First Chiral Chelated *N*-Heterocyclic *Bis*-Carbene Complexes

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Supporting Information

Experimental Section

2,2′-Dimethyl-1,1′-binaphthalene (4) To a mixture of (*S*)-1,1′-bi-2-naphthol bis (trifluoromethane sulfonate) (3.243 g, 5.892 mmol) and (dppp)$NiCl_2$ (321.4 mg, 0.5951 mmol) in diethyl ether (30 mL) was added a solution of methylmagnesium bromide (5.9 mL, 3 M) in diethyl ether and the reaction was stirred for 1 h. The reaction was quenched with dilute hydrochloric acid (2 M) and diluted with diethyl ether. The organic layer was washed with water and brine, dried ($MgSO_4$) and filtered. Column chromatography of the concentrated residue with 5% ethyl acetate in petroleum ether as eluant gave naphthalene **4** (1.64 g, 99%) as a viscous oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.2 Hz, 2H), 7.86 (d, *J* = 8.5 Hz, 2H), 7.49 (d, *J* = 8.5 Hz, 2H), 7.37 (dd, *J* = 7.5, 8.5 Hz, 2H), 7.18 (dd, *J* = 7.5, 8.5 Hz, 2 H), 7.04 (d, *J* = 8.5 Hz, 2 H), 2.02 (s, 6H).

2,2′-Di(bromomethyl)-1,1′-binaphthalene (5) Naphthalene **4** (3.67 g, 13.0 mmol), *N*-bromosuccinimide (4.63 g, 26.0 mmol) and AIBN (cat.) were stirred in carbon tetrachloride (40 mL) with reading lamp irradiation for 5 h. A scoop of dry silica was added and the reaction was concentrated in vacuo. Column chromatography of the resultant residue with initially 5% ethyl acetate in petroleum ether followed by 20% ethyl acetate in petroleum ether as eluant gave dibromide **5** (5.08 g, 89%) as a white solid. rev. phase HPLC (1% water in methanol, 1 mL/min, Zorbax ODS): $Ar(CH_2Br)_2$ (5.07 min, 90%), $Ar(CH_2Br)(CHBr_2)$ (6.03 min, 10%).

1,1′-(2,2′-dimethyl-1,1′-binaphthyl) diimidazole (6) Imidazole (0.449 mg, 6.59 mmol) and sodium hydride (0.264 g, 6.59 mmol) were stirred in dimethoxyethane (10 mL) at 0 °C for 10 min. A solution of dibromide **5** (0.967 g, 2.20 mmol) in dimethoxyethane (10 mL) was added via cannula and the reaction was stirred with slow warming to rt over 4 h. The reaction was quenched with water, and diluted with CH_2Cl_2. The aqueous layer was extracted twice with

CH_2Cl_2, and the organics were combined, washed with brine, dried ($MgSO_4$) and filtered. Column chromatography of the resultant residue with 10% methanol in CH_2Cl_2 as eluant gave imidazole **6** (0.733 g, 80%) as a cream coloured solid. ^{1}H NMR (250 MHz, $CDCl_3$): δ 8.04 (d, *J* = 8.7 Hz, 2H), 7.98 (d, *J* = 7.8 Hz, 2H), 7.55 (dd, *J* = 7.8, 7.8 Hz, 2H), 7.36 (d, *J* = 8.7 Hz, 2H), 7.34 (dd, *J* = 7.8, 7.8 Hz, 2H), 7.12 (d, *J* = 7.8 Hz, 2H), 7.01 (s, 2H), 6.97 (s, 2H), 6.64 (s, 2H), 4.55 (d, *J* = 15.3 Hz, 2H), 4.35 (d, *J* = 15.3 Hz, 2H).

1,1′-(2,2′-dimethyl-1,1′-binaphthyl)-3,3′-dimethyldiimidazolium diiodide (7) Imidazole **6** (117 mg, 0.283 mmol) and methyl iodide (351 uL, 5.64 mmol) were stirred in CH_2Cl_2 (4 mL) for 21 h. The reaction was concentrated to give diiodide **7** (214 mg, quant) as a white solid. ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.39 (s, 2H), 8.25 (d, *J* = 8.7 Hz, 2H), 8.07 (d, *J* = 7.2 Hz, 2H), 7.79 (d, *J* = 8.7 Hz, 2H), 7.54 (dd, *J* = 7.2, 7.2 Hz, 2H), 7.23 (s, 2H), 7.20 (dd, *J* = 7.2, 7.2 Hz, 2H), 7.09 (s, 2H), 6.61 (d, *J* = 8.7 Hz, 2H), 5.32 (d, *J* = 15.2 Hz, 2H), 5.10 (d, *J* = 15.2 Hz, 2H), 3.47 (s, 6H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 136.29, 133.79, 132.86, 131.73, 130.36, 129.60, 128.19, 127.61, 126.88, 126.84, 124.80, 123.08, 122.15, 51.09, 35.38; MSFAB (SIMS(+)) *m/z* (relative intensity): 697 ($C_{30}H_{28}N_4I_2$, M^+-1, 0.4), 571 (M^+-I, 99).

***Trans*-diiodo-[1,1′-(2,2′-dimethyl-1,1′-binaphthyl)-3,3′-dimethyldiimidazoline-2,2′-diylidene] palladium (II) (1a) and *cis*-diiodo-[1,1′-(2,2′-dimethyl-1,1′-binaphthyl)-3,3′-dimethyldiimidazoline-2,2′-diylidene] palladium (II) (1b)** (a) Preparation in hot DMSO Imidazolium salt **7** (358 mg, 0.512 mmol) and palladium acetate (125 mg, 0.559 mmol) were stirred in DMSO (30 mL) at 140 °C for 6 hours. The solvent was removed by distillation under high vacuum, and the residue was dissolved in CH_2Cl_2. Chromatography of the residue with CH_2Cl_2 as eluant gave complex **1a** (167 mg, 41%), and with ethyl acetate gave complex **1b** (135 mg, 33%) both as yellow solids. **1a (*trans*)** ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.97 (d, *J* =

7.8 Hz, 2H), 7.94 (d, *J* = 7.5 Hz, 2H), 7.48 (dd, *J* = 7.3, 7.5 Hz, 2H), 7.36 (dd, *J* = 7.3, 8.7 Hz, 2H), 7.29 (d, *J* = 8.7 Hz, 2H), 7.28 (d, *J* = 7.8 Hz, 2H), 7.17 (d, *J* = 1.8 Hz, 2H), 6.90 (d, *J* = 1.8 Hz, 2H), 5.70 (d, *J* = 16.5 Hz, 2H), 4.70 (d, *J* = 16.5 Hz, 2H), 3.81 (s, 6H); ^{13}C NMR (75.469 MHz, $CDCl_3$): δ 170.95 (2), 133.72 (2), 133.43 (2), 132.92 (2), 132.71 (2), 129.00 (2), 128.86 (2), 126.92 (2), 126.01 (2), 125.93 (2), 125.38 (2), 123.71 (2), 121.61 (2), 53.37 (2), 38.60 (2); MSFAB (SIMS(+)) *m/z* (relative intensity): 803 ($C_{30}H_{26}N_4PdI_2$, M^++1, 42), 802 (M^+, 26), 675 (100); rev. phase HPLC (10% water in methanol, 1 mL/min, Zorbax ODS, 300 nm): 3.87 min (100%). **1b (*cis*)** ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.11 (d, *J* = 8.7 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 7.5 Hz, 1H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.61 (d, *J* = 8.7 Hz, 1H), 7.51 (dd, *J* = 7.5, 7.5 Hz, 1H), 7.47 (dd, *J* = 7.8, 8.4 Hz, 1H), 7.35 (d, *J* = 1.8 Hz, 1H), 7.30-7.35 (m, 2H), 7.22 (dd, *J* = 7.8, 8.7 Hz, 1H), 7.10 (d, *J* = 8.4 Hz, 1H), 6.98 (d, *J* = 1.8 Hz, 1H), 6.80 (d, *J* = 8.7 Hz, 1H), 6.41 (d, *J* = 1.8 Hz, 1H), 5.98 (d, *J* = 1.8 Hz, 1H), 5.80 (d, *J* = 17.1 Hz, 1H), 5.71 (d, *J* = 15.6 Hz, 1H), 4.87 (d, *J* = 17.1 Hz, 1H), 4.69 (d, *J* = 15.6 Hz, 1H), 3.89 (s, 3H), 3.73 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.21, 163.71, 134.03, 133.18, 133.08 (2), 133.02, 131.91, 131.44, 130.78, 129.91, 128.86, 128.77, 128.21, 127.47, 126.93, 126.65, 126.30, 126.14, 125.20, 124.28, 124.01, 123.34, 122.60, 121.27, 113.15, 55.31, 52.89, 39.58, 39.52; MSFAB (SIMS(+)) *m/z* (relative intensity): 803 ($C_{30}H_{26}N_4PdI_2$, M^++1, 6), 802 (M^+, 12), 675 (100); rev. phase HPLC (10% water in methanol, 1 mL/min, Zorbax ODS, 300 nm): 3.83 min (100%).

(b) Preparation via pre-formation of free carbene at rt Imidazolium salt **7** (9.9 mg, 0.14 mmol) and potassium *t*-butoxide (3.4 mg, 0.030 mmol) were stirred in THF (7 mL) at rt under N_2 for 10 minutes. Palladium acetate (3.8 mg, 0.017 mmol) was added in THF (1 mL) and the reaction was stirred for two hours and then concentrated. Column chromatography of the resultant residue with CH_2Cl_2 as eluant gave complex **1a** (2.4 mg, 21%) as a yellow solid.

***Trans*-diiodo-[1,1′-(2,2′-dimethyl-1,1′-binaphthyl)-3,3′-dimethyldiimidazoline-2,2′-diylidene] nickel (II) (2a)** (a) Preparation in hot NMP Imidazolium salt **7** (29 mg, 0.041 mmol) and nickel acetoacetate (21 mg, 0.082 mmol) were stirred in NMP (0.20 mL) at 200 °C for 1 h. The solvent was removed by distillation under high vacuum, and the residue was dissolved in CH_2Cl_2. Chromatography of the residue with CH_2Cl_2 as eluant gave complex **2a** (7.9 mg, 26%) as a red solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.98 (d, *J* = 8.4 Hz, 2H), 7.97 (d, *J* = 7.7 Hz, 2H), 7.48-7.52 (m, 2H), 7.34-7.37 (m, 4H), 7.34 (d, *J* = 8.7 Hz, 2H), 7.05 (d, *J* = 1.8 Hz, 2H), 6.78 (d, *J* = 1.8 Hz, 2H), 6.21 (d, *J* = 16.3 Hz, 2H), 4.79 (d, *J* = 16.3 Hz, 2H), 4.07 (s, 6H); ^{13}C NMR (75.469 MHz, $CDCl_3$): δ 176.41 (2), 133.71 (2), 133.54 (2), 133.30 (2), 133.00 (2), 128.91 (2), 128.83 (2), 126.95 (2), 126.09 (2), 126.00 (2), 125.48 (2), 124.46 (2), 122.23 (2), 52.93 (2), 38.24 (2); MSFAB (SIMS(+)) *m/z* (relative intensity): 755 ($C_{30}H_{26}N_4NiI_2$, M^+, 6), 500 (M^+-I_2, 100); rev. phase HPLC (10% water in methanol, 1 mL/min, Zorbax ODS, 300 nm): 3.97 min (100%).

(b) Preparation from pre-formed carbene at rt Imidazolium salt **7** (15 mg, 0.022 mmol) and potassium *t*-butoxide (6.0 mg, 0.053 mmol) were stirred in THF (8 mL) at rt under N_2 for 10 minutes. Bis(triphenylphosphine)nickel chloride (17 mg, 0.026 mmol) was added in THF (2 mL) and the reaction was stirred for 19 hours and then concentrated. Column chromatography of the resultant residue with CH_2Cl_2 as eluant gave complex **2a** (7.4 mg, 45%) as a red solid.

Details of Crystal Structure Analysis

(a) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-137339 (**1a**), CCDC-137340 (**1b**), and CCDC-137338 (**2a**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge

CB12EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk. See Supporting information for details of the crystal structure analysis.

(b) Crystal structure analysis (Rigaku AFC5S diffractometer) of **1a**: $C_{30}H_{26}I_2N_4Pd$, M_r = 802.77, orange plate of dimensions 0.12 x 0.27 x 0.35 mm^3, monoclinic, space group *C*2/c, *a* = 18.229 (3), *b* = 17.368 (2), *c* = 12.682 (2) Å, β = 116.10 (1)°, *V* = 3605.6 (8) $Å^3$, ρ_{calcd} = 1.48 mg m^{-3}, $2\theta_{max}$ 55°, MoK(α) radiation with graphite monochromator, λ = 0.71069 Å, scan mode ω-2θ, *T* = 296 K, 4444 measured reflections ($2 < \theta < 27.5°$), 2677 reflections with $I>1\sigma(I)$, 2677 reflections were used in the refinement, μ = 2.22 mm^{-1}, transmission factors min/max 0.740/1.0. The structure was solved by the Patterson method and expanded using DIRDIF.[e] There was a disorded solvent channel, which was modeled with random carbon atoms. Full matrix least squares refinement based on F was performed with teXsan.[14f] 198 parameters were used, the hydrogen atoms were fixed at calculated positions, *R* = 0.053, *wR* = 0.047, GOF = 2.21, maximum residual electron density 0.83 e $Å^{-3}$.

(c) Crystal structure analysis (Rigaku AFC5S diffractometer) of **1b**.2$CHCl_3$: $C_{30}H_{26}I_2N_4Pd$ with 2$CHCl_3$, M_r = 1041.48, yellow plate of dimensions 0.06 x 0.31 x 0.31 mm^3, monoclinic, space group $P2_1/n$ (#14), *a* = 10.630 (1), *b* = 26.301 (2), *c* = 13.994 (1) Å, β = 103.656 (8)°, *V* = 3801.7 (6) $Å^3$, ρ_{calcd} = 1.82 mg m^{-3}, $2\theta_{max}$ 55°, MoK(α) radiation with graphite monochromator, λ = 0.71069 Å, scan mode ω, *T* = 293 K, 9447 measured reflections ($2 < \theta < 27.5°$), 8981 independant reflections, 7083 reflections with I > 0 were used in the refinement, μ = 2.56 mm^{-1}, transmission factors min/max 0.618/1.0. The structure was solved by the Patterson method using SHELXS-86.[g] One of the $CHCl_3$ molecules was disordered and was removed from the model by the SQUEEZE[i] program in PLATON.[j] Full matrix least squares refinement based on F^2 was performed with SHELXL-93.[h] 372 parameters were used, the hydrogen

atoms were fixed at calculated positions, R = 0.086, wR = 0.121, GOF = 1.02, maximum residual electron density 0.70 e Å^{-3}.

(d) Crystal structure analysis (Rigaku AFC5S diffractometer) of **2a**.2CH_2Cl_2: $C_{30}H_{26}I_2N_4Ni$ with 2CH_2Cl_2, M_r = 924.61, dark red crystal of dimensions 0.19 x 0.35 x 0.38 mm^3, triclinic, space group *P*1bar (#2), a = 12.014 (2), b = 12.737 (2), c = 13.120 (1) Å, α =77.07 (1), β = 74.44 (1), γ = 65.53 (1)°, V = 1745.6 (5) Å^3, ρ_{calcd} = 1.76 mg m^{-3}, 2θ_{max} 50°, MoK(α) radiation with graphite monochromator, λ = 0.71069 Å, scan mode ω-2θ, T = 213 K, 6488 measured reflections (2 < θ < 25°), 6168 independant reflections, 6166 reflections were used in the refinement, μ = 2.66 mm^{-1}, transmission factors min/max 0.832/1.0. The structure was solved by the Patterson method using SHELXS-86.[g] Full matrix least squares refinement based on F^2 was performed with SHELXL-93.[h] One of the CH_2Cl_2 molecules was disordered and modeled in terms of two orientations. 386 parameters were used, the hydrogen atoms were fixed at calculated positions, R = 0.044, wR = 0.086, GOF = 1.08, maximum residual electron density 1.43 e Å^{-3}.

(e) teXsan: Crystal Structure Analysis Package, version 1.7-2, Molecular Structure Corporation, The Woodlands, TX, **1995**.

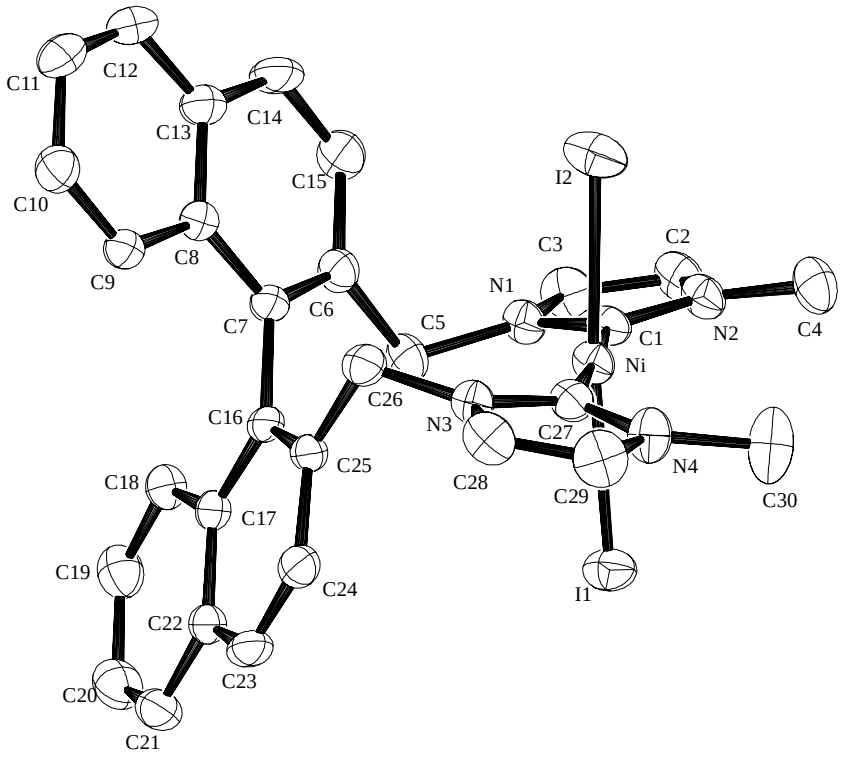
(f) DIRDIF: V. Parthasarathi; P. T. Beurskens; H. J. B. Slot, *Acta Cryst.* **1983**, *A39*, 860.

(g) SHELXS-86: G. M. Sheldrick, *Acta Cryst.* **1990**, *A46*, 467.

(h) SHELXL-93: G. M. Sheldrick, Universität Gottingen, Germany, **1993**.

(i) P. van der Sluis; A. L. Spek, *Acta Cryst.* **1990**, *A46*, 194.

(j) A. L. Spek, *Acta Cryst.* **1990**, *A46*, C-34.



2a

ORTEP drawing of the molecular structure of the *trans* Ni-complex **2a** (thermal ellipsoids at the 50% probability level). Selected bond lengths [Å] and angles [°]: Ni-C1 1.889 (4), Ni-C27 1.901 (4), Ni-I1 2.5094 (8), Ni-I2 2.4937 (8), C1-Ni-C27 177.7 (2), I1-Ni-I2 174.81 (3), I1-Ni-C1 89.90 (12), I2-Ni-C27 92.03 (13).