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Ultra-small Palladium Nano-particles Synthesized Using Bulky S/Se and N Donor Ligands as a Stabilizer: Application as Catalysts for Suzuki-Miayaura Coupling

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S1. Syntheses of ligands L1’ and L2’

Synthesis of L1’ and L2’: 9-Anthracencarboxaldehyde (0.412 g, 2.0 mmol) was stirred in dry ethanol (5 mL) for 10 minutes at room temperature. The solution of 2-(phenylthio)ethylamine (0.306 g, 2.0 mmol) / 2-(phenylseleno)ethylamine (0.398 g, 2.0 mmol) was added drop wise with stirring. The mixture was further stirred for 8 h at room temperature. After completion of the reaction, the solvent was removed with a rotary evaporator resulting L1’/L2’ as a yellow solid.

L1’: Yield: Yellow solid (0.30 g) 86%. ¹H NMR (500 MHz, CDCl₃, 25 °C, TMS): δ(ppm): 3.62 (t, 2H, SCH₂), 4.36 (t, 2H, NCH₂), 7.20 (m, 1H, Ar-H), 7.35-7.40 (m, 2H, Ar-H), 7.48-7.60 (m, 6H, Ar-H), 8.03 (m, 2H, Ar-H), 8.49-8.60 (m, 3H, Ar-H), 9.40 (s,1H,CH=N). ¹³C{¹H}NMR (125 MHz, CDCl₃, 25 °C, TMS):34.5 (SCH₂), 61.3(NCH₂), 124.6, 124.8, 125.2, 126.7, 128, 128.5, 129, 129.5, 131.1, 135.8 (Ar-C), 162.1 (N=C).

L2’:¹H NMR (500 MHz, CDCl₃, 25 °C, TMS): δ(ppm): 3.43 (t, 2H, SeCH₂), 4.18 (t, 2H, C-CH₂-N ), 7.21-7.28 (m, 3H, Ar-H), 7.43-7.51 (m, 4H, Ar-H ), 7.59 (m, 2H,Ar-H ), 7.9 (m, 2H, Ar-H), 8.4-8.51 (m, 3H, Ar-H ), 9.31 (s, 1H, CH=N).¹³C{¹H}NMR (125MHz, CDCl₃, 25°C, TMS):28.5(SeCH₂), 62.2 (NCH₂), 124.7, 125.18, 126.2, 126.9, 127.8, 128.7, 129.1, 129.4, 129.7, 129.8, 131.1,131.7 (Ar-C), 161.7 (N=C).
### TABLE S1. Crystal data and structural refinements for ligand L1

|                          | L1                                                                 |
|--------------------------|--------------------------------------------------------------------|
| **Empirical formula**    | C\(_{23}\)H\(_{21}\)NS                                               |
| **Formula weight**       | 343.47                                                             |
| **Temperature**          | 150.01(10) K                                                       |
| **Wavelength**           | 1.541                                                              |
| **Crystal system, space group** | Triclinic, \(P\overline{1}\)                                       |
| **Unit cell dimension**  |                                                                    |
| a                        | 5.3825(7) Å                                                        |
| b                        | 15.3166(13) Å                                                      |
| c                        | 21.472(3) Å                                                        |
| \(\alpha\)               | 89.910(8)°                                                        |
| \(\beta\)                | 84.752(10)°                                                       |
| \(\gamma\)               | 89.905(9)°                                                        |
| **V**                    | 1762.8 (4) Å³                                                      |
| **Z**                    | 4                                                                 |
| **Absorption coefficient**| 1.639                                                              |
| F(000)                   | 728                                                                |
| **Crystal color**         | Light yellow                                                       |
| **Theta range for data collection** | 3.5470 to 67.0830 deg.                                           |
| **Density**              | 1.294                                                              |
| **Limiting indices**     |                                                                    |
|                         | \(-6<h<4, -15<h<18, -24<h<25\)                                     |
| **Goodness –of –fit on \(F^2\)** | 1.131                                                             |
| **\(R_1\)^a [I \(>\) 2\(\sigma(I)\)]** | 0.0821                                                             |
| **\(R_1\) [all data]**   | 0.1042                                                             |
| **\(wR^2\) [I \(>\) 2\(\sigma(I)\)]** | 0.2427                                                             |
| **\(wR^2\) [all data]**  | 0.2912                                                             |
| **CCDC**                 | 1887878                                                             |

### Table S2. Selected bond distances and bond angles of L1

| Bond Length(Å) | Bond Angles(°) |
|----------------|----------------|
| S(2)–C(27)     | 1.765(6)       |
| S(2)–C(13)     | 1.826(6)       |
| N(3)–C(45)     | 1.436(8)       |
| N(3)–C(33)     | 1.492(7)       |
| C(27)–S(2)–C(13)| 104.5(3)       |
| C(45)–N(3)–C(33)| 113.9(4)       |
Fig. S1. $^1$H NMR of ligand L1’
Fig. S2. $^{13}\text{C}\{^1\text{H}\}$ NMR of ligand L1′
Fig. S3. $^1$H NMR of ligand L2’

Fig. S4. $^{13}$C{$^1$H} NMR of ligand L2’
Fig. S5. $^1$H NMR of ligand L1
Fig. S6. $^{13}$C{${}^1$H} NMR of ligand L1
Fig. S7. $^1$H NMR of ligand L2
Fig. S8. $^{13}$C($^1$H) NMR of ligand L2
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Fig. S15. PXRD analysis of ligand L2
S2. NMR Data of Coupled Products of Suzuki reaction

4-Nitrobiphenyl.  
Pale yellow solid.  
$^1$H NMR (500 MHz, CdCl$_3$): $\delta$ 7.406-7.515 (m, 3H), 7.609 (d, 2H), 7.709 (d, 2H), 8.266 (d, 2H).

4-Phenylbenzonitrile.  
Pale yellow solid.  
$^1$H NMR (500 MHz, CdCl$_3$): $\delta$ 7.339-7.447 (m, 3H, aromatic), 7.490-7.521(m, 3H, aromatic), 7.539-7.608(m, 3H, aromatic).

Biphenyl-4-carboxaldehyde.  
Light yellow solid.  
$^1$H NMR (500 MHz, CdCl$_3$): $\delta$ 7.391-7.508 (m, 3H), 7.628-7.655 (m, 3H), 7.755 (d, 2H), 7.955 (d, 2H), 10.058 (s, 1H).

Biphenyl-4-carboxylic acid.  
White solid.  
$^1$H NMR (500 MHz, CdCl$_3$): $\delta$ 7.393-7.523 (m, 3H), 7.727 (d, 2H), 7.793 (d, 2H), 8.026 (d, 2H).

4-Methylbiphenyl.  
Colorless solid.  
$^1$HNMR (300 MHz, CDCl$_3$): $\delta$ 2.375 (s, 3H), 7.228 (d, 2H), 7.274-7.323 (m, 1H), 7.378-7.427 (m, 2H), 7.479 (d, 2H), 7.552-7.580(m, 2H).

4-Phenylaniline.  
Brown solid.  
$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 3.722 ( s, 2H), 6.752 (d, 2H), 7.246–7.286 (m, 1H), 7.364–7.428 (m, 4H), 7.533 (d, 2H).

4-Hydroxybiphenyl.  
Brown solid.  
$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 4.915 (s, 1H, OH), 6.998 (d, 2H), 7.300–7.548 (m, 7H).

S3. References

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