Equilibrium Study of Pd(dba)₂ and P(OPh)₃ in the Palladium-Catalyzed Allylation of Aniline by Allyl Alcohol

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Supporting Information

Contents:
General Information S-2
Stability of Pd complexes S-3
Preparation of Pd[P(OPh)₃]₃ S-3
Variable-temperature ³¹P NMR study of Pd(dba)₂/P(OPh)₃ S-3
The allylation of aniline by isolated Pd(dba)[P(OPh)₃]₂ S-3
The allylation of aniline by isolated Pd[P(OPh)₃]₃ S-4
ESI-MS Procedures S-4
Reference S-7
Copies of spectral data S-8
X-ray crystal structure analysis of Pd[P(OPh)₃]₃ S-13
X-ray crystal structure analysis of Pd(dba)[P(OPh)₃]₂ S-17
### General Information

All reactions were conducted in oven-dried glassware under an argon atmosphere using standard Schlenk techniques or a nitrogen atmosphere glove box. Solvents were purified by passage through alumina \(^1\) or distilled according to literature procedures. \(^2\) Allylic alcohol was distilled from magnesium and stored under argon. Aniline was distilled under reduced pressure and stored under argon. All other reagents were purchased from commercial suppliers and used without further purification. Toluene-\(d_8\) (C\(_7\)D\(_8\)) was purified by refluxing over sodium metal, distilled under argon atmosphere and stored over molecular sieve (4 Å) prior to use. \(^1\)H NMR spectra were recorded on a Varian 300 (300 MHz), or a Varian 400 (400 MHz), or a Varian 500 (500 MHz) spectrometer. \(^13\)C NMR spectra were recorded on a Varian 300 (75 MHz), or a Varian 400 (101 MHz), or a Varian 500 (126 MHz) spectrometer with complete proton decoupling. Coupling constants (\(J\)) are reported in hertz, and chemical shifts are reported in parts per million (\(\delta\)) using the solvent signal [CDCl\(_3\) (7.26 ppm for \(^1\)H and 77.00 ppm for \(^13\)C), C\(_7\)D\(_8\) (2.09 ppm ppm for \(^1\)H)] and C\(_6\)D\(_6\) (7.16 ppm for \(^1\)H and 128.06 ppm for \(^13\)C)] as an internal reference for \(^1\)H and \(^13\)C and phosphoric acid as an external reference for \(^31\)P. The following abbreviations are used: s = singlet, d = doublet, m = multiplet, and br= broad. IR spectra were recorded on a Perkin Elmer FT-IR Spectrometer. High resolution mass spectra (HRMS) were recorded on a Bruker MicroTOF ESI spectrometer. ESI-MS and MS/MS experiments were performed using a 3200 Q Trap mass spectrometer manufactured by AB Sciex (Concord, ON, Canada). Crystallographic data were collected on a Bruker SMART APEX diffractometer equipped with an APEXII CCD detector, a graphite monochromator and a 3-circles goniometer.
Stability of Pd complexes

Generally, all complexes prepared in situ were stable under strict inert conditions even in solvent. Also, the Pd[P(OPh)$_3$]$_3$ complex was stable under inert conditions. The Pd(dba)[P(OPh)$_3$]$_2$ was very unstable even under inert atmosphere, where equilibration to other complexes and decomposition to palladium black occurred within minutes.

Preparation of Pd[P(OPh)$_3$]$_3$

The complex (Pd[P(OPh)$_3$]$_3$) was prepared according to a literature procedure. The white precipitate was washed by acetone, and recrystallized from hot acetone to give Pd[P(OPh)$_3$]$_3$ (0.218 mg, 55%) as a white solid. $^1$H NMR (300 MHz, C$_6$D$_6$): δ 7.05-7.01 (m, 48H), 6.92-6.88 (m, 12H). $^{13}$C NMR (75 MHz, C$_6$D$_6$): δ 152.4, 129.59, 129.48, 124.1, 121.76, 121.64. $^{31}$P{$^1$H} NMR (121 MHz, C$_6$D$_6$): δ 138.8. MS (ESI-MS) for [C$_{54}$H$_{46}$O$_9$P$_3$Pd]$^+$ 1037.1389, found 1037.1388 (M+H$^+$). NMR Spectral data were in accordance to the literature.

Variable-temperature $^{31}$P NMR study of Pd(dba)$_2$/P(OPh)$_3$

A flame-dried Schlenk tube containing a stir bar was charged with Pd(dba)$_2$ (16 mg, 0.0278 mmol). The tube was capped with a rubber septum, evacuated and backfilled with argon. 0.6 mL of CH$_2$Cl$_2$ and P(OPh)$_3$ (30 µL, 0.112 mmol) was added via syringe. The slurry was degassed by three freeze-pump-thaw cycles and stirred at room temperature for 30 min. The residual was evaporated in vacuo. The complex was dissolve in dry degassed toluene-$d_8$ (C$_7$D$_8$) (2.4 mL). In a glove box, C$_7$D$_8$ stock solution of Pd(0) complex (0.6 mL of a 11.6 mM solution) was added to the NMR tube. The NMR tube was shaken, and inserted into the spectrometer pre-cooled to -60 ºC. The sample was allowed to equilibrate in the spectrometer for 10 min before acquiring spectra. The equilibrium of Pd(0) species was studied by $^{31}$P NMR spectroscopy at -60 ºC, -40 ºC, -20 ºC and 25 ºC.

The allylation of aniline by isolated Pd(dba)[P(OPh)$_3$]$_2$

A flame-dried Schlenk tube was charged with Pd(dba)[P(OPh)$_3$]$_2$ (8 mg, 0.00878 mmol), dissolved in 2.0 mL of C$_6$D$_6$, and aniline (40 µL, 0.439 mmol) was added via syringe. The slurry was degassed by three freeze-pump-thaw cycles. Degassed allyl alcohol (120 µL, 1.764 mmol)
was added via syringe and the mixture was stirred at 60 °C. The reaction was followed with $^1$H NMR spectroscopy by integrating the ratio of $N$-allylaniline at $\delta$ 3.35, and $N,N$-diallylaniline at $\delta$ 3.60 and the ferrocene signal at $\delta$ 4.00.

**The allylation of aniline by isolated Pd[P(OPh)$_3$)$_3$**

A flame-dried Schlenk tube was charged with Pd[P(OPh)$_3$)$_3$ (9 mg, 0.00878 mmol), dissolved in 2.0 mL of C$_6$D$_6$, and aniline (40 µL, 0.439 mmol) was added via syringe. The slurry was degassed by three freeze-pump-thaw cycles. Degassed allyl alcohol (120 µL, 1.764 mmol) was added via syringe and the mixture was stirred at 60 °C. The reaction was followed with $^1$H NMR spectroscopy by integrating the ratio of $N$-allylaniline at $\delta$ 3.35, and $N,N$-diallylaniline at $\delta$ 3.60 and the ferrocene signal at $\delta$ 4.00.

**ESI-MS Procedures**

**Allylation of allyl alcohol by Pd(dba)[P(OPh)$_3$]$_2$ complex generated in situ from Pd(dba)$_2$ and P(OPh)$_3$,**

According to the general procedure, Pd(dba)[P(OPh)$_3$]$_2$ (0.0175 mmol) generated in situ from Pd(dba)$_2$ and P(OPh)$_3$, and allylic alcohol (100 µL, 1.5 mmol) was stirred at 60 °C for 5 min.

**Allylation of allyl alcohol by isolated Pd[P(OPh)$_3$]$_3$**

According to the general procedure, Pd[P(OPh)$_3$]$_3$ (0.0175 mmol) and allylic alcohol (100 µL, 1.5 mmol) was stirred at 60 °C for 5 min.

**ESI-MS analysis**

An aliquot of the reaction mixture (50 µL) was diluted with dry degassed toluene (0.5 mL) in an pre-dried vial and analyzed by ESI(+)MS. The reaction mixture was introduced by continuous infusion with the aid of a syringe pump at a flow-rate of 10 µL/min through a fused silica capillary (with a 50 µm inner and a 184 µm outer diameter). The ion source used was a Turbo V source in positive ESI mode. The following MS conditions were used: temperature (TEM) ambient, curtain gas (CUR) 15 psi, ion source gas 1 (GS1) 5 psi, ion source gas 2 (GS2) 10 psi,
ion spray voltage (IS) 5500 V, the declustering potential (DP) was 40 V and entrance potential (EP) 10 V for all measurements. MS data were collected in enhanced MS mode (EMS) and MS/MS data were collected in enhanced product ion mode (EPI). The collision gas parameter (CAD) was set to high for EMS (linear ion trap MS scan) and an arbitrary number, 11, for the EPI, which corresponds to a pressure reading of 4.1•10^-5 Torr. The collision energy (CE) was 25 eV for all experiments aside from the EMS where it was set to 10 eV. Acquisition and processing of the MS data was performed with Analyst 1.4.2 (AB Sciex).
Figure S1: CID mass spectrum of the signal at (a) m/z 457 (b) m/z 691 (c) m/z 767 and m/z 792 of allylation of allyl alcohol by Pd[P(OMe)3]3.
**Figure S2:** CID mass spectrum of the signal at m/z 691 of allylation of allyl alcohol by in situ generated Pd[P(OPh)₃]₃ from Pd(dba)₂ + P(OPh)₃ (4 equiv relative to Pd).

**Reference**

1. Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.
2. Armarego, W. L. F.; Chai, C. L. L. *Purification of Laboratory Chemicals*, 5th ed.; Butterworth-Heinemann: London, 2003.
3. Kayaki, Y.; Koda, T.; Ikariya, T. *J. Org. Chem.* **2004**, *69*, 2595.
Figure S3. $^1$H NMR spectra of Pd(P(OPh)$_3$)$_3$
Figure S4. $^{13}$C NMR spectra of Pd(P(OPh)$_3$)$_3$
Figure S5. $^{31}$P NMR spectra of Pd(P(O)(Ph)$_3$)$_3$
Figure S6. $^1$H NMR spectra of Pd(dba)(P(OPh)$_3$)$_2$
Figure S7. $^{31}$P NMR spectra of Pd(dba)(P(OPh)$_3$)$_2$. 
X-ray crystal structure analysis of Pd(P(OPh)\textsubscript{3})\textsubscript{3} and Pd(dba)[P(OPh)\textsubscript{3}]\textsubscript{2}

Crystallographic data sets were collected from single crystal samples mounted on a loop fiber and coated with Fomblin® (molecular weight 6 300 Da) at 100(2)K. Collection was performed using a Bruker SMART APEX diffractometer equipped with an APEXII CCD detector, a graphite monochromator and a 3-circles goniometer. The crystal-to-detector distance was 5.0 cm, and the data collection was carried out in 512 x 512 pixel mode. The initial unit cell parameters were determined by a least-squares fit of the angular setting of strong reflections, collected by a 10.0 degrees scan in 12 frames over three different parts of the reciprocal space (36 frames total). Cell refinement and data reduction were performed with SAINT V7.68A (Bruker AXS).\textsuperscript{1} Absorption correction was done by multi-scan methods using SADABS.\textsuperscript{2} The structure was solved by direct methods and refined using SHELX-2013\textsuperscript{3} using WinGX.\textsuperscript{4} Graphical representations are prepared with ORTEP\textsuperscript{5} for Windows and POV-Ray. All non-H atoms were refined by full-matrix least-squares with anisotropic displacement parameters while hydrogen atoms were placed in idealized positions. Refinement of F2 was performed against all reflections. The weighted R-factor wR and goodness of fit S are based on F2. Full details concerning the data sets and crystal resolutions can be found in the respective CIF files deposited at the Cambridge Crystallographic Data Centre under the allocated deposition numbers CCDC (963489) and (963490) for Pd\{P(OPh)\textsubscript{3}\}\textsubscript{3} and Pd(dba)[P(OPh)\textsubscript{3}]\textsubscript{2}.

Pd\{P(OPh)\textsubscript{3}\}\textsubscript{3}:

![ORTEP representation of Pd\{P(OPh)\textsubscript{3}\}\textsubscript{3} at thermal ellipsoids of 50%. Only one of the two independent units is displayed. Hydrogen atoms and acetone solvate molecules are omitted for clarity.]

Selected bond lengths and angles:

\begin{tabular}{ll}
P1 & \text{- Pd1} 2.2501(  2) \\
P2 & \text{- Pd1} 2.2525(  3) \\
P3 & \text{- Pd1} 2.2572(  3) \\
P4 & \text{- Pd2} 2.2437(  2) \\
P5 & \text{- Pd2} 2.2430(  3) \\
P6 & \text{- Pd2} 2.2498(  3) \\
\end{tabular}
| Atoms | Bond Lengths (Å) |
|-------|-----------------|
| O1    | P1 1.6160(2)    |
| O2    | P1 1.6438(2)    |
| O3    | P1 1.6275(2)    |
| O4    | P2 1.6307(2)    |
| O5    | P2 1.6308(1)    |
| O6    | P2 1.6087(2)    |
| O7    | P3 1.6202(1)    |
| O8    | P3 1.6211(2)    |
| O9    | P3 1.6373(2)    |
| P1    | Pd1 2.2501(2)   |
| P2    | Pd1 2.2525(3)   |
| P3    | Pd1 2.2572(3)   |
| C1    | O1 124.56(1)    |
| C7    | O2 120.47(1)    |
| C13   | O3 121.80(1)    |
| C19   | O4 125.75(1)    |
| C25   | O5 119.92(1)    |
| C31   | O6 123.19(1)    |
| C37   | O7 122.80(2)    |
| C43   | O8 122.32(1)    |
| C49   | O9 118.15(1)    |
| O1    | P1 100.55(1)    |
| O1    | P1 98.37(1)     |
| O1    | Pd1 118.48(1)   |
| O2    | P1 97.33(1)     |
| O2    | Pd1 117.70(1)   |
| O3    | P1 120.19(1)    |
| O4    | P2 97.41(1)     |
| O4    | P2 96.42(1)     |
| O4    | P2 123.99(1)    |
| O5    | P2 100.73(1)    |
| O5    | P2 117.67(1)    |
| O6    | P2 116.07(1)    |
| O7    | P3 96.97(1)     |
| O7    | P3 102.37(1)    |
| O7    | Pd1 118.78(1)   |
| O8    | P3 96.94(1)     |
| O8    | P3 121.09(1)    |
| O9    | P3 116.52(1)    |
| P1    | Pd1 116.02(1)   |
| P1    | Pd1 120.93(1)   |
| P2    | Pd1 122.94(1)   |
| O10   | P4 96.79(1)     |
| Identification code | josa2_1 |
|---------------------|---------|
| **CCDC**            |         |
| **Empirical formula** | C_{54}H_{45}O_{9}P_{3}Pd, C_{3}H_{6}O |
| **Formula weight**  | 1095.28 |
| **Crystal description** | Colorless block |
| **Crystal size [mm]**  | 0.28x0.33x0.40 |
| **Crystal system, space group** | Orthorhombic, Pna21 |
| **Unit cell dimensions:** | |
| a                   | 19.337(3) |
| b                   | 12.3753(19) |
| c                   | 43.227(6) |
| α, β, γ             | 90 |
| **Volume [Å³]**     | 10344(3) |
| Z                   | 8 |
| **Calculated density [Mg/m³]** | 1.407 |
| **F(000)**          | 4512 |
| **Linear absorption coefficient μ** | 0.511 |
| Absorption correction          | Multi-scan       |
|-------------------------------|-----------------|
| Min. and max. transmission    | 0.6399 / 0.7461  |
| Temperature                   | 100(2)          |
| Diffractometer                | Bruker SMART –APEX-II |
| Radiation source              | Mo Kα          |
| Radiation and wavelength      | 0.71073         |
| Scan type                     | φ-ω-scan        |
| Range for data collection θ   | 0.99-29.99      |
| Index ranges                  | -27≤h≤16, -15≤k≤16, -53≤l≤56 |
| Reflections collected / unique| 51885, 24778    |
| Significant unique reflections| 20826           |
| R(int), R(sigma)              | 0.0540, 0.0815  |
| Completeness                  | 0.949           |
| Θ-max                         | 29.99           |
| Refinement method             | Full-matrix least-squares on F² |
| Data / parameters / restraints| 24778/1283/0    |
| Goodness-of-fit on F²         | 1.024           |
| Final R indices [I > (I)]σ2   | 0.0468          |
| R indices (all data)          | 0.1062          |
| Weighting scheme              | w=1/[σ²(Fo²)+(aP)²] where P=(Fo²+2Fc²)/3 |
| Weighting scheme parameters a | 0.0411,         |
| Largest/mean σ/Δ in last cycle| 0.025/0.0      |
| Largest difference peak and hole| 0.757 / -0.706 |
| Structure Solution Program    | ShelXS-2013     |
| Structure Refinement Program  | ShelXL-2013     |
**Pd(dba)[P(OPh)₃]₂:**

![ORTEP representation of Pd(dba)[P(OPh)₃]₂](image)

**Figure S9.** ORTEP representation of Pd(dba)[P(OPh)₃]₂ at thermal ellipsoids of 50%. Only one of the two independent units is displayed. Hydrogen atoms and acetone solvate molecules are omitted for clarity.

Selected bond lengths and angles:

| Bond    | Length (Å) | Error (Å) |
|---------|------------|-----------|
| Pd - C97 | 2.126(15)  |           |
| Pd - C98 | 2.159(15)  |           |
| Pd - P1  | 2.247(5)   |           |
| Pd - P2  | 2.254(5)   |           |
| P1 - O20 | 1.589(11)  |           |
| P1 - O30 | 1.594(11)  |           |
| P1 - O10 | 1.621(10)  |           |
| O10 - C11| 1.390(11)  |           |
| O30 - C31| 1.376(12)  |           |
| P2 - O50 | 1.585(11)  |           |
| P2 - O60 | 1.590(10)  |           |
| P2 - O40 | 1.615(10)  |           |
| C105 - C10| 1.329(19)  |           |
| C106 - C107| 1.406(19) |           |
| C107 - C108| 1.372(2)  |           |
| Cl(1A) - C1| 1.749(16)  |           |
| C1 - Cl(1B)| 1.762(16) |           |
| C97 - Pd | C98       | 36.7(5)   |
| C97 - Pd | - P1      | 151.3(5)  |
| C98 - Pd | - P1      | 115.4(5)  |
| C97 - Pd | - P2      | 102.7(5)  |
| C98 - Pd | - P2      | 139.3(5)  |
| P1 - Pd  | - P2      | 105.14(17)|
O20 -P1 -O30 98.4(6)  
O20 -P1 -O10 102.9(5)  
O30 -P(1) -O10 96.4(5)  
O20 -P1 -Pd 111.0(4)  
O30 -P1 -Pd 124.8(4)  
O10 -P(1) -Pd 119.5(4)  
C11 -O10 -P1 121.6(8)  
C21 -O20 -P1 124.7(8)  
O20 -C21 -C22 120.9(8)  
C31 -O30 -P1 122.6(8)  
O30 -C31 -C32 118.6(9)  
O30 -C31 -C36 121.1(9)  
O50 -P2 -O60 100.3(6)  
O50 -P2 -O40 95.8(5)  
O60 -P2 -O40 104.5(5)  
O50 -P2 -Pd 118.7(4)  
O60 -P2 -Pd 112.0(4)  
O40 -P2 -Pd 122.2(4)  
C41 -O40 -P2 124.7(8)  
C61 -O60 -P2 123.8(8)  
C62 -C61 -O60 122.0(8)  
C66 -C61 -O60 117.9(8)  
C98 -C97 -Pd 73.0(9)  
C91 -C97 -Pd 113.8(11)  
C97 -C98 -Pd 70.3(9)  
C99 -C(98) -Pd 106.6(10)  

| Identification code | josa2_2 |
|---------------------|---------|
| CCDC                | 963490  |
| Empirical formula   | C_{55} H_{48} Cl_{14} O_{7} P_{2} Pd |
| Formula weight      | 1131.07 |
| Crystal description | Colorless block |
| Crystal size [mm]   | 0.1x0.05x0.04 |
| Crystal system, space group | Monoclinic, P21/n |
| Unit cell dimensions: | a | 13.8329(8) |
|                      | b | 25.3965(15) |
|                      | c | 14.4809(7)  |
|                      | α, β, γ | 90 |
| Volume [Å³]         | 5040.7(5) |
| Z                   | 4 |
| Calculated density [Mg/m³] | 1.490 |
|                                |       |
|--------------------------------|-------|
| **F(000)**                    | 2312  |
| Linear absorption coefficient $\mu$ | 0.511 |
| Absorption correction         | Multi-scan |
| Min. and max. transmission     | 0.6399 / 0.7461 |
| Temperature                   | 100(2) |
| Diffractometer                | Bruker SMART - APEX-II |
| Radiation source              | Mo $K\alpha$ |
| Radiation and wavelength      | 0.71073 |
| Scan type                     | $\phi$ / $\omega$-scan |
| Range for data collection $\Theta$ | 3.22-15.86 |
| Index ranges                  | $-10 \leq h \leq 10$, $-19 \leq k \leq 19$, $-11 \leq l \leq 10$ |
| Reflections collected / unique| 9269, 2391 |
| $R$(int), $R$(sigma)           | 0.0745, 0.1416 |
| Completeness                  | 15.86, 99.1% |
| Refinement method             | Full-matrix least-squares on $F^2$ |
| Data / parameters / restraints | 24778/1283/0 |
| Goodness-of-fit on $F^2$       | 1.175 |
| Final $R$ indices [I > (I)]$\sigma^2$ | 0.0745 |
| $R$ indices (all data)        | 0.1416 |
| Largest difference peak and hole | 0.542 / -0.387 |
| Structure Solution Program    | ShelXS-2013 |
| Structure Refinement Program  | ShelXL-2013 |