (0.8 mmol g<sup>-1</sup>) was observed in SiO<sub>2</sub>/Cl. After the reaction of SiO<sub>2</sub>/Cl with DABCO, the ratio of Cl (0.6 mmol g<sup>-1</sup>) to N (1.4 mmol g<sup>-1</sup>) was approximately 1:2, suggesting that quaternarized DABCO had formed on the SiO<sub>2</sub> surface (SiO<sub>2</sub>/DABCO). SiO<sub>2</sub>/DABCO/PP-Pd contained 0.17 mmol g<sup>-1</sup> of the Pd species. In the case of SiO<sub>2</sub>/PP-Pd, the amounts of Pd, N, and Cl were almost identical (ca. 0.3 mmol g<sup>-1</sup>). P/Pd ratio in SiO<sub>2</sub>/PP-Pd was determined by XPS analysis: the atomic ratio was approxi-



Scheme 1. Synthesis of (A)  $\rm SiO_2/DABCO$  and (B)  $\rm SiO_2/DABCO/PP-Pd$  and  $\rm SiO_2/PP-Pd.$ 

mately 2:1 for P/Pd, suggesting that the PP-Pd complex structure had been maintained.

The successful silane-coupling reaction between surface Si-OH groups and Si(OR)<sub>3</sub> moieties in the coupling partners was determined by <sup>29</sup>Si cross polarization magic angle spinning (CP/MAS) NMR spectroscopy (Figure S1 in the Supporting Information). The carbon skeletons in the prepared samples were determined by <sup>13</sup>C CP/MAS NMR measurements, as shown in Figure 1(<sup>13</sup>C). After the reaction of SiO<sub>2</sub>/Cl and DABCO, the chloropropyl functionality (Figure 1A) had been completely converted to quaternarized DABCO (Figure 1B). Comparison of the <sup>13</sup>C NMR spectra of PP-Pd before (Figure 1 C) and after immobilization on SiO<sub>2</sub> (Figure 1D) indicated the presence of the bisphosphine ligand (signals a-d, and Ph).<sup>[12]</sup> In the <sup>13</sup>C NMR spectrum of SiO<sub>2</sub>/DABCO/PP-Pd (Figure 1E), both the signals observed in Figure 1B and D were detected, indicating that both functionalities were immobilized on the SiO<sub>2</sub> surface and had maintained their carbon skeleton structure.

To determine the detailed structure of the immobilized Pd complexes, <sup>31</sup>P MAS NMR, XPS, and XAFS measurements were also conducted. The signal for the homogeneous PP-Pd complex was detected at 3.1 ppm in the <sup>31</sup>P NMR (Figure 1A, (<sup>31</sup>P)).<sup>[12]</sup> These signal positions were unchanged after immobilization of PP-Pd (Figure 1B and 1C), indicating that almost all

phosphorus atoms remained coordinated to Pd after immobilization. A small signal originated from phosphine oxide was also detected around 30 ppm, however, the intensity was much lower than that of the main signal around 0 ppm. XPS spectra and signal positions are shown in Figure S2 (in the Supporting Information) and Table 1, respectively. The Pd<sub>3d5/2</sub> signal position in both immobilized complexes, SiO<sub>2</sub>/DABCO/ PP-Pd and SiO<sub>2</sub>/PP-Pd, indicated the formation of a monomeric bisphosphine complex.<sup>[8]</sup> In SiO<sub>2</sub>/DABCO/PP-Pd, two N1s signals were detected at 399.4 and 402 eV, whereas only one signal was present in SiO<sub>2</sub>/PP-Pd (399.5 eV), supporting the presence of quaternarized DABCO in SiO<sub>2</sub>/DABCO/PP-Pd.<sup>[13]</sup>

Figure 2 shows the Pd-K edge X-ray absorption near-edge structure (XANES) spectra for SiO<sub>2</sub>/DABCO/PP-Pd, SiO<sub>2</sub>/PP-Pd, and the reference samples. The spectra for SiO<sub>2</sub>/DABCO/PP-Pd (Figure 2A) and SiO<sub>2</sub>/PP-Pd (Figure 2B) were almost identical. In addition, their spectral features were consistent with those of  $[Pd^{II}CI_2(PPh_3)_2]$  (Figure 2C), whereas other Pd references, such as Pd foil and PdO, were completely different (Figure 2D–G). The  $k^3$ -weighted extended XAFS (EXAFS) spectrum of SiO<sub>2</sub>/DABCO/PP-Pd was also similar to that of SiO<sub>2</sub>/PP-Pd, as shown in Figure S3 (in the Supporting Information). These XANES and EXAFS results indicated that local Pd structure at the SiO<sub>2</sub> surface was not affected by the presence of quaternarized DABCO on the same surface.

Figure 3 shows the Fourier transform (FT) of the  $k^3$ -weighted EXAFS spectra of SiO<sub>2</sub>/DABCO/PP-Pd, SiO<sub>2</sub>/PP-Pd, and the reference samples. The spectra of SiO<sub>2</sub>/DABCO/PP-Pd and SiO<sub>2</sub>/PP-Pd have strong peaks at 1.8 Å, together with a weak shoulder around 1.4 Å (Figure 3 A and B). Comparison of spectra (A) and (B) with those of  $[Pd^{II}Cl_2(PPh_3)_2]$  (C) and  $[Pd^{II}Cl(\eta^3-allyl)]_2(D)$  suggested that the aforementioned signals could be assigned to Pd-P or Pd-Cl, denoted as Pd-P/Cl and Pd-C, because the Pd atom in the PP-Pd complex precursor has P, Cl, and C ligands. Figure 3A and B indicates the presence of a Pd-C bond, but the contribution of the Pd-C bond into the first shell is much lower than that of Pd-P/Cl. Therefore, the peak at 1.8 Å in SiO<sub>2</sub>/DABCO/PP-Pd and SiO<sub>2</sub>/PP-Pd was fitted by using the Pd-P/CI parameter. The curve-fitting analysis results of the EXAFS data are summarized in Table 2. In both SiO<sub>2</sub>/DABCO/PP-Pd and SiO<sub>2</sub>/PP-Pd, the peak was well fitted, with a coordination number (N) of approximately 3 and Pd–P/Cl bond length (r) of 2.29 Å. This bond length is close to that of the Pd-P/Cl bond in the [Pd<sup>II</sup>Cl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] reference,<sup>[14]</sup> and the coordination number suggests the presence of two Pd-P bonds and one Pd-Cl bond based on the XPS and elemental analysis data. Conclusively, this curve-fitting result supported the observation that the Pd complex structure was maintained after immobilization onto the SiO<sub>2</sub> surface, both with and without DABCO.

By combining the above elemental analysis, NMR, XPS, and XAFS spectroscopies, we proposed the surface structures of SiO<sub>2</sub>/DABCO/PP-Pd and SiO<sub>2</sub>/PP-Pd as shown in Scheme 1. Based on the elemental analysis results (Table S1), the PP-Pd/DABCO ratio was approximately 1:3 in SiO<sub>2</sub>/DABSO/PP-Pd. The average number of Pd-bisphosphine complex and DABCO moieties were calculated to be 0.6 and 1.8 nm<sup>-2</sup>, respectively. The local structure of the Pd complex was not strongly affect-



**Figure 1.** <sup>13</sup>C NMR spectra for: (A) SiO<sub>2</sub>/CI, (B) SiO<sub>2</sub>/DABCO, (C) PP-Pd, (D) SiO<sub>2</sub>/PP-Pd, and (E) SiO<sub>2</sub>/DABCO/PP-Pd. <sup>13</sup>C CP/MAS NMR was conducted for SiO<sub>2</sub>-supported materials. Asterisks (\*) indicate spinning side bands. <sup>31</sup>P NMR spectra for: (A) PP-Pd in CDCI<sub>3</sub> solution, and <sup>31</sup>P MAS NMR spectra of (B) SiO<sub>2</sub>/PP-Pd and (C) SiO<sub>2</sub>/PP-Pd/DABCO.

Table 1. XPS analysis of SiO <sub>2</sub> -supported Pd catalysts.										
Sample		Bin								
	$Pd_{3d5/2}$	P <sub>2p</sub>	N <sub>1s</sub>	Si <sub>2p</sub>	Cl <sub>2p</sub>					
SiO <sub>2</sub> /DABCO/PP-Pd	337.1	131.3	399.4, 402	103.3	197.8					
SiO <sub>2</sub> /PP-Pd	337.3	131.4	399.5	103.4	198.1					
PdCl <sub>2</sub> <sup>[a]</sup>	338.1	-	-	-	199.2					
[a] Data from ref. [8].										

ed by the presence of quaternarized DABCO on the same surface, indicating that the catalytic activity of the Pd complex should be unchanged in supported Pd complexes, SiO<sub>2</sub>/DABCO/PP-Pd and SiO<sub>2</sub>/PP-Pd. On the other hand, the  $\Delta\sigma^2$  value for SiO<sub>2</sub>/DABCO/PP-Pd was twice that of SiO<sub>2</sub>/PP-Pd (Table 2), implying that the Pd complex structure in SiO<sub>2</sub>/DABCO/PP-Pd was slightly distorted by interactions with co-immobilized DABCO. In other words, the Pd complex and DABCO exist closely in SiO<sub>2</sub>/DABCO/PP-Pd, allowing the potential for dual activation of substrate molecules by both DABCO and the catalytically active Pd complex.

To evaluate the synergistic effect of immobilized DABCO in Pd-catalyzed reactions, the Tsuji-Trost allylation of ethyl ace-

toacetate was conducted by using the prepared SiO<sub>2</sub>-supported Pd complex catalysts. The Tsuji-Trost allylation is wellknown to be accelerated by basic sites, which activate nucleophiles.<sup>[15, 16]</sup> As shown in Scheme 2, SiO<sub>2</sub>/DABCO/PP-Pd achieved a high yield and selectivity for the diallylated product in the reaction. In the absence of DABCO, yield and selectivity were moderate. These results indicated that heterogeneous synergistic catalysis had been created between the PP-Pd complex and DABCO on the silica surface.<sup>[17]</sup> The catalytic activity of the bifunctional catalyst, SiO<sub>2</sub>/DABCO/PP-Pd, was maintained after the reaction, with six subsequent additions of new substrate to the reaction mixture (total amount of ethyl acetoacetate: 19 mmol) inducing further transformation to the corresponding allylated products, achieving turnover numbers (TON) up to > 10000 (Table S3 in the Supporting Information). This high TON and high selectivity to diallylated product clearly demonstrate the higher performance of the new SiO<sub>2</sub>/DABCO/PP-Pd catalyst compared with previously reported Pd catalysts, including our SiO<sub>2</sub>-supported diaminopalladium-tertiary amine bifunctional catalyst.<sup>[6a,b]</sup>

Next, we examined the rarely reported allylation of nitroethane, as shown in Scheme 3. In the case of  $SiO_2/DABCO/PP$ -Pd, a 64% yield of the diallylated product was obtained. In the absence of DABCO, the total yield of allylated products was







Figure 2. Pd K-edge XANES spectra for (A) SiO<sub>2</sub>/DABCO/PP-Pd, (B) SiO<sub>2</sub>/PP-Pd, (C) [Pd<sup>II</sup>Cl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>], (D) [Pd<sup>II</sup>Cl( $\eta^3$ -allyl)]<sub>2</sub>, (E) [(Ph<sub>3</sub>P)<sub>4</sub>Pd<sup>0</sup>], (F) Pd foil, and (G) PdO.

much lower (33%), suggesting that the accelerating effect of DABCO on the allylation reaction also suppressed side reactions. Interestingly, the activity of the homogeneous PP-Pd complex was lower than its  $SiO_2$ -supported counterpart. The product yield increased with the addition of DABCO to homogeneous PP-Pd, but the yield and selectivity were much lower than with  $SiO_2$ /DABCO/PP-Pd.

In summary, a Pd-bisphosphine complex and quaternarized DABCO were successfully immobilized on the same  $SiO_2$  surface. The supported metal complex and organic functionalities were characterized by spectroscopic techniques. The silica-sup-



**Figure 3.** FT of  $k^3$ -weighted Pd K-edge EXAFS spectra for: (A) SiO<sub>2</sub>/DABCO/ PP-Pd, (B) SiO<sub>2</sub>/PP-Pd, (C) [Pd<sup>II</sup>Cl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>], (D) [Pd<sup>II</sup>Cl( $\eta^3$ -allyl)]<sub>2</sub>, (E) [(Ph<sub>3</sub>P)<sub>4</sub>Pd<sup>0</sup>], (F) Pd foil, and (G) PdO. The *k* range for FT was *k*=2.8–15 Å<sup>-1</sup> or 2.8–14 Å<sup>-1</sup> (for (D) and (E)).

ported Pd complex/DABCO catalyst synergistically accelerated Tsuji–Trost allylations.

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Table 2. Curve-fitting analysis of EXAFS spectra for SiO2-supported Pd complexes. <sup>[a]</sup>										
Sample	Shell	<i>N</i> <sup>[b]</sup>	<i>r</i> <sup>[c]</sup> [Å]	$\Delta\sigma^{\mathrm{2[d]}}$ [Å × 10 <sup>-3</sup> ]	$\Delta E$ [eV]	<i>R</i> <sub>f</sub> [%]				
$SiO_2/DABCO/PP-Pd$ $SiO_2/PP-Pd$ $[Pd^{II}CI_2(PPh_3)_2]^{[e]}$	Pd-P/Cl Pd-P/Cl Pd-P Pd-Cl	3.3±0.5 2.7±0.4 2 2	$\begin{array}{c} 2.29 \pm 0.01 \\ 2.29 \pm 0.01 \\ 2.34^{[f]} \\ 2.30^{[f]} \end{array}$	5.43±0.17 2.96±0.14 - -	-2.20 ± 1.94 -8.53 ± 1.97 - -	0.232 0.085 - -				
[a] The fitting range of [d] Debye–Waller factor. [	<i>R</i> -space was 1.4–2.5 e] Data from ref. [14]	Å. The <i>k</i> range for . [f] Average value re	Fourier transformation ported.	was $k = 2.8 - 15 \text{ Å}^{-1}$ . [b] Co	ordination number. [c] B	ond length.				

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Scheme 2. Allylation of ethyl acetoacetate with SiO<sub>2</sub>-supported Pd catalysts.



Scheme 3. Allylation of nitroethane with various catalysts.

**Keywords:** immobilized catalysts • organic bases • Pd complexes • synergistic catalysis • XAFS

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