*Supporting Information*

# Syntheses of Pd(II)/Pt(II) Complexes with non-Chelating 4-Pyridylselenolate Ligand ranging from Mononuclear to Macrocyclic Structures and their utility as Catalysts in Suzuki C–C Coupling Reaction

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## Supporting Information

**General Procedures:** Solvents were dried and distilled prior to use by standard methods. All reactions were carried out in Schlenk flasks under a nitrogen atmosphere. 4-Bromopyridine, 1-(4-pyridyl)-pyridinium chloride hydrochloride, silver triflate, sodium borohydride were used as purchased from commercial sources without further purification. The complexes *cis*-$[MCl_2(PR_3)_2]$, *cis*-$[MCl_2(P^{\frown}P)]$, $[M_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2]$ (M = Pd, Pt; $PR_3$ = $PEt_3$, $PMe_2Ph$, $PPh_3$; $P^{\frown}P$ = dppm, dppe, dppp)[s1-3] and *cis*-$[Pt(PEt_3)_2(OTf)_2]$[s4] (OTf = $CF_3SO_3^-$) were prepared according the literature methods. Melting points were determined in capillary tubes and are uncorrected. Elemental analysis for C, H, N and S were carried out on an Carlo-Erba EA-1110 CHNS Analyser. Absorption spectra were recorded on a JASCO aaaaaV-630 spectrophotometer. Infrared spectra were recorded with a JASCO FTIR-6100 spectrometer. Mass spectra were recorded on a Waters Q-TOF micro (YA-105) time of flight mass spectrometer. $^1H$, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, $^{77}Se\{^1H\}$ and $^{195}Pt\{^1H\}$ NMR spectra were recorded on a Bruker Avance II-300 NMR spectrometers operating at 300, 75.47, 121.5, 57.25, 64.29 MHz, respectively. Chemical shifts are relative to internal chloroform peak (δ 7.26 $^1H$ and

77.0 for $^{13}C$), external 85% $H_3PO_4$ for $^{31}P\{^1H\}$, external $Ph_2Se_2$ in $CDCl_3$ for $^{77}Se\{^1H\}$ ( δ 463 relative to $Me_2Se_2$ as 0 ppm) and $Na_2PtCl_6$ for $^{195}Pt\{^1H\}$.

**Crystallography**

**A.** Crystals of *trans*-[Pt(4-$SeC_5H_4N)_2(PEt_3)_2$] were grown from a dichloromethane-hexane mixture at room temperature. Data were collected as outlined in Table 1. Cell parameters were obtained from 60 data frames taken at widths of 0.5°. Integrated intensity information for each reflection was obtained by reduction of the data frames with the program APEX2. Data were collected for Lorentz and polarization factors, and using SADABS.[s6] absorption and crystal decay effects. The structure was solved by direct methods using SHELXTL (XS).[s7] All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were placed in idealized positions, and refined using a riding model. The parameters were refined by weighted least squares refinement on $F^2$ to convergence.[s7]

**B.** Crystals of *trans*-[PtCl(4-$SeC_5H_4N)(PEt_3)_2$] were grown in a tightly sealed round bottomed flask kept at -5°C. Data were collected as outlined in Table 1. Cell parameters were obtained from 60 data frames taken at widths of 0.5°. Integrated intensity information for each reflection was obtained by reduction of the data frames with the program APEX2. Data were collected for Lorentz and polarization factors, and using SADABS.[s6] absorption and crystal decay effects. The structure was solved by direct methods using SHELXTL.[s7] All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were placed in idealized positions, and refined using a riding model. The parameters were refined by weighted least squares refinement on $F^2$ to convergence.[s7]

**C.** Crystals of [Pt(4-$SeC_5H_4N)_2$(dppp)] were grown by slow evaporation of solvent mixture of acetone-hexane at room temperature. Data were collected as outlined in Table 1. Cell parameters were obtained from 180 data frames taken at widths of 0.5$^o$. Integrated intensity information for each reflection was obtained by reduction of the data frames with the program APEX2. TWINABS was used for adsorption correction as well as to separate one twin component. The integration method employed a three dimensional profiling algorithm and all the data were collected for Lorentz and polarization factors, as well as for crystal decay effects. The structure was solved by direct methods using SHELXTL.[s7] All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were placed in idealized positions, and were set riding on the parent atom. The parameters were refined by weighted least squares refinement on $F^2$ to convergence.[s7] Olex2 was employed for the final data presentation and structure plots.[s8]

**D.** Crystals of *trans*-[Pd(4-$SeC_5H_4N)_2(PPh_3)_2$] were grown in a tightly sealed round bottomed flask kept at -5$^o$C. Data were collected as outlined in Table 1. Cell parameters were obtained from 60 data frames taken at widths of 0.5$^o$. Integrated intensity information for each reflection was obtained by reduction of the data frames with the program APEX2. Data were collected for Lorentz and polarization factors, and using SADABS.[s6] absorption and crystal decay effects. The structure was solved by direct methods using SHELXTL (XS).[s7] All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were placed in idealized positions, and refined using a riding model. The parameters were refined by weighted least squares refinement on $F^2$ to convergence.[s7] Olex2 was employed for the final data presentation and structure plots.[s8]

**E.** Crystals of *trans*-[PdCl(4-$SeC_5H_4N)(PPh_3)_2$] were grown from dichloromethane-hexane solvent mixture at room temperature. Data were collected as outlined in Table 1. Cell

parameters were obtained from 180 data frames taken at widths of 0.5°. Integrated intensity information for each reflection was obtained by reduction of the data frames with the program APEX2. The integration method employed a three dimensional profiling algorithm and all the data were collected for Lorentz and polarization factors, as well as for crystal decay effects. Finally the data was merged and scaled to produce a suitable data set SADABS.[s6] was used to correct the data for absorption effects. The structure was solved by direct methods using SHELXTL.[s7] All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were placed in idealized positions, and refined using a riding model. The parameters were refined by weighted least squares refinement on $F^2$ to convergence.[s7] X-seed was employed for the final data presentation and structure plots.[s9]

**F.** Crystals of [Pd(4-$SeC_5H_4N)_2$(dppe)] were grown by slow evaporation of solvent mixture of acetone-hexane at room temperature. Crystal data were collected as outlined in Table 1. Cell parameters were obtained from 180 data frames taken at widths of 0.5°. Integrated intensity information for each reflection was obtained by reduction of the data frames with the program APEX2. TWINABS was used for adsorption correction as well as to separate one twin component. The integration method employed a three dimensional profiling algorithm and all the data were collected for Lorentz and polarization factors, as well as for crystal decay effects. Finally the data was merged and scaled to produce a suitable data set. TWINABS was used to correct the data for absorption effects as well as to separate the twin components. The structure was solved by direct methods using SHELXTL.[s7] All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in idealized positions, and were set riding on the parent atom. The parameters were

refined by weighted least squares refinement on $F^2$ to convergence.[s7] Olex2 was employed for the final data presentation and structure plots.[s8]

**G.** Crystals of $[PdCl(4\text{-}SeC_5H_4N)(PPh_3)]_2$ were grown from dichloromethane-hexane solvent mixture at room temperature. Data were collected as outlined in Table 1. Cell parameters were obtained from 60 data frames taken at widths of $0.5^o$. Integrated intensity information for each reflection was obtained by reduction of the data frames with the program APEX2. The integration method employed a three dimensional profiling algorithm and all the data were collected for Lorentz and polarization factors, as well as for crystal decay effects. Finally the data was merged and scaled to produce a suitable data set. The absorption correction program SADABS.[s6] was employed to correct the data for absorption effects. The structure was solved by direct methods using SHELXTL (XS).[s7] All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were placed in idealized positions, and were set riding on the respective parent atoms. The parameters were refined by weighted least squares refinement on $F^2$ to convergence.[s7] Olex2 was employed for the final data presentation and structure plots.[s8]

**H.** The crystals of $[PdCl(SeC_5H_4N)(PEt_3)]_3$ and $[PtCl(SeC_5H_4N)(PEt_3)]_3$ were isolated from dichloromethane-hexane solvent mixture and $CDCl_3$ solution (in NMR tube), respectively at room temperature.

**References:**

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(s8) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, "OLEX2: A Complete Structure Solution, Refinement and Analysis Program", *J. Appl. Cryst*., 2009, **42**, 339-341.

(s9) L. J. Barbour (2001) "X-Seed (version 2.0): A Software Tool for Supramolecular Crystallography" *J. Supramol. Chem*., 2001, **1**, 189-191.

**Table S1**. Crystallographic and structure refinement data for complexes

| Compound | [PdCl(4-$SeC_5H_4N$)($PPh_3$)$_2$]·acetone | [PtCl(4-$SeC_5H_4N$)($PEt_3$)$_2$] | [Pd($PPh_3$)$_2$(4-$SeC_5H_4N$)$_2$] | [Pt($PEt_3$)$_2$(4-$SeC_5H_4N$)$_2$] |
|---|---|---|---|---|
| Chemical formula | $C_{44}H_{40}ClNOP_2PdSe$ | $C_{17}H_{34}ClNP_2PtSe$ | $C_{46}H_{38}N_2P_2PdSe_2$ | $C_{22}H_{38}N_2P_2PtSe_2$ |
| Formula weight | 881.52 | 623.89 | 945.04 | 745.49 |
| Crystal Size ($mm^3$) | 0.12 × 0.06 × 0.03 | 0.42 × 0.31 × 0.25 | 0.50 × 0.43 × 0.16 | 0.43 × 0.41 × 0.24 |
| Diffractometer | BRUKER GADDS | BRUKER APEX 2 | BRUKER APEX 2 | BRUKER APEX 2 |
| T/K | 110(2) | 110(2) | 110(2) | 110(2) |
| λ/Å | 1.54178 | 0.71073 | 0.71073 | 0.71073 |
| Crystal system | Monoclinic | Monoclinic | Monoclinic | Orthorhombic |
| Space group | P2(1)/n | P2(1)/n | P2(1) | Pca2(1) |
| a/Å | 10.4301(3) | 14.4320(6) | 10.1330(11) | 19.975(3) |
| b/Å | 16.8918(6) | 10.6073(5) | 12.8723(14) | 9.0763(15) |
| c/Å | 43.8939(14) | 15.4103(7) | 15.0542(16) | 14.380(2) |
| α/° | 90 | 90 | 90 | 90 |
| β/$^0$ | 93.019(2) | 105.0360(10) | 91.1260 | 90 |
| γ/$^0$ | 90 | 90 | 90 | 90 |
| V/$Å^3$ | 7722.6(4) | 2278.31(18) | 1963.2(4) | 2607.1(7) |
| $\rho_{calc}$, g $cm^{-3}$ | 1.516 | 1.819 | 1.599 | 1.899 |
| Z | 8 | 4 | 2 | 4 |
| μ/$mm^{-1}$ | 6.646 | 8.014 | 2.444 | 8.309 |
| Reflections collected | 135477 | 47227 | 30774 | 27666 |
| Data/restraints /parameters | 11447 / 0 / 923 | 5237 / 2 / 222 | 8936 / 1 / 479 | 5919 / 15 / 262 |
| Final R1,*w*R2 indices | R1 = 0.0382, wR2 = 0.0863 | R1 = 0.0162, wR2 = 0.0396 | R1 = 0.0440, wR2 = 0.1128 | R1 = 0.0238, wR2 = 0.0499 |
| $R_1$, $wR_2$ (all data) | R1 = 0.0511, wR2 = 0.0894 | R1 = 0.0177, wR2 = 0.0405 | R1 = 0.0485, wR2 = 0.1162 | R1 = 0.0281, wR2 = 0.0511 |
| Largest diff.peak & hole [e$Å^{-3}$] | 0.408 and -0.822 | 0.675 and -0.985 | 3.155 and -0.849 | 1.445 and -1.015 |

**Table S2**. Crystallographic and structure refinement data for complexes

| Compound | [Pd(dppe)(4-$SeC_5H_4N)_2$]·$2H_2O$ | [Pt(dppp)(4-$SeC_5H_4N)_2$]·$0.5H_2O$ | [PdCl(4-$SeC_5H_4N$)($PPh_3$)]$_2$ |
|---|---|---|---|
| Chemical formula | $C_{36}H_{36}N_2O_2P_2PdSe_2$ | $C_{37}H_{35}N_2O_{0.5}P_2PtSe_2$ | $C_{46}H_{38}Cl_2N_2P_2Pd_2Se_2$ |
| Formula weight | 854.93 | 930.62 | 1122.34 |
| Crystal Size ($mm^3$) | 0.13 × 0.08 × 0.03 | 0.06 × 0.05 × 0.03 | 0.25 × 0.18 × 0.12 |
| Diffractometer | BRUKER GADDS | BRUKER GADDS | BRUKER APEX 2 |
| T/K | 110(2) | 110(2) | 110(2) |
| λ/Å | 1.54178 | 1.54178 | 0.71073 |
| Crystal system | Monoclinic | Triclinic | Monoclinic |
| Space group | P2(1)/c | P-1 | P2(1)/n |
| a/Å | 15.7931(8) | 10.5487(12) | 10.1799(12) |
| b/Å | 10.5303(5) | 10.7006(13) | 14.6690(17) |
| c/Å | 21.2888(11) | 14.9796(16) | 14.8568(17) |
| α/° | 90 | 91.771(9) | 90 |
| β/$^0$ | 105.650(3) | 94.027(9) | 93.4050 |
| γ/$^0$ | 90 | 95.391(9) | 90 |
| V/$Å^3$ | 3409.2(3) | 1678.0(3) | 2214.6(4) |
| $\rho_{calc}$, g $cm^{-3}$ | 1.666 | 1.842 | 1.683 |
| Z | 4 | 2 | 2 |
| μ/$mm^{-1}$ | 7.999 | 11.443 | 2.683 |
| Reflections collected | 9607 | 9931 | 24421 |
| Data/restraints/parameters | 5063 / 0 / 406 | 9942 / 0 / 407 | 5068 / 0 / 253 |
| Final R1,*w*R2 indices | R1 = 0.0347, wR2 = 0.0828 | R1 = 0.0373, wR2 = 0.1104 | R1 = 0.0178, wR2 = 0.0437 |
| $R_1$, $wR_2$ (all data) | R1 = 0.0446, wR2 = 0.0848v | R1 = 0.0423, wR2 = 0.1151 | R1 = 0.0193, wR2 = 0.0443 |
| Largest diff.peak & hole [e$Å^{-3}$] | 1.067 and -0.774 | 1.065 and -1.036 | 0.492 and -0.445 |

**Table S3**. Crystallographic and structure refinement data for complexes

| Compound | [PdCl(4-$SeC_5H_4N$)($PEt_3$)]$_3$ | [PtCl(4-$SeC_5H_4N$)($PEt_3$)]$_3$•$CHCl_3$ |
|---|---|---|
| Chemical formula | $C_{33}H_{57}Cl_3N_3P_3Pd_3Se_3$ | $C_{34}H_{58}Cl_6N_3P_3Pt_3Se_3$ |
| Formula weight | 1251.16 | 1636.59 |
| Crystal Size ($mm^3$) | 0.25 × 0.20 × 0.10 | 0.30 × 0.15 × 0.15 |
| Diffractometer | RIGAKU AFC7S | RIGAKU AFC7S |
| T/K | 298 (2) | 298 (2) |
| λ/Å | 0.71069 | 0.71069 |
| Crystal system | Monoclinic | Monoclinic |
| Space group | P 1 21/n 1 | P 1 21/a 1 |
| a/Å | 14.2500(12) | 14.501(3) |
| b/Å | 13.984(6) | 24.574(3) |
| c/Å | 24.400(5) | 14.763(4) |
| α/$^o$ | 90 | 90 |
| β/$^0$ | 105.330(13) | 102.72(2) |
| γ/$^0$ | 90 | 90 |
| V/$Å^3$ | 4689(2) | 5131.7(18) |
| $\rho_{calc}$, g $cm^{-3}$ | 1.772 | 2.026 |
| Z | 4 | 4 |
| μ/$mm^{-1}$ | 3.766 | 10.567 |
| Reflections collected | 14523 | 14086 |
| Data/restraints/parameters | 10760/20/410 | 11757/63/363 |
| Final R1,*w*R2 indices | 0.0745, 0.1409 | 0.0696, 0.1331 |
| $R_1$, $wR_2$ (all data) | 0.1803, 0.3474 | 0.2161, 0.3843 |
| Largest diff.peak & hole [e$Å^{-3}$] | 1.032 & -0.886 | 1.000, -1.247 |

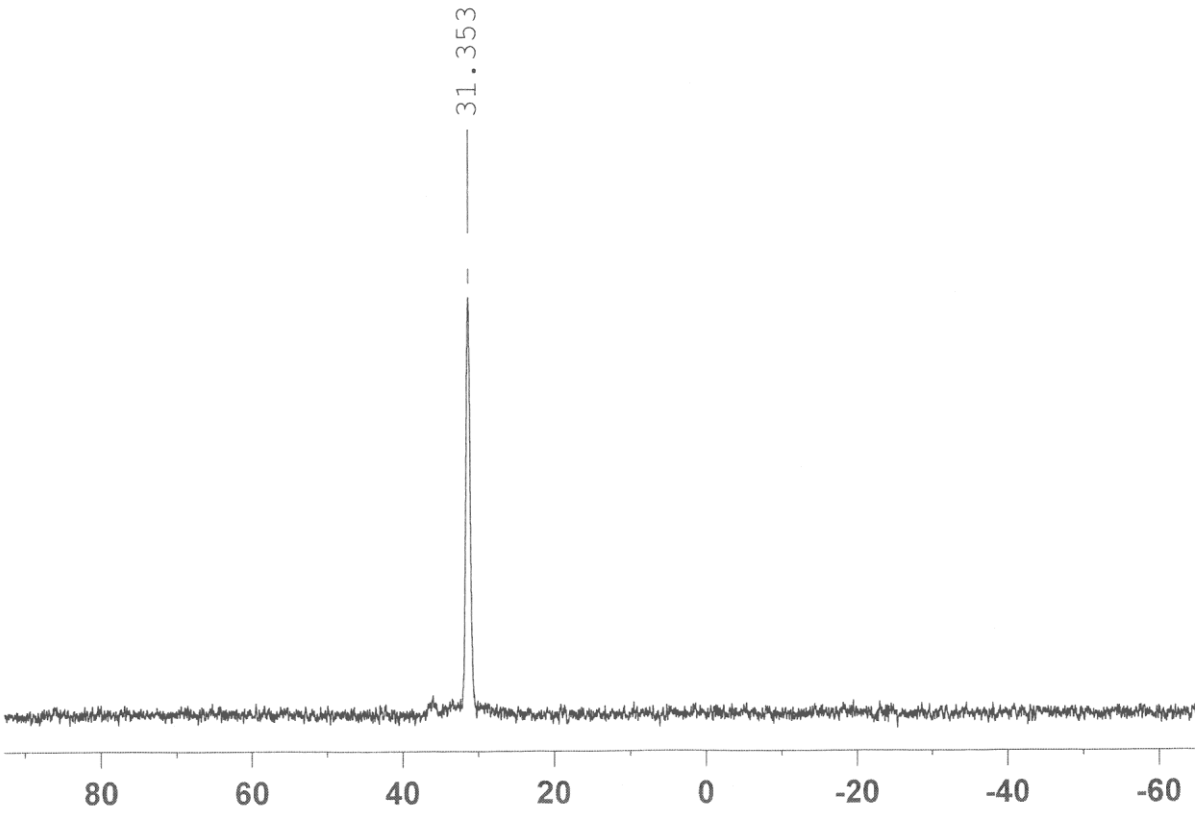


**Figure S1.** $^{31}P\{^{1}H\}$ NMR spectra of $[PdCl(4\text{-}SeC_5H_4N)(PEt_3)]_n$ in $CDCl_3$

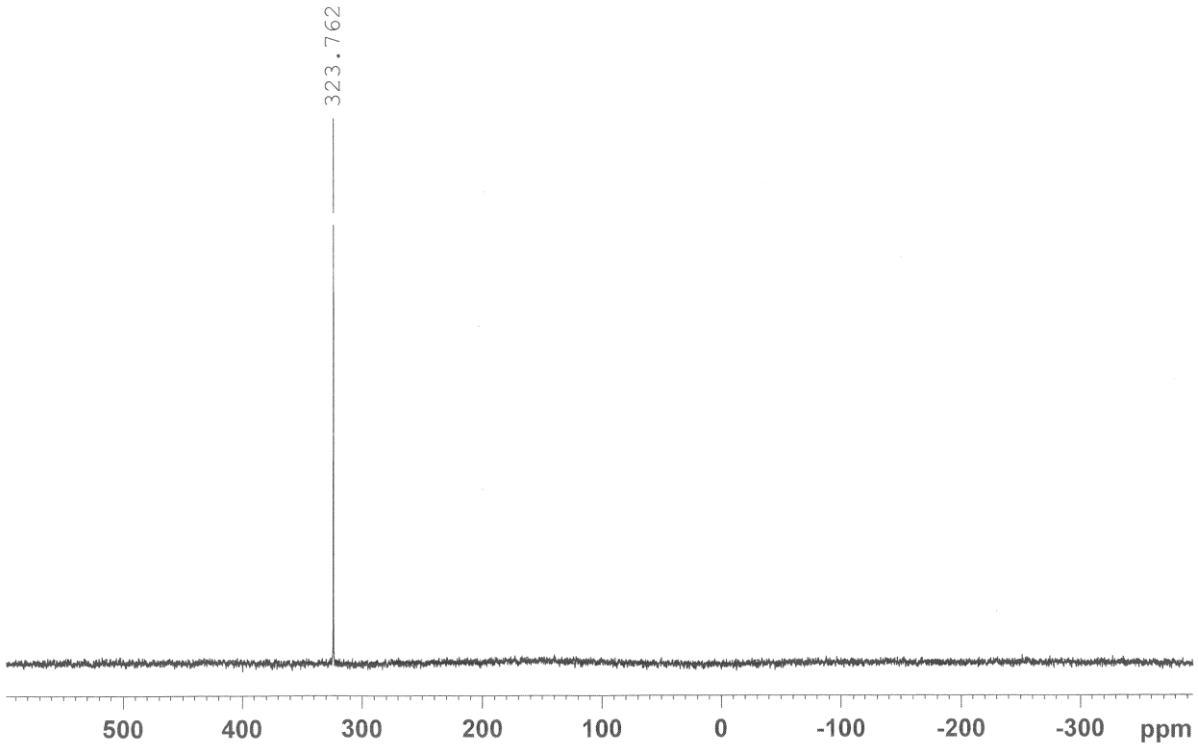


**Figure S2.** $^{77}Se\{^{1}H\}$ NMR spectra of $[PdCl(4\text{-}SeC_5H_4N)(PEt_3)]_n$ in $CDCl_3$

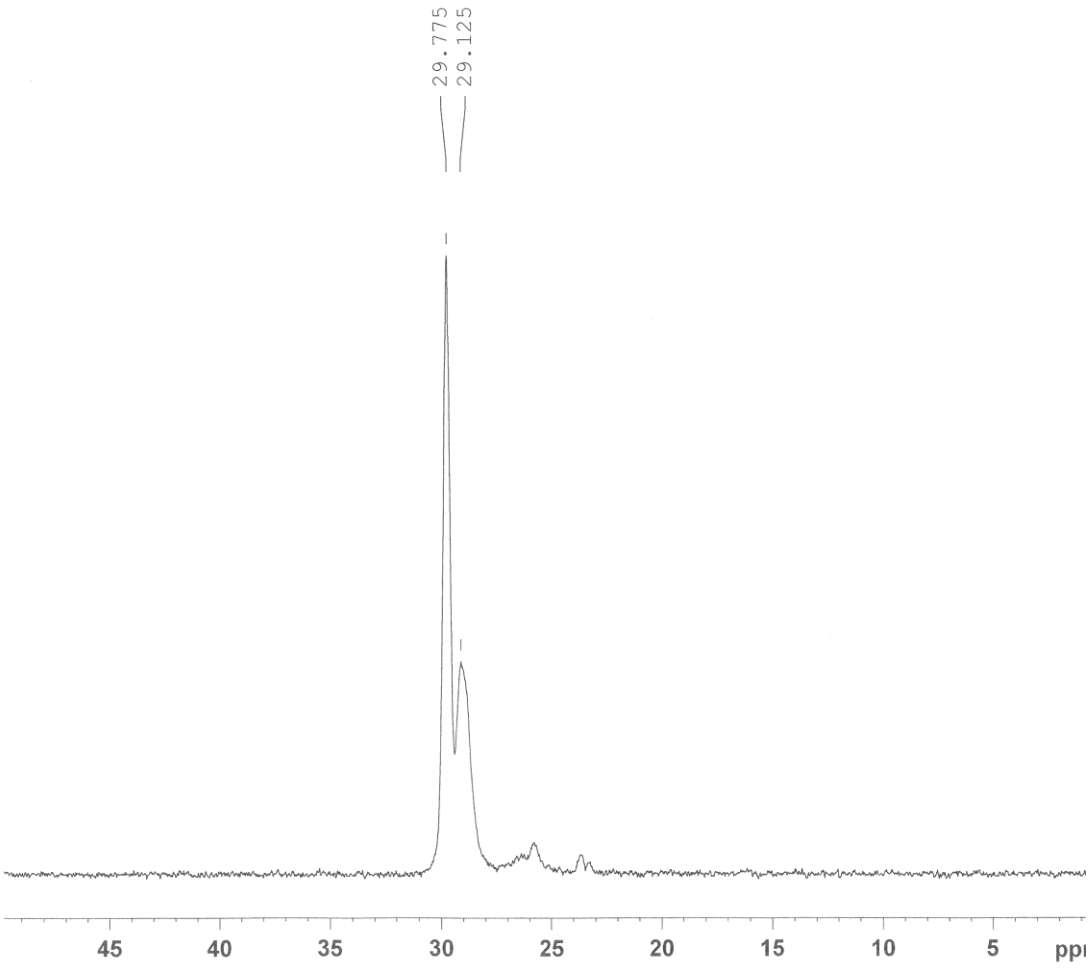


**Figure S3.** $^{31}P\{^{1}H\}$ NMR spectra of $[PdCl(4\text{-}SeC_5H_4N)(PPh_3)]_n$ in $CDCl_3$

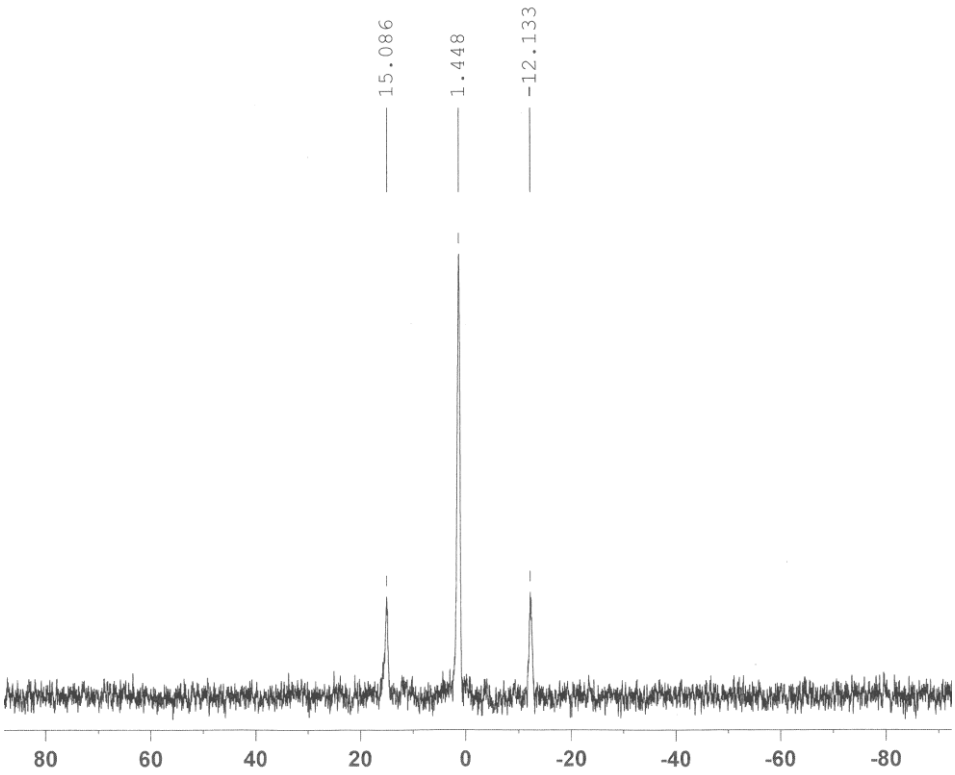


**Figure S4.** $^{31}P\{^{1}H\}$ NMR spectra of $[PtCl(4\text{-}SeC_5H_4N)(PEt_3)]_n$ in $CDCl_3$

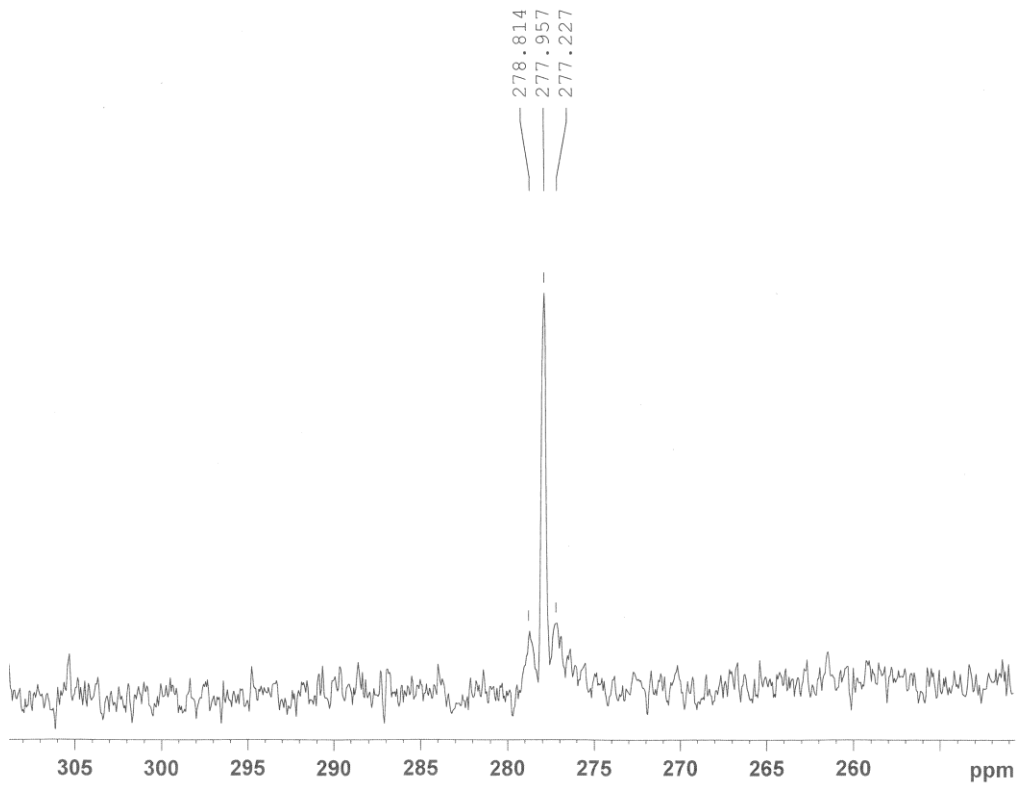


**Figure S5.** $^{77}Se\{^{1}H\}$ NMR spectra of $[PtCl(4\text{-}SeC_5H_4N)(PEt_3)]_n$ in $CDCl_3$

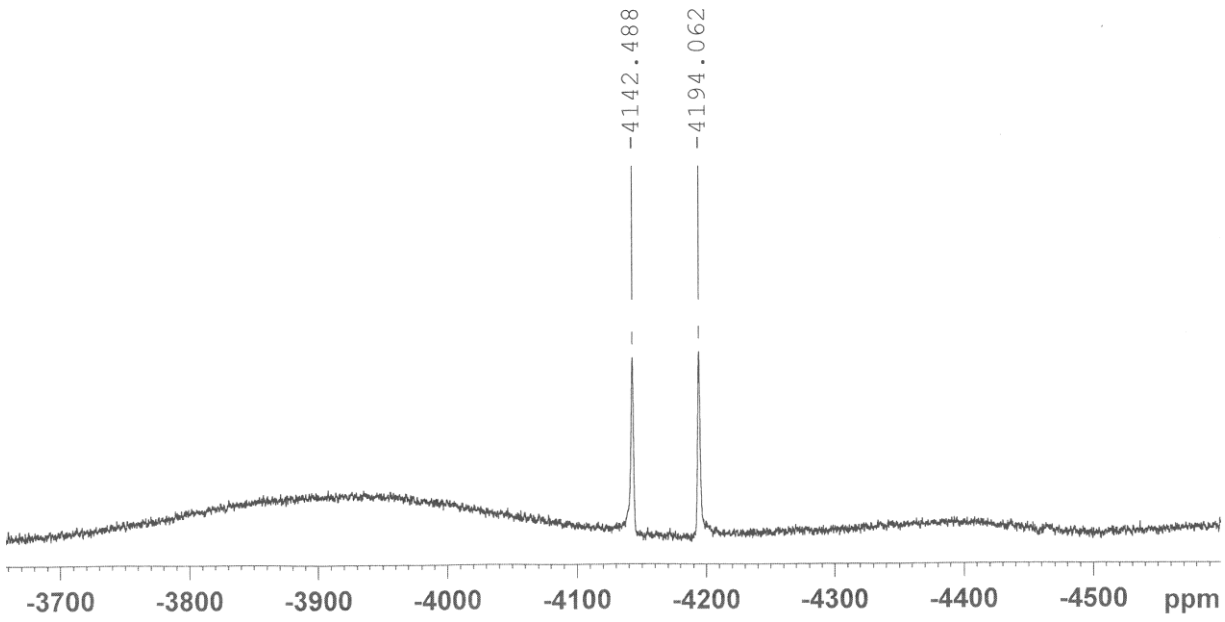


**Figure S6.** $^{195}Pt\{^{1}H\}$ NMR spectra of $[PtCl(4\text{-}SeC_5H_4N)(PEt_3)]_n$ in $CDCl_3$

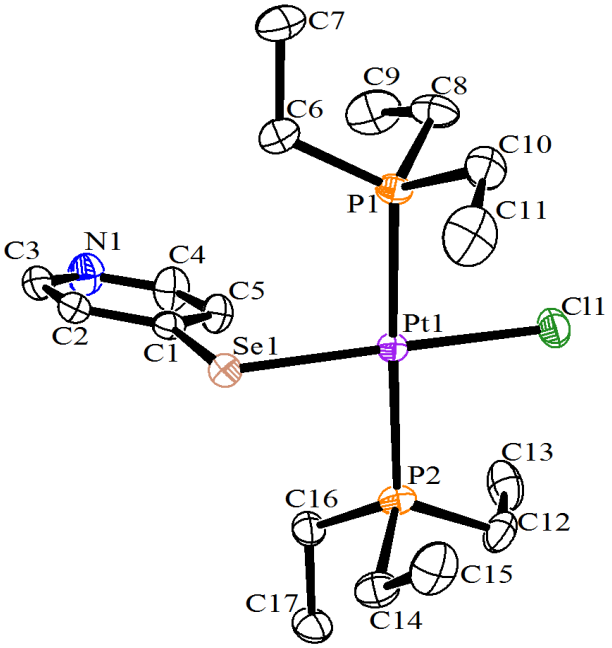


**Figure S7.** Molecular structure of *trans*-[PtCl(4-$SeC_5H_4N$)($PEt_3$)$_2$] (**4b**) ellipsoids drawn at 50% probability. (Hydrogen atoms are omitted for clarity)

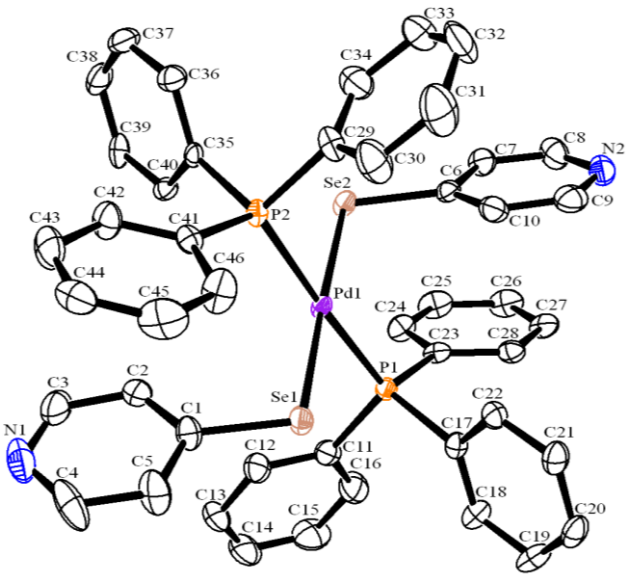


**Figure S8.** Molecular structure of *trans*-[Pd(4-$SeC_5H_4N)_2(PPh_3)_2$] (**5a**) ellipsoids drawn at 50% probability. (Hydrogen atoms are omitted for clarity)

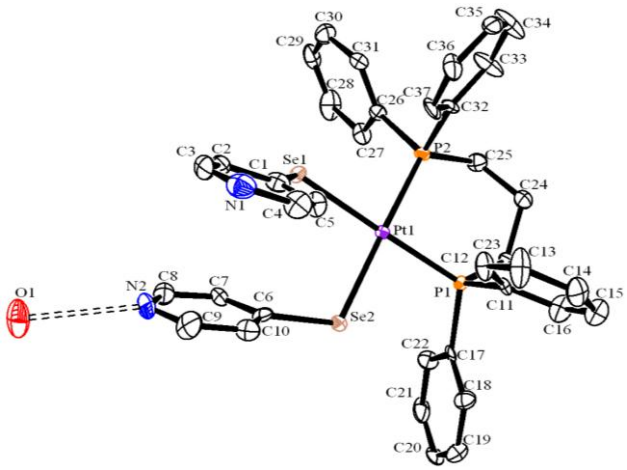


**Figure S9.** Molecular structure of *cis*-[Pt(4-$SeC_5H_4N)_2$(dppp)]·$0.5H_2O$ (**6c**·$0.5H_2O$) ellipsoids drawn at 50% probability.