Supplementary Material (ESI) for Chemical Communications

Supporting Information

Dual Chirality Control of Palladium(II) Complexes Bearing *Tropos* Biphenyl Diamine Ligands

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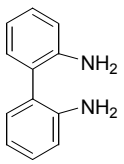
General:

^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra were measured on Varian GEMINI 300 (300 MHz) and Varian GEMINI 400 (400 MHz) spectrometers. Chemical shifts of ^{1}H NMR were expressed in parts per million downfield from tetramethylsilane as an internal standard (δ= 0) in $CDCl_3$. Chemical shifts of ^{13}C NMR were expressed in parts per million downfield from $CDCl_3$ as an internal standard (δ = 77.1) in $CDCl_3$. Chemical shifts of ^{31}P NMR were expressed in parts per million downfield from 85% H_3PO_4 as an external standard (δ= 0) in $CDCl_3$. Optical rotations were measured on a JASCO DIP-370. Analytical thin layer chromatography (TLC) were performed on a glass plates (Merck Kieselgal 60 F_{254}, layer thickness 0.25 and 0.2 mm). Column chromatography was performed on KANTO Silica Gel 60N (spherical, neutral). All experiments were carried out under argon atmosphere otherwise noted.

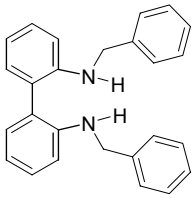
2,2'-Diaminobiphenyl (DABP)



A slurry of 10% palladium on carbon (90 mg) was stirred in methanol (15 ml) while bubbling argon through the mixture. A solution of sodium borohydride (181.6 mg, 4.8 mmol) in water (5.0 ml) was added, and purging continued. Over the next 10 min, 2,2'-dinitro-1,1'-biphenyl (195.4 mg, 0.8 mmol) in methanol (15 ml) was added. The mixture was stirred at room temperature for 1 h, filtered with celite and taken to

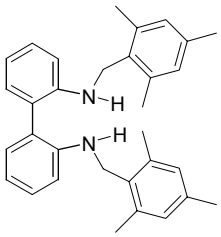
dryness by evaporation. The residue was extracted with dichloromethane and ether. The organic layer was dried over $MgSO_4$. The $MgSO_4$ was filtered off on celite, and then the filtrate was evaporated under reduced pressure. Without further purification, 2,2'-diamino-1,1'-biphenyl (DABP) was obtained in 94% yield.
^{1}H NMR (300 MHz, $CDCl_3$) δ 3.71 (br s, 4H, N*H*$_2$), 6.76 (dd, *J* = 7.8, 1.2 Hz, 2H), 6.82 (ddd, *J* = 7.8, 7.4, 1.5 Hz, 2H), 7.12 (dd, *J* = 7.5, 1.5 Hz, 2H), 7.16 (ddd, *J* = 7.5, 7.4, 1.2 Hz, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 115.2, 118.5, 124.3, 128.5, 130.8, 143.9.

_N_,_N_'-Dibenzyl-2,2'-diamino- 1,1'-biphenyl (1a)



To a solution of 2,2'-diamino-1,1'-biphenyl (184.2 mg, 1.0 mmol) in toluene (5.0 ml) was added benzaldehyde (254 μl, 2.5 mmol) under argon atmosphere. The mixture was refluxed (about 140 °C) with a Dean-Stark for 24 h. After evaporation under reduced pressure, the diimine product was obtained through quantitative reaction (confirmed by ^{1}H NMR analysis in $CDCl_3$). To a mixture of the diimine and $NaBH_4$ (756.6 mg 20 mmol) in toluene (10 ml) was added MeOH (10 ml) at -78 °C under argon atmosphere. The mixture was stirred at room temperature for 2 h. The reaction mixture was poured into 1*N* HCl and extracted with dichloromethane. The organic layer was washed with sat.$NaHCO_3$, brine and then dried over $MgSO_4$. The $MgSO_4$ was filtered off on celite, and then the filtrate was evaporated under reduced pressure. The residue was purified by silica-gel chromatography (hexane/ethyl acetate = 5/1) to give the product (yield 82%).
^{1}H NMR (300 MHz, $CDCl_3$) δ 4.33 (br, 2H), 4.37 (br s, 2H), 4.38 (br s, 2H), 6.70 (dd, *J* = 8.4, 0.9 Hz, 2H), 6.82 (td, *J* = 7.5, 0.9 Hz, 2H), 7.17 (dd, *J* = 7.4, 1.5 Hz, 2H), 7.21-7.32 (m, 12H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 47.8, 110.8, 117.4, 123.9, 126.9, 128.5, 129.1, 131.0, 139.5, 145.6.
Anal. Calcd for $C_{26}H_{24}N_2$: C, 85.68; H, 6.64; N, 7.69%. Found: C, 85.67; H, 6.83; N, 7.56%.

_N_,_N_'-Bis(2,4,6-trimethylbenzyl)-2,2'-diamino-1,1'-biphenyl (1b)



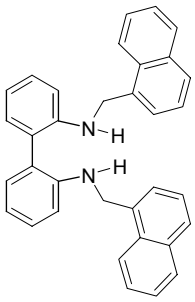
The titled compound was prepared from DABP according to the procedure as described for *N*,*N*'-dibenzyl-2,2'-diamino- 1,1'-biphenyl **(1a)** (yield 86%)
^{1}H NMR (300 MHz, $CDCl_3$) δ 2.21 (s, 12H), 2.24 (s, 6H), 3.41 (br s, 2H), 4.06 (dd, *J* = 11.4, 2.7 Hz, 2H),

4.55 (dd, J = 11.4, 3.9 Hz, 2H), 6.71 (td, J = 7.5, 0.9 Hz, 2H), 6.80 (s, 4H), 6.81 (d, J = 7.2 Hz, 2H), 7.01 (dd, J = 7.2, 1.5 Hz, 2H), 7.21-7.27 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 19.3, 20.9, 42.9, 110.9, 117.1, 123.8, 128.9, 129.0, 130.7, 131.9, 137.1, 137.4, 146.5.

Anal. Calcd for $C_{32}H_{36}N_2 \cdot 2H_2O$: C, 79.30; H, 8.32; N, 5.78%. Found: C, 78.16; H, 8.04; N, 5.20%.

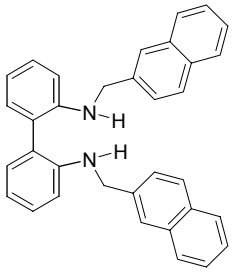
_N_,_N_'-Bis(1-naphthyl)-2,2'-diamino-1,1'-biphenyl (1c)



The titled compound was prepared from DABP according to the procedure as described for *N*,*N*'-dibenzyl-2,2'-diamino-1,1'-biphenyl **(1a)** without purification by silica-gel chromatography (yield 74%). The compound **5c** was insoluble in all solvents.

Anal. Calcd for $C_{34}H_{28}N_2 \cdot H_2O$: C, 84.61; H, 6.27; N, 5.80%. Found: C, 86.79; H, 6.31; N, 5.78%.

_N_,_N_'-Bis(2-naphthyl)-2,2'-diamino-1,1'-biphenyl (1d)



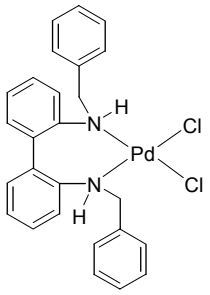
The titled compound was prepared from DABP according to the procedure as described for *N*,*N*'-dibenzyl-2,2'-diamino- 1,1'-biphenyl **(1a)** (yield 81%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 4.43 (br, 2H), 4.53 (br s, 4H), 6.73 (dd, J = 8.4, 0.9 Hz, 2H), 6.81 (td, J = 7.2, 0.9 Hz, 2H), 7.17-7.22 (m, 4H), 7.39-7.44 (m, 6H), 7.66-7.80 (m, 8H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 48.1, 111.0, 117.5, 124.0, 125.2, 125.4, 125.5, 126.0, 127.6, 127.7, 128.3, 129.1, 131.0, 132.6, 133.4, 137.0, 145.7.

Anal. Calcd for $C_{34}H_{28}N_2$: C, 87.90; H, 6.07; N, 6.03%. Found: C, 86.58; H, 6.28; N, 5.87%.

_N_$_2$PdCl$_2$ complex (2a)



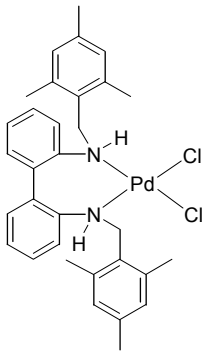
A solution of $PdCl_2(CH_3CN)_2$ (77.8 mg, 0.3 mmol) and *N*,*N*'-dibenzyl-2,2'-diamino-1,1'-biphenyl **(5a)** (109.3 mg, 0.3 mmol) in dichloromethane (10 ml) was stirred for 12 h at room temperature under argon atmosphere, and then evaporated. The complex was dissolved in a minimum amount of dichloromethane and precipitated by addition of hexane, washed with hexane, and then dried *in vacuo* (yield 97%). Recrystallization from dichloromethane-hexane gave single crystals, which allowed the 3D structure of the complex to be clarified by X-ray crystallographic analysis (*vide infra*).

^{1}H NMR (300 MHz, $CDCl_3$) δ 3.61 (dd, *J* = 13.7, 10.8 Hz, 2H, C*H*N), 4.58 (dd, *J* = 13.7, 2.7 Hz, 2H, C*H*N), 5.53 (br, 2H, N*H*), 6.74 (d, *J* = 7.8 Hz, 2H), 6.86-6.89 (m, 4H), 7.11-7.23 (m, 8H), 7.32 (dd, *J* = 7.8, 1.5 Hz, 2H), 7.48 (td, *J* = 7.8, 1.5 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 55.3, 124.4, 128.9, 129,2, 130.1, 131.8, 132.6, 133.7, 139.1.

Anal. Calcd for $C_{26}H_{24}Cl_2N_2Pd$: C, 57.64; H, 4.46; N, 5.17%. Found: C, 57.51; H, 4.42; N, 5.00%.

N_2PdCl_2 complex (2b)



The titled compound was prepared from *N*,*N*'-bis(2,4,6-trimethylbenzyl)-2,2'-diamino-1,1'- biphenyl **(1b)** according to the procedure as described for **2a** (yield 81%).

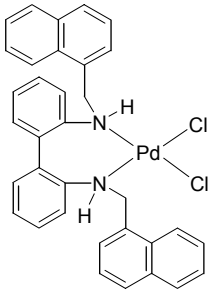
^{1}H NMR (300 MHz, $CDCl_3$) δ 2.19 (s, 6H), 2.45 (s, 12H), 3.47 (dd, *J* = 13.5, 1.2 Hz, 2H, C*H*N), 4.04 (dd, *J* = 13.5, 8.4 Hz, 2H, C*H*N), 5.22 (br, 2H, N*H*), 6.79 (s, 4H), 7.25 (d, *J* = 7.5 Hz, 2H), 7.41 (td, *J* = 7.5, 1.5 Hz, 2H), 7.47 (dd, *J* = 7.5, 1.5 Hz, 2H), 7.55 (t, *J* = 7.5 Hz, 2H).

^{1}H NMR (300 MHz, CD_2Cl_2) δ 2.22 (s, 6H), 2.48 (s, 12H), 3.45 (dd, *J* = 13.5, 1.2 Hz, 2H, C*H*N), 3.97 (dd, *J* = 13.5, 8.4 Hz, 2H, C*H*N), 5.18 (br, 2H, N*H*), 6.83 (s, 4H), 7.23 (d, *J* = 7.5 Hz, 2H), 7.45 (td, *J* = 7.5, 1.5 Hz, 2H), 7.51 (dd, *J* = 7.5, 1.5 Hz, 2H), 7.57 (td, *J* = 7.5, 0.9 Hz, 2H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ 20.5, 20.8, 53.4, 122.0, 128.0, 129.0, 129.6, 130.4, 132.4, 133.4, 138.0, 139.0, 143.3.

Anal. Calcd for $C_{32}H_{36}Cl_2N_2Pd{\cdot}2H_2O$: C, 58.06; H, 6.09; N, 4.23%. Found: C, 58.50; H, 5.65; N, 4.18%.

N_2PdCl_2 complex (2c)



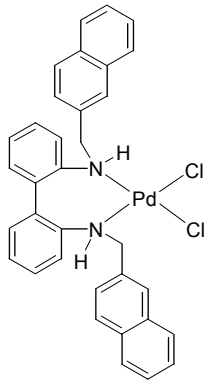
The titled compound was prepared from *N*,*N*'-bis(1-naphthyl)-2,2'-diamino-1,1'-biphenyl **(1c)** according to the procedure as described for **2a** (yield 90%). Recrystallization from dichloromethane -hexane gave single crystals, which allowed the 3D structure of the complex to be clarified by X-ray crystallographic analysis (*vide infra*).

^{1}H NMR (300 MHz, CD_2Cl_2) δ 4.00 (dd, *J* = 13.8, 11.1 Hz, 2H, C*H*N), 5.22 (dd, *J* = 13.8, 2.7 Hz, 2H, C*H*N), 6.00 (br, 2H, N*H*), 6.48 (d, *J* = 7.8 Hz, 2H), 6.88 (d, *J* = 6.3 Hz, 2H), 7.03-7.08 (m, 2H), 7.17 (d, *J* = 7.7 Hz, 2H), 7.46-7.49 (m, 4H), 7.54 (d, *J* = 7.8 Hz, 2H), 7.67 (d, *J* = 7.8 Hz, 2H), 7.73 (d, *J* = 8.1 Hz, 2H), 7.85 (d, *J* = 7.8 Hz, 2H), 8.46 (d, *J* = 8.4 Hz, 2H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ 53.3, 123.2, 124.0, 124.9, 126.6, 127.7, 128.6, 129.3, 129.4, 130.0, 130.1, 131.4, 131.8, 133.3, 134.2, 139.3.

Anal. Calcd for $C_{34}H_{28}Cl_2N_2Pd$: C, 63.62; H, 4.40; N, 4.36%. Found: C, 63.25; H, 4.20; N, 4.22%.

N_2PdCl_2 complex (2d)

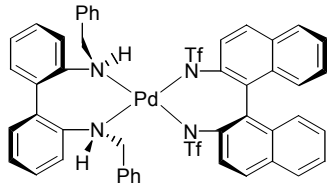


The titled compound was prepared from *N*,*N*'-bis(2-naphthyl)-2,2'-diamino-1,1'-biphenyl **(1d)** according to the procedure as described for **2a** (yield 96%). Recrystallization from dichloromethane -hexane gave single crystals, but X-ray crystallographic analysis is not tried yet.

^{1}H NMR (300 MHz, $CDCl_3$) δ 3.81 (dd, *J* = 13.8, 11.3 Hz, 2H, C*H*N), 4.79 (dd, *J* = 13.8, 2.4 Hz, 2H, C*H*N), 5.70 (br, 2H, N*H*), 6.78 (d, *J* = 8.1 Hz, 2H), 6.99 (dd, *J* = 8.7, 1.5 Hz, 2H), 7.18 (td, *J* = 7.8, 1.5 Hz, 2H), 7.37-7.54 (m, 10H), 7.65 (d, *J* = 8.7 Hz, 2H), 7.69-7.76 (m, 4H).

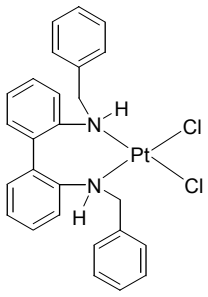
^{1}H NMR (300 MHz, CD_2Cl_2) δ 3.81 (dd, *J* = 13.8, 11.3 Hz, 2H, C*H*N), 4.75 (dd, *J* = 13.8, 2.4 Hz, 2H, C*H*N), 5.70 (br, 2H, N*H*), 6.85 (d, *J* = 8.1 Hz, 2H), 7.07 (dd, *J* = 8.7, 1.5 Hz, 2H), 7.21 (td, *J* = 7.8, 1.5 Hz, 2H), 7.39-7.56 (m, 10H), 7.70 (d, *J* = 8.7 Hz, 2H), 7.73-7.78 (m, 4H).
^{13}C NMR (75 MHz, CD_2Cl_2) δ 55.5, 124.5, 126.1, 126.8, 126.9, 127.9, 128.1, 128.7, 128.9, 129.5, 130.2, 131.4, 132.0, 133.0, 133.3, 133.4, 139.2.
Anal. Calcd for $C_{34}H_{28}Cl_2N_2Pd{\cdot}CH_2Cl_2$: C, 57.83; H, 4.16; N, 3.85%. Found: C, 59.09; H, 4.03; N, 3.83%.

(*R*)-*N*$_2$Pd/(*R*)-DABNTf complex (*R*/*R*,*R*/*R*-3a)



To a solution of N_2PdCl_2 complex **(2a)** (56.9 mg, 0.105 mmol) in dichloromethane (6.0 ml) was added a solution of (*R*)-DABNTf (57.6 mg, 0.105 mmol) and ^{t}BuOK (23.7 mg, 0.210 mmol) in THF (4.0 ml) under argon atmosphere. The mixture was stirred at room temperature for 18 h. The KCl was filtered off on celite, and then the filtrate was evaporated under reduced pressure. The residue was purified by recrystallization from dichloromethane-acetone-hexane to give the product (*R*)/(*R*,*R*)/(*R*)-**8a** (yield 81%). Recrystallization from dichloromethane-MeOH gave single crystals, which allowed the 3D structure of the complex to be clarified by X-ray crystallographic analysis (*vide infra*).
^{1}H NMR (300 MHz, $CDCl_3$) δ 3.69 (dd, *J* = 13.8, 10.8 Hz, 2H, C*H*N), 4.64 (dd, *J* = 13.8, 4.2 Hz, 2H, C*H*N), 7.06-7.26 (m, 20H), 7.39-7.46 (m, 6H), 7.82 (t, *J* = 9.0 Hz, 4H), 8.48 (br, 2H, N*H*).
^{19}F NMR (376 MHz, $CDCl_3$) δ -76.1 (s, 6F). *cf*. (*R*)-DABNTf ; δ -76.8 (s, 6F).
$[\alpha]_D^{26}$ = +846.0 (c = 1.71 in $CHCl_3$). *cf*. (*R*)-DABNTf; $[\alpha]_D^{27}$ = +115.3 (c = 0.3 in $CHCl_3$)
Anal. Calcd for $C_{48}H_{36}F_6N_4O_4PdS_2{\cdot}H_2O$: C, 55.68; H, 3.70; N, 5.41%. Found: C, 55.16; H, 3.69; N, 5.04%.

DB-DABP-PdCl$_2$ complex



A solution of $PtCl_2(CH_3CN)_2$ (34.8 mg, 0.1 mmol) and diamine ligand **1a** (36.4 mg, 0.1 mmol) in dichloroethane (4.0 ml) was stirred for 24 h at 80 °C under argon atmosphere. The mixture was filtered off on celite, and then the filtrate was evaporated under reduced pressure. The residue was dissolved in a minimum amount of dichloromethane and precipitated by addition of ether, washed with ether, and then dried *in vacuo* (yield 65%).

Supplementary Material (ESI) for Chemical Communications

^{1}H NMR (300 MHz, $CDCl_3$) δ 3.60 (dd, *J* = 13.2, 11.1 Hz, 2H, C*H*N), 4.63 (dd, *J* = 13.2, 2.4 Hz, 2H, C*H*N), 6.11 (br, 2H, N*H*), 6.69 (d, *J* = 8.1 Hz, 2H), 6.89 (dd, *J* = 7.5, 1.8 Hz, 4H), 7.14-7.25 (m, 8H), 7.39 (dd, *J* = 7.5, 1.8 Hz, 2H), 7.46 (td, *J* = 7.2, 0.9 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 57.6, 123.9, 128.8, 128.9, 129.0, 130.1, 131.5, 132.8, 133.7, 140.0.