Supplementary Material (ESI) for Chemical Communications

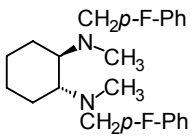
Supplementary Material

Highly selective *R,S* – Coordination of non racemic (1*R*,2*R)*- (1,2 dialkyl)-1,2 diamine cyclohexane derivatives to palladium dichloride.

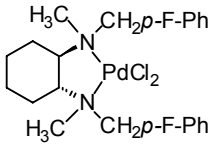
Esfandiar Rafii, Benjamin Dassonneville and Andreas Heumann

Table 1. Proton and fluorine shift differences (ppm) in selected alkyl substituted chiral *trans*-1.2 diamino cyclohexanes coordinated to $PdCl_2$ (**3**).

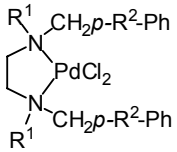
	Substituents at N	$\Delta\delta$ H_1-H_2	$\Delta\delta$ H_7-H_8	$\Delta\delta$ $H_{7'}$-$H_{8'}$	$\Delta\delta$ NH	$\Delta\delta$ X
3a	CH_2Ph, H	1.7	0.11	0.4	0.17	-
3b	CH_2*p*-F-Ph, H	1.69	0.25	0.2	0.2	0.8 X=F
3c	CH_2*p*-CF_3-Ph, H	1.28	0.13	0.35	0.73	0.16 X=F
3d	CH_2*p*-OMe-Ph, H	1.64	0.19	0.28	0.2	0.06 X=OMe
3e	CH_2*m*-CF_3-Ph, H	1.78	0.18	0.34	0.05	0.16 X=F
3f	CH_2*m*-NO_2-Ph, H	1.6	0.26	0.32	0	-
3g	CH_2*o*-NO_2-Ph, H	1.78	0.18	0.34	0.05	-
3h	CH_2mesityl, H	1.53	0.41	0.45	0.13	0.1 X=Me
3i	1-naphthyl, H	1.62	0.06	0.91	0.73	-
3j	CH_2-1-furfuryl, H	1.93	0.07		0.08	-
3k	$CH_2C(CH_3)_3$, H	0.43	0.19	0.64	0.45	0.11 X=Me



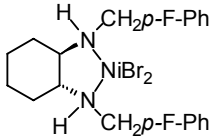
(1*R*,2*R*)-**4**



(1*R*,2*R*)-**5**

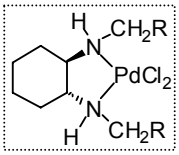


6a R^1 = Me, R^2 = H
6b R^1 = H, R^2 = F



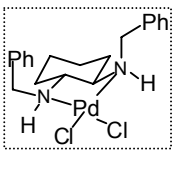
(1*R*,2*R*)-**7**

Scheme 4



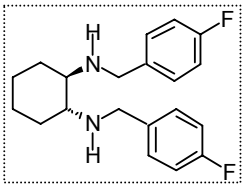
Pd[(*R*,*R*)-*N*,*N*'-Cyclohexane-1,2-diamine]Cl_2
Palladium dichloride bisacetonitrile (0.2 mmol) is added at room temperature to a stirred solution of the chiral diamine (0.2 mmol) in 1 mL of methylene chloride. In general the reaction is finished after 15 min. After evaporation of the solvent a bright yellow palladium complex is recovered. Purification by recrystallisation from acetonitrile, methylene choride, or by flash chromatography. Some complexes, e.g. **3i** are extremely insoluble in common solvents and are difficult to handle.

Pd[(*R*,*R*)-*N*,*N*'-Dibenezycylclohexane-1,2-diamine]Cl_2 3a, ($C_{20}H_{26}Cl_2N_2Pd$) yellow solid (90% yield), **^{1}H NMR** (500MHz, $CDCl_3$) δ : 8.05 (d, 2H, *J* = 7.0 Hz), 7.55 - 7.25 (m,

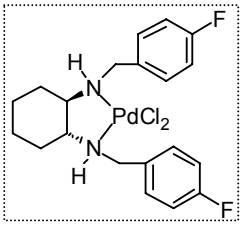


8H), 5.62 (br, 1H, NH), 5.46 (br, 1H, NH), 4.36 (dd, 2H, *J* = 13.3, 4.2 Hz), 4.22 (br, 1H), 4.22 (d, 1H, *J* = 14.2 Hz), 3.78 (dd, 1H, *J* = 13.4, 2.3 Hz), 3.36 (dd, 1H, *J* = 14.5, 8.9 Hz), 2.50 (m, 1H), 2.05 (m, 1H), 1.6 – 1.35 (m, 5H), 1.2 - 1.05 (m, 2H), 0.9 – 0.8 (m, 1H). **^{13}C NMR** (75MHz, $CDCl_3$) δ 137.2, 135.2, 130.7, 128.9, 128.77, 128.73, 128.66, 128.0, 66.4, 62.2, 52.1, 51.1, 31.4, 30.1, 24.3, 24.2. $[\alpha]_D$ + 219 (c = 0.2, CH_2Cl_2).

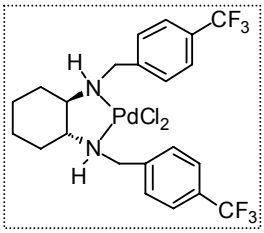
***(R,R)*-*N,N'*-Bis((4-fluorophenyl)methyl)cyclohexane-1,2-diamine *2*b,** colourless oil (84%); **^{1}H NMR** (200 MHz, $CDCl_3$) δ 7.24 (m, 4H), 6.97 (m, 4H), 3.88 (d, 2H, *J* = 13.2 Hz), 3.6 (d, 2H, *J* = 13.2Hz), 2.20 (m, 4H), 1.75 (m, 4H), 1.4 – 0.9 (m, 4H). **^{13}C NMR** (50 MHz, $CDCl_3$): δ 161.6 (d, *J*= 244 Hz), 136.7, 129.3 (d, *J*= 8 Hz), 114.9 (d, *J*= 21 Hz), 60.8, 50.0, 31.4, 24.8; **^{19}F NMR** (188 MHz): δ -116.8; **IR** ν (cm^{-1}) 3301, 2925, 2843, 1560, 1490, 1465, 1334. Anal. Calcd. for $C_{20}H_{24}F_2N_2$ (330.41): C, 72.7; H, 7.32; N, 8.48. Found: C, 71.93; H, 7.68; N 8.61. $[\alpha]_D$ – 79.7 (c = 1, CH_2Cl_2).



Pd[*(R,R)*-*N,N'*-Bis((4-fluorophenyl)methyl)cyclohexane-1,2-diamine]Cl_2 3b, ($C_{20}H_{24}Cl_2F_2N_2Pd$) yellow solid (92% yield), **^{1}H NMR** (200MHz, $CDCl_3$) δ 8.04 (m, 2H,), 7.53 (m, 2H), 7.19 (t, 2H, *J* = 8.6 Hz), 7.0 (t, 2H, *J* = 8.6 Hz), 5.72 (m, 1H, NH), 5.49 (br, 1H, NH), 4.44 (dd, 1H, *J* = 13.6, 3.2 Hz), 4.15 (br, 1H), 4.14 (d, 1H, *J* = 14.4 Hz), 3.67 (dd, 1H, *J* = 13.3, 2.4 Hz), 3.46 (dd, 1H, *J* = 14.4, 10 Hz), 2.45 (m, 1H), 2.17 (m, 1H), 1.75 – 1.6 (m, 5H), 1.6 - 1.1 (m, 2H), 1.0 – 0.5 (m, 1H). **^{13}C NMR** (75MHz, $CDCl_3$) δ 163.0 (d, *J*= 249 Hz), 162.5 (d, *J*= 249 Hz), 132.7, 132.57 (d, *J*= 7.5 Hz), 130.7 (d, *J*= 8.3 Hz), 130.57 (d, *J*= 3 Hz),116.3 (d, *J*= 22 Hz), 115.8 (d, *J*= 22 Hz), 66.0, 62.1, 50.4, 50.2, 31.4, 30.0, 24.4, 24.2. **^{19}F NMR** (188 MHz): δ -112.9, -113,7. $[\alpha]_D$ + 165 (c = 0.08, CH_2Cl_2).

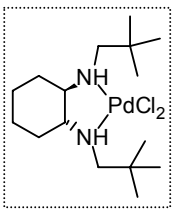


Pd[*(R,R)*-*N,N'*-Bis((4-trifluoromethylphenyl)methyl)cyclohexane-1,2-diamine]Cl_2 3c, (**$C_{22}H_{24}F_6N_2PdCl_2$**) yellow solid (89%); **^{1}H NMR** (200MHz, $CDCl_3$) δ 8.26 (d, 2H, *J* = 8.2 Hz), 7.78 (d, 2H, *J* = 8.2 Hz), 7.63 (s, 4H), 5.81 (br, 1H), 5.68 (br, 1H), 4.53, (dd, 1H, *J* = 13.6, 3.0 Hz), 4.40 (d, 1H, *J* = 14.0 Hz), 4.07 – 4.28 (m, 1H), 3.83 (dd, 1H, *J* = 13.4, 2.0 Hz), 3.48 (dd, 1H, *J* = 15.0, 9.0 Hz), 2.6 – 2.3 (m, 1H), 2.25 – 2.1 (m, 1H), 1.7 – 1.3 (m, 4H), 1.25 – 1.1 (m, 2H), 1.0 – 0.7 (m, 1H); **^{13}C NMR** (50MHz, with som drops of $DMSOd_3$) δ 141.7, 139.5, 131.3, 129;1, 126.3, and 126.1 (2q, *J*= 4 Hz), 66.4, 63.1, 51.3, 51.2, 31.8, 30.6, 24.8, 24.3; **^{19}F NMR** (188MHz) δ - 63.08, - 63.15. $[\alpha]_D$ + 133 (c = 0.12, $CHCl_3$).



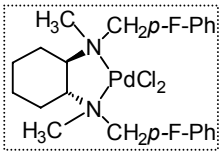
Pd[*(R,R)*-*N,N'*-Bis((3-trifluoromethylphenyl)methyl)cyclohexane-1,2-diamine]Cl_2 3e, (**$C_{22}H_{24}F_6N_2PdCl_2$**) yellow solid (89%); **^{1}H NMR** (200MHz, $CDCl_3$) δ 8.66 (d, 1H, *J* = 6.8 Hz), 8.08 (s, 1H), 7.89 (d, 1H, *J* = 6.9 Hz), 7.73 – 7.53 (m, 5H), 5.76 (br, 2H), 4.59 (dd, 1H, *J* = 13.6, 3.0 Hz), 4.40 (d, 1H, *J* = 14.4 Hz), 4.18 (br, 1H), 3.83 (dd, 1H, *J* = 13.6, 2.0 Hz), 3.50 (dd, 1H, *J* = 14.5, 9.0 Hz), 2.5 – 2.3 (m, 1H), 2.25 – 2.1 (m, 1H), 1.7 – 1.3 (m, 4H), 1.25 – 1.1 (m, 2H), 1.0 – 0.8 (m, 1H); **^{13}C NMR** (75MHz) δ 138.1, 135.9, 134.0, 132.1, 129.9, 129.7, 127.2 (t, *J*= 3 Hz), 125.9 – 125.7 (m), 125.3 – 125.1 (m), 66.0, 62.9, 51.1, 50.8, 31.5, 30.2, 24.4, 24.1; **^{19}F NMR** (188MHz) δ -63.01, -63.17. $[\alpha]_D$ + 148 (c = 0.2, CH_2Cl_2).

Pd[*(R,R)*-*N*,N'-Bis(2,2-dimethypropyl)cyclohexane -1,2-diamine]Cl_2 3k: ($C_{16}H_{34}N_2PdCl_2$) **^{1}H NMR** (300MHz, $CDCl_3$) δ 5.05 - 4.95 (m, 1H), 4.55 – 4.45, (m, 1H), 4.45 – 4.40 (m, 1H), 3.20 (dd, 1H, *J* = 13.4, 5.3 Hz), 3.08 (dd, 1H, *J* = 14.0, 6.1 Hz), 2.90 (dd, 1H, *J* = 14.0, 1.9 Hz), 2.74 (ddd, 1H, *J* = 14.5, 10.6, 3.9 Hz), 2.55 (dd, 1H, *J* = 13.4, 4.7 Hz), 2.31 (dm, 1H, *J* =

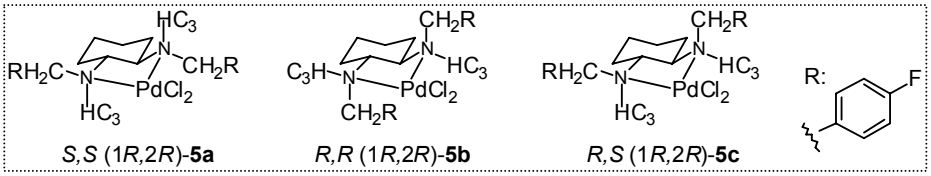


12.0 Hz), 1.85 - 1.5 (m, 3H), 1.5 – 0.9 (m, 4H), 1.26, (s, 9H); 1.15, (s, 9H); **^{13}C NMR** (75 MHz) δ 67.0, 64.1, 60.3, 59.4, 31.8, 31.2, 31.1, 30.8, 29.9, 29.5, 24.5, 23.9. $[\alpha]_D$ + 122 (c 0.5, CH_2Cl_2).

Pd[(*R*,*R*)-*N*,*N*',*N*,*N*'-Dimethylbis((4-Fluorophenyl)methyl)cyclohexane-1,2-diamine]Cl_2 5a-c,



($C_{22}H_{28}Cl_2F_2N_2Pd$) yellow solid (90% yield), mixture of 3 complexes
^{19}F NMR (188 MHz): δ: - 111.2 (21%, *dl*-1), -111.7 and –112.0 (55%, *meso*), -111.8 (20%, *dl*-2), -114.5 (3%, unknown).
^{1}H NMR (200MHz, $CDCl_3$) δ 8.82 (m, integrates for 0.4), 8.34 (dd, integrates for 2.0, *J* = 8.5, 5.3 Hz), 7.94 (dd, integrates for 1.18, *J* = 8.5, 5.3 Hz), 7.73 (m, integrates for 0.66), 7.65 (dd, integrates for 1.18, *J* = 8.5, 5.3 Hz), 7.3 - 7.18 (m, integrates for 4.5), 7.15 – 7;05 (m, integrates for 4.5), benzylic protons vide infra, methyl groups at 3.03, 2.97, 2.52, 2.49, 2.17, cyclohexane protons: 3.2 – 0.8 (several multiplets).
After chromatography:
^{19}F NMR (188 MHz): dl-1 (10%) δ -111.3; dl-2 (26%) δ -111.8; **5c** (63%) δ -111.7, -112,6.



dl-1	10% (F); 15% (H)
dl-2	26% (F); 35% (H)
meso	63% (F); 47% (H)

(F:^{19}F NMR, H: ^{1}H NMR)

^{1}H NMR (300MHz, $CDCl_3$) δ of benzylic protons (all d)
dl-1 (**5a**) 4.47 (d, 2H, *J* = 13.2 Hz), 3.26 (d, 2H, *J* = 13.4 Hz) (integrates for 0.30)
dl-2 (**5b**) 4.96 (d, 2H, *J* = 13.0 Hz), 2.96 (d, 2H, *partially hidden*)(integrates for 0.70)
meso (**5c**) 4.23 (d, 1H, *J* = 13.2 Hz), 3.54 (d, 1H, *J* = 13.4 Hz (integrates for 0.5) and 4.74 (d, 1H, *J* = 13.4 Hz), 3.67 (d, 1H, *J* = 13.2 Hz (integrates for 0.5)