A Modular Approach to Achiral and Chiral Ni(II), Pd(II), and Pt(II) PCP Pincer Complexes based on Diaminobenzenes

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Supporting Information

Ni(PCP-Bu^t)Cl (4c). This complex has been prepared analogously to **4a** with $NiCl_2 \cdot 6H_2O$ (65 mg, 0.50 mmol) and **1c** (200 mg, 0.50 mmol) as the starting materials. Yield: 220 mg (90 %). Anal. Calcd. for $C_{21}H_{41}ClN_2NiP_2$: C, 53.96; H, 8.44; N, 5.72. Found: C, 53.74; H, 8.17; N, 5.55. ^{1}H NMR (δ, CD_2Cl_2, 20°C): 6.67 (s, 1H, Ph^4), 5.95 (d, *J* = 6.7 Hz, 2H, Ph^{3,5}), 4.12 (s, 2H, N*H*), 1.47 (s, 36H, C(C*H*$_3$)$_3$). ^{13}C{1H} NMR (δ, CD_2Cl_2, 20°C): 160.1 (t, *J* = 14.4 Hz, C^{Ph}), 134.6 (C^{Ph}), 127.1 (C^{Ph}), 100.1 (t, *J* = 6.0 Hz, C^{Ph}), 37.7 (*C*(CH$_3$)$_3$), 28.2 (t, *J* = 2.6 Hz, C(*C*H$_3$)$_3$). ^{31}P{^{1}H} NMR (δ, CD_2Cl_2, 20°C): 113.5.

Pd(PCP-Bu^t)Cl (5c). This complex has been prepared analogously to **4a** with $Pd(COD)Cl_2$ (144 mg, 0.50 mmol) and **1c** (200 mg, 0.50 mmol) as the starting materials. Yield: 233 mg (83 %). Anal. Calcd. for $C_{22}H_{41}ClN_2P_2Pd$: C, 49.17; H, 7.69; N, 5.21. Found: C, 49.23; H, 7.66; N, 5.12. ^{1}H NMR (δ, CD_2Cl_2, 20°C): 6.73 (t, *J* = 7.8 Hz, 1H, Ph^4), 6.12 (d, *J* = 7.9 Hz, 2H, Ph^{3,5}), 4.18 (s, 2H, N*H*), 1.45-1.39 (t, *J* = 7.3 Hz, 36H, C(C*H*$_3$)$_3$). ^{13}C{1H} NMR (δ, CD_2Cl_2, 20°C): 157.9 (t, *J* = 11.2 Hz, C^{Ph}), 126.7 (C^{Ph}), 117.0 (t, *J* = 11.5 Hz, C^{Ph}), 101.4 (t, *J* = 7.8 Hz, C^{Ph}), 38.1 (t, *J* = 8.9 Hz, *C*(CH$_3$)$_3$), 28.0 (t, *J* = 3.7 Hz, C(*C*H$_3$)$_3$). ^{31}P{^{1}H} NMR (δ, CD_2Cl_2, 20°C): 120.4.

Pd(PCP-BIPOL)Cl (5d). This complex has been prepared analogously to **4a** with $Pd(COD)Cl_2$ (106 mg, 0.37 mmol) and **1d** (200 mg, 0.37 mmol) as the starting materials. Yield: 115 mg (86%). Anal. Calcd. for $C_{30}H_{21}ClN_2O_4P_2Pd$: C, 53.20; H, 3.13; N, 4.14. Found: C, 52.84; H, 3.26; N, 4.21. ^{1}H NMR (δ, DMSO, 20°C): 7.68 – 7.17 (m, 16H Biph), 7.07 (t, *J* = 8.2 Hz, Ph^4), 6.28 (d, *J* = 7.9 Hz, 2H, Ph^{3,5}), 5,49 (2H, N*H*). ^{13}C{1H} NMR (δ, DMSO, 20°C): 150.7 (C^{Biph}), 149.4 (C^{Ph}), 149.2 (C^{Ph}), 140.5 (C^{Ph},), 131.1

(C^{Biph}),, 131.0 (C^{Biph}), 130.8 (C^{Ph}), 130.0 (C^{Biph}), 129.2 (C^{Biph}), 126.3 (C^{Biph}), 123.7 (C^{Ph}). $^{31}P\{^1H\}$ NMR (δ, DMSO, 20°C): 147.2.

Pd(PCP-TAR^{Me})Cl (R,R-5e). Pd(COD)Cl_2 (115 mg, 0.40 mmol) and **R,R-1e** (209 mg, 0.40 mmol) were stirred in THF (15 mL) at 50°C overnight. The solvent was then removed under vacuum, and the product was washed twice with pentane (10 mL) and dried. Yield: 210 mg (79%). Anal. Calcd. for $C_{18}H_{21}ClN_2O_{12}P_2Pd$: C, 32.70; H, 3.20; N, 4.24. Found: C, 32.34; H, 3.15; N, 4.15. ^1H NMR (δ, CD_3CN, 20°C): 7.45 (t, *J* = 8.0 Hz, 1H, Ph^4), 7.18 (s, 2H, $Ph^{3,5}$), 6.95 (s, 2H, N*H*), 5.50 – 5.06 (m, 4H, C*H*), 3.83 (6H, CH_3), 3.80 (6H, CH_3). $^{13}C\{1H\}$ NMR (δ, CD_3CN, 20°C): 167.4 (*C*O), 167.1 (*C*O), 142.1 (C^{Ph}), 130.1 (C^{Ph}), 126.4 (C^{Ph}), 125.2 (C^{Ph}), 77.2 (*C*H), 77.1 (*C*H), 76.3 (*C*H), 76.0 (*C*H), 53.1 (CH_3), 52.9 (CH_3). $^{31}P\{^1H\}$ NMR (δ,CD_3CN, 20°C): 119.5.

Pd(PCP-TAR^{Pr})Cl (R,R-5f). Pd(COD)Cl_2 (105 mg, 0.37 mmol) and **R,R-1f** (233mg, 0.37 mmol) were stirred in THF (ca. 15 mL) at room temperature overnight. The solvent was then evaporated under vacuum, and the product was washed twice with pentane (10 mL) and dried. Yield: 211 mg (74 %). Anal. Calcd. for $C_{26}H_{37}N_2O_{12}P_2PdCl$: C, 40.38; H, 4.38; N, 3.62. Found: C, 40.04; H, 4.43; N, 3.55. ^1H NMR (δ, CD_2Cl_2, 20°C): 7.40 (t, *J* = 8.3 Hz, 1H, Ph^4), 7.17 (s, 2H, $Ph^{3,5}$), 6.98 (s, 2H, N*H*), 5.18 – 4.85 (m, 8H, C*H*, C*H*(CH_3)$_2$), 1.30 - 1.28 (m, 24H, CH(CH_3)$_2$). $^{13}C\{1H\}$ NMR (δ, CD_2Cl_2, 20°C): 168.8 (*C*O), 166.0 (*C*O), 137.1 (C^{Ph}), 131.0 (C^{Ph}), 128.9 (C^{Ph}), 124.2 (C^{Ph}), 77.2 (*C*H), 77.1 (*C*H), 71.7 (*C*H(CH_3)$_2$), 21.9 (CH(CH_3)$_2$). $^{31}P\{^1H\}$ NMR (δ, CD_2Cl_2, 20°C): 117.3.

Pd(PCP^F-TAR^{Me})Cl (R,R-6e). This complex has been prepared analogously to **R,R-5e** with Pd(COD)Cl_2 (73 mg, 0.26 mmol) and **R,R-2e** (150 mg, 0.26 mmol) as the starting materials. Yield: 160 mg (86%). Anal. Calcd. for $C_{19}H_{20}ClF_3N_2O_{12}P_2Pd$: C, 31.30; H, 2.76; N, 3.84. Found: C, 31.39; H, 2.80; N, 3.77. ^1H NMR (δ,CD_3CN, 20°C): 7.01 (s, 2H, $Ph^{3,5}$), 6.84 (s, 2H, N*H*), 5.24 – 5.15 (m, 4H, C*H*), 3.76 (s, 6H, CH_3), 3.67 (s, 6H, CH_3). $^{13}C\{1H\}$ NMR (δ, CD_3CN, 20°C): 168.2 (*C*O), 167.9 (*C*O), 140.3 (C^{Ph}), 128.5 (C^{Ph}), 111.9 (C^{Ph}), 77.3 (*C*H), 77.2 (*C*H), 75.5 (*C*H), 75.3 (*C*H), 52.8 (CH_3), 52.5 (CH_3). $^{31}P\{^1H\}$ NMR (δ, CD_3CN, 20°C): 119.3.

Pt(PCP-Bu^t)Br (7c). This complex has been prepared analogously to **5a** with Pt(COD)Br_2 (50 mg, 0.11 mmol), **1c** (44 mg, 0.11 mmol) and triethylamine (20 μL, 0.13 mmol) as the starting materials. Yield: 58 mg (79 %). Anal. Calcd. for $C_{22}H_{41}BrN_2P_2Pt$: C, 39.41; H, 6.16; N, 4.18. Found: C, 39.24; H, 6.25; N, 4.02. ^1H NMR (δ, CD_2Cl_2, 20°C): 6.88 (t, *J* = 8.1 Hz, 1H, Ph^4), 6.16 (q, *J* = 7.9 Hz, 2H, $Ph^{3,5}$), 4.47 (t, *J* = 38.2 Hz, 2H, N*H*), 1.14 (s, 36H, C(CH_3)$_3$). $^{13}C\{1H\}$ NMR (δ, CD_2Cl_2, 20°C): 155.7 (t, *J* = 9.8

Hz, C^{Ph}), 134.6 (C^{Ph}), 126.6 (d, *J* = 11.4 Hz, C^{Ph}), 101.1 (t, *J* = 6.3 Hz, C^{Ph}), 39.4 (t, *J* = 13.0 Hz, *C*$(CH_3)_3$), 28.0 (C(*C*$H_3)_3$). $^{31}P\{^1H\}$ NMR (δ, CD_2Cl_2, 20°C): 109.5 (t, *J* = 1568.0 Hz).

Pd(PCP-Bu^t)(TFA) (8c). This complex has been prepared analogously to **8a** with $Pd(CF_3COO)_2$ (100 mg, 0.30 mmol) and **1c** (120 mg, 0.30 mmol) as the starting materials. Yield: 140 mg (78 %). Anal. Calcd. for $C_{24}H_{41}F_3N_2OP_2Pd$: C, 48.13; H, 6.90; N, 4.68. Found: C, 48.23; H, 7.05; N, 4.45. ^1H NMR (δ, CD_2Cl_2, 20°C): 6.73 (t, *J* = 7.8 Hz, 1H, Ph^4), 6.13 (d, *J* = 7.9 Hz, 2H, $Ph^{3,5}$), 4.18 (s, 2H, N*H*), 1.45 - 1.39 (m, 36H, C(C*H*$_3)_3$). $^{13}C\{1H\}$ NMR (δ, CD_2Cl_2, 20°C): 158.0 (t, *J* = 11.5 Hz, C^{Ph}), 129.8 (C^{Ph}), 126.7 (C^{Ph}), 101.4 (t, *J* = 8.1 Hz, C^{Ph}), 38.1 (t, *J* = 8.9 Hz, *C*$(CH_3)_3$), 28.0 (t, *J* = 3.7 Hz, C(*C*$H_3)_3$). $^{31}P\{^1H\}$ NMR (δ, CD_2Cl_2, 20°C): 120.4.

Pd(PCP^E-TAR^{Me})Cl (R,R-9e). This complex has been prepared analogously to **9a** with **R,R-23** (127 mg, 0.20 mmol) and $Pd_2(dba)_3$, (90 mg, 0.10 mmol) as the starting materials. Yield: 80 mg (55 %). Anal. Calcd. for $C_{23}H_{29}N_2O_{14}P_2PdCl$: C, 36.29; H, 3.84; N, 3.68. Found: C, 36.24; H, 3.78; N, 3.77. ^1H NMR (δ, $CDCl_3$, 20°C): 6.99 (s, 2H, Ph), 6.20 (s, 2H, N*H*), 4.06 – 3.82 (m, 6H: 4H, C*H*$COOCH_3$; 2H, CH_2^{iBu}), 2.05 (m, 1H, CH^{iBu}), 1.00 (d, *J* = 6.6 Hz, 6H, CH_3^{iBu}). $^{13}C\{1H\}$ NMR (δ, $CDCl_3$, 20°C): 188.9 (*C*OO^{i}Bu), 166.9, (*C*O), 143.6 (C^{Ph}), 139.6 (C^{Ph}), 134.8 (C^{Ph}), 110.1 (C^{Ph}), 78.0 (*C*H), 77.8 (*C*H), 77.6 (*C*H), 76.4 (*C*H), 71.1 (CH_2^{iBu}), 54.3 (CH_3), 53.7 (CH_3), 27.8 (CH^{iBu}), 19.2 (CH_3^{iBu}). $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$, 20°C): 147.5.

Table S1. Details for the crystal structure determinations of complexes **4a**·½C_6H_6, **4c**, **5a**·2DMF, **6a**·CH_3CN, **7a**·[NEt_3H]Br·CH_2Cl_2, **8b**, and **8d**·2Et_2O.

	4a·½C_6H_6	**4c**	**5a**·2DMF	**6a**·CH_3CN	**7a**·[NEt_3H]Br·CH_2Cl_2	**8b**	**8d**·2Et_2O
formula	$C_{33}H_{28}ClN_2NiP_2$	$C_{22}H_{41}ClN_2NiP_2$	$C_{36}H_{39}ClN_4O_2P_2Pd$	$C_{33}H_{27}ClF_3N_3P_2Pd$	$C_{37}H_{43}Br_2Cl_2N_3P_2Pt$	$C_{20}H_{33}F_3N_2O_2P_2Pd$	$C_{40}H_{41}F_3N_2O_8P_2Pd$
fw	608.67	489.67	763.50	726.37	1017.49	558.82	903.09
cryst.size, mm	0.47 x 0.22 x 0.15	0.58 x 0.25 x 0.05	0.40 x 0.27 x 0.23	0.38 x 0.28 x 0.204	0.18 x 0.12 x 0.10	0.62 x 0.55 x 0.38	0.46 x 0.28 x 0.24
space group	$P2_1/c$ (no. 14)	$Pna2_1$ (no. 33)	$P2_12_12_1$ (no. 19)	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/n$ (no. 14)	$P2_12_12_1$ (no. 19)
a, Å	9.3016(5)	22.614(2)	12.9104(6)	11.1604(5)	8.7928(5)	12.4771(6)	13.6286(12)
b, Å	21.4580(12)	7.9747(8)	14.3253(6)	19.9505(9)	18.5713(11)	14.3627(7)	15.5379(14)
c, Å	15.0813(8)	13.7454(14)	18.6546(8)	13.6931(6)	24.1001(14)	13.8741(7)	18.6978(17)
α, deg	90	90	90	90	90	90	90
β, deg	99.619(1)	90	90	94.624(1)	97.161(1)	94.266(1)	90
γ, deg	90	90	90	90	90	90	90
V, $Å^3$	2967.8(3)	2478.8(4)	3450.1(3)	3038.9(2)	3904.7(4)	2479.4(2)	3959.4(6)
Z	4	4	4	4	4	4	4
ρ_{calc}, g cm^{-3}	1.362	1.312	1.470	1.588	1.731	1.497	1.515
T, K	297(2)	100(2)	173(2)	100(2)	173(2)	173(2)	100(2)
μ, mm^{-1} (Mo Kα)	0.877	1.030	0.747	0.851	5.889	0.918	0.618
F(000)	1260	1048	1568	1464	1992	1144	1848
θ_{max}, deg	28	30	30	30	30	30	30
no. of rflns measd	20760	17862	45267	44927	57788	33847	57753
no. of unique rflns	7147	6018	9963	8788	11370	7185	11504
no. of rflns I>2σ(I)	3374	5453	9661	8429	9338	6630	10637
no. of params	352	265	427	389	424	281	505
R_1 (I > 2σ(I)) [a]	0.0391	0.0335	0.0234	0.0203	0.0293	0.0263	0.0397
R_1 (all data)	0.1026	0.0409	0.0246	0.0213	0.0412	0.0290	0.0467
wR_2 (all data)	0.0788	0.0821	0.0628	0.0533	0.0722	0.0678	0.1026
Diff.Four.peaks min/max, $eÅ^{-3}$	-0.34/0.33	-0.44/0.56	-0.31/0.83	-0.55/0.74	-1.60/1.48	-0.61/0.95	-1.12/2.37

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma(w(F_o^2-F_c^2)^2)/\Sigma(w(F_o^2)^2)]^{½}$

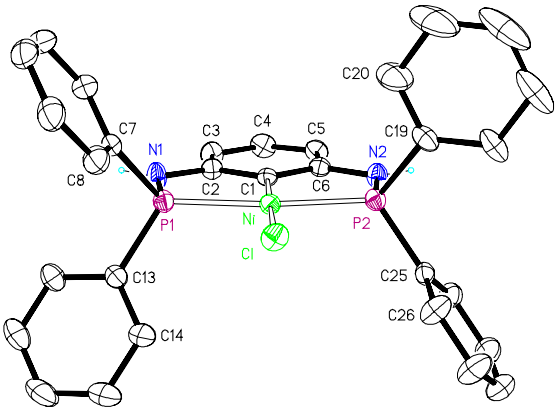

Figure S1. Structural view of Ni(PCP-Ph)Cl·C_6H_6 (**4a**·C_6H_6) showing 20% thermal ellipsoids (C-bonded H atoms and benzene omitted for clarity). Selected bond lengths (Å) and bond angles (°): Ni-C(1) 1.894(3), Ni-P(1) 2.1768(8), Ni-P(2) 2.1774(8), Ni-Cl 2.2137(8), P(1)-N(1) 1.664(2), P(2)-N(2) 1.670(2), P(1)-Ni-P(2) 167.32(3), C(1)-Ni-P(1) 83.73(8), C(1)-Ni-P(2) 83.59(8), Cl-Ni-P(1) 96.75(3), Cl-Ni-P(2) 95.91(3).

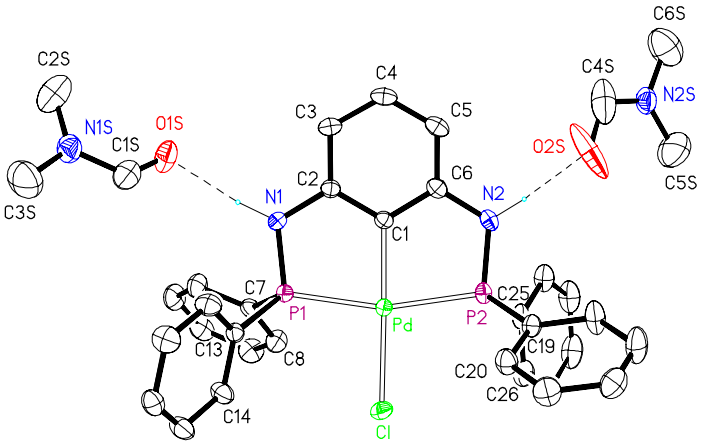

Figure S2. Structural view of Pd(PCP-Ph)Cl·2DMF (**5a**·2DMF) showing 40% thermal ellipsoids (C-bonded H atoms omitted for clarity). Selected bond lengths (Å) and bond angles (°): Pd-C(1) 2.002(2), Pd-P(1) 2.2748(4), Pd-P(2) 2.2851(5), Pd-Cl 2.3699(4), P(1)-N(1) 1.673(2), P(2)-N(2) 1.671(2), P(1)-Pd-P(2) 163.54(2), C(1)-Pd-P(1) 81.80(5), C(1)-Pd-P(2) 81.79(5), Cl-Pd-P(1) 96.97(2), Cl-Pd-P(2) 99.46(2); hydrogen bonds: N(1)---O(1S) 2.889(2), N(2)---O(2S) 2.833(3).

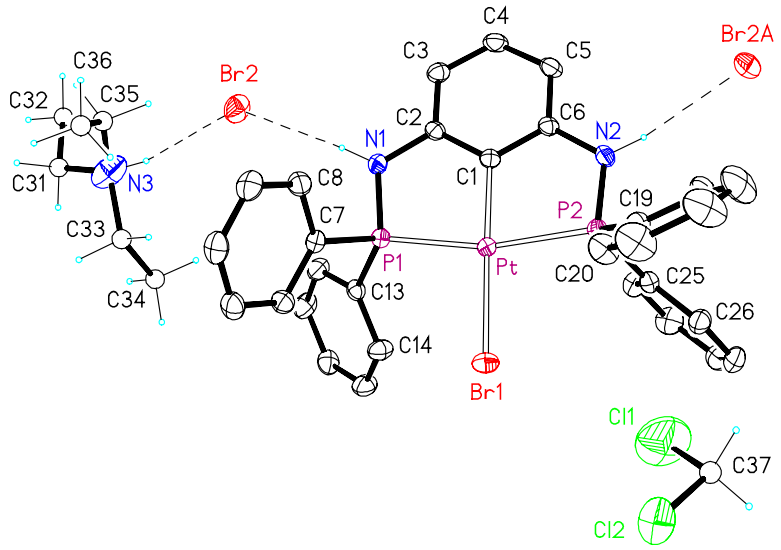

Figure S3. Structural view of Pt(PCP-Ph)Br·[NEt_3H]Br·CH_2Cl_2 (**7a**·[NEt_3H]Br·CH_2Cl_2) showing 40% thermal ellipsoids (arene-bonded H atoms omitted for clarity, solvent carbon atoms displayed as spheres, Br2A is a symmetry equivalent of Br). Selected bond lengths (Å) and bond angles (°): Pt-C(1) 2.006(3), Pt-P(1) 2.2750(8), Pt-P(2) 2.2712(8), Pt-Br(1) 2.5100(4), P(1)-N(1) 1.672(3), P(2)-N(2) 1.666(3), P(1)-Pt-P(2) 164.33(3), C(1)-Pt-P(1) 81.90(9), C(1)-Pt-P(2) 82.50(9), Br(1)-Pt-P(1) 99.31(2), Br(1)-Pt-P(2) 96.27(2); hydrogen bonds: N(1)---Br(2) 3.429(3), N(2)---Br(2A) 3.451(3), N(3)---Br(2) 3.260(5).