*Eur. J. Inorg. Chem.* **2004** · © WILEY-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, 2004 · ISSN 1434–1948

## ***SUPPORTING INFORMATION***

***Title:*** Synthesis, Structure and Complexation Ability of Novel Metalloreceptors Containing Two Pincer Complexes of Palladium(II)
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Synthesis of **3a**, **3b**, **5a**, **5b**, **6a**, **6b**, **7a**, and **7b**

**General.** All chemical reagents were purchased and used without further purification. Acetonitrile was distilled from calcium hydride under nitrogen atmosphere prior to use. Diols **2a**,[13] **2b**[14] and dithiol **4**[15] was prepared by the procedures described in the literature. Melting points were determined on a Yanaco melting point apparatus and were uncorrected. $^1$H NMR spectra were recorded on a Bruker ARX400 at 400 MHz. $^{13}$C NMR spectra were recorded on a Bruker ARX400 at 100 MHz. Coupling constants (*J*) were reported in Hz. NMR chemical shifts were reported in ppm downfield from a tetramethylsilane peak. NMR solvents were purchased and used without further purification. ESI-MS spectra were recorded with a Perkin-Elmer Sciex API-100 and an Applied Biosystems QStar/Pulsar *i* spectrometer. Elemental analyses were performed at Chemical Analysis Center, University of Tsukuba.

**Synthesis of tosylate 3a.** To a solution of **2a** (18.47 g, 64.5 mmol) in THF (150 mL) was added a solution of NaOH (4.593 g, 115 mmol) in water (50 mL), and the mixture was stirred for 1 h below 0 °C. A solution of *p*-toluenesulfonyl chloride (14.81 g, 77.2 mmol) in THF (60 mL) was then added dropwise to the reaction mixture during 1 h below 0 °C, and then the mixture was stirred for further 3 h. The mixture was poured onto 3 M hydrochloric acid and the organic solvent was evaporated. The residue was extracted with chloroform (3 × 150 mL), and the organic layer was dried over anhydrous $MgSO_4$. After removal of the solvent, the crude product was purified by column chromatography ($SiO_2$, $CHCl_3$/EtOAc (1:1) then EtOAc) to afford **3a** as a pale yellow oil (22.71 g, 80%). $^1$H NMR (400 MHz, $CDCl_3$) *d* 2.21 (brs, 1H), 2.41 (s, 3H), 3.66-3.68 (m, 2H), 3.72-3.74 (m, 2H), 3.78 (t, *J* = 4.8 Hz, 2H), 3.82 (t, *J* = 4.8 Hz, 2H), 3.88 (t, *J* = 4.8 Hz, 2H), 4.09 (t, *J* = 4.8 Hz, 2H), 4.15 (t, *J* = 4.8 Hz, 2H), 4.20 (t, *J* = 4.8 Hz, 2H), 6.86-6.94 (m, 4H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.80 (d, *J* = 8.2 Hz, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) *d* 21.59 ($CH_3$), 61.67, 68.61, 68.68, 68.83, 69.39, 69.47, 69.77, 72.59 ($CH_2$), 114.31, 114.38, 121.64 (×2), 127.95, 129.80 (CH), 132.93, 144.77, 148.71 (×2) (C). Anal. Calcd. for $C_{21}H_{28}O_8S$: C, 57.26; H, 6.41. Found: C, 56.91; H, 6.26.

**Synthesis of tosylate 3b.** To a solution of **2b** (33.43 g, 89.3 mmol) in THF (100 mL) was added a solution of NaOH (5.553 g, 139 mmol) in water (50 mL), and the mixture was stirred for 30 min below 0 °C. A solution of *p*-toluenesulfonyl chloride (20.13 g, 106 mmol) in THF (50 mL) was then added dropwise to the reaction mixture during 1 h below 0 °C, and then the mixture was stirred for further 6 h. The mixture was poured onto 3 M hydrochloric acid and the organic solvent was evaporated. The residue was extracted with chloroform (3 × 100 mL), and the organic layer was dried over anhydrous $MgSO_4$. After removal of the solvent, the crude product was purified by column chromatography ($SiO_2$, EtOAc) to afford **3b** as a pale yellow oil (29.65 g, 63%).

$^1$H NMR (400 MHz, $CDCl_3$) *d* 2.40 (brs, 1H), 2.43 (s, 3H), 3.60-3.62 (m, 4H), 3.67-3.75 (m, 10H), 3.84 (t, *J* = 4.8 Hz, 2H), 3.87 (t, *J* = 4.8 Hz, 2H), 4.14-4.18 (m, 6H), 6.91 (s, 4H), 7.33 (d, *J* = 8.2 Hz, 2H), 7.79 (d, *J* = 8.2 Hz, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) *d* 21.62 ($CH_3$), 61.72, 68.47,

68.60, 68.70, 69.28, 69.71, 69.75, 70.27, 70.72, 70.76, 70.82, 72.74 ($CH_2$), 114.24, 114.37, 121.60 (×2), 127.98, 129.82 (CH), 133.00, 144.80, 148.67, 148.69 (C). Anal. Calcd for $C_{25}H_{36}O_{10}S$: C, 56.80; H, 6.86. Found: C, 56.42; H, 6.82.

**Synthesis of diol 5a.** To a solution of dithiol **4** (1.701 g, 9.99 mmol) and tosylate **3a** (8.800 g, 20.0 mmol) in acetonitrile (120 mL) was added $K_2CO_3$ (3.326 g, 24.1 mmol), and then the mixture was refluxed for 16 h. After removal of the solvent, water (60 mL) was added to the residue. The mixture was extracted with chloroform (3 × 60 mL), and the organic layer was dried over anhydrous $MgSO_4$. The solvent was evaporated, and the crude product was purified by column chromatography ($SiO_2$, EtOAc) to afford **5a** as a yellow oil (3.722 g, 53%). $^1$H NMR (400 MHz, $CDCl_3$) *d* 2.63 (t, *J* = 6.8 Hz, 4H), 2.78 (brs, 2H), 3.65-3.69 (m, 8H), 3.71-3.75 (m, 4H), 3.73 (s, 4H), 3.82 (t, *J* = 4.8 Hz, 4H), 3.87 (t, *J* = 4.6 Hz, 4H), 4.13-4.16 (m, 8H), 6.91 (s, 8H), 7.16-7.26 (m, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$) *d* 30.75, 36.52, 61.73, 68.48, 68.72, 69.40, 69.52, 70.91, 72.74 ($CH_2$), 114.26, 114.38, 121.55, 121.69, 127.65, 128.62, 129.47 (CH), 138.69, 148.66, 148.77 (C). Anal. Calcd for $C_{36}H_{50}O_{10}S_2$: C, 61.17; H, 7.13. Found: C, 60.87; H, 7.10.

**Synthesis of diol 5b.** To a solution of dithiol **4** (1.338 g, 7.86 mmol) and tosylate **3b** (9.00 g, 15.4 mmol) in acetonitrile (200 mL) was added $K_2CO_3$ (2.660 g, 19.2 mmol) , and then the mixture was stirred for 16 h. After removal of the solvent, water (50 mL) was added to the residue. The mixture was extracted with chloroform (3 × 50 mL), and the organic layer was dried over anhydrous $MgSO_4$. The solvent was evaporated, and the crude product was purified by column chromatography ($SiO_2$, EtOAc then EtOAc/EtOH (4:1)) to afford **5b** as a pale yellow oil (5.536 g, 80%). $^1$H NMR (400 MHz, $CDCl_3$) *d* 2.62 (t, *J* = 7.0 Hz, 4H), 2.75 (brs, 2H), 3.59-3.62 (m, 12H), 3.67-3.69 (m, 4H), 3.71-3.75 (m, 12H), 3.73 (s, 4H), 3.86 (t, *J* = 5.0 Hz, 4H × 2), 4.16 (t, *J* = 5.0 Hz, 4H × 2), 6.91 (s, 8H), 7.16-7.26 (m, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$) *d* 30.74, 36.51, 61.70, 68.53, 68.62, 69.68, 69.74, 70.30, 70.32, 70.74, 70.77, 70.82, 72.74 ($CH_2$), 114.34, 114.43, 121.57, 121.62, 127.64, 128.60, 129.40 (CH), 138.69, 148.68, 148.74 (C). Anal. Calcd for $C_{44}H_{66}O_{14}S_2 \cdot 0.5H_2O$: C, 59.24; H, 7.57. Found: C, 59.17; H, 7.34.

**Synthesis of ditosylate 6a.** To a solution of diol **5a** (3.722 g, 5.27 mmol) in THF (40 mL) was added a solution of NaOH (0.631 g, 15.8 mmol) in water (25 mL), and the mixture was stirred for 1 h below 0 °C. A solution of *p*-toluenesulfonyl chloride (2.512 g, 13.2 mmol) in THF (40 mL) was then added dropwise to the reaction mixture during 40 min below 0 °C, and the mixture was stirred for further 5 h. The mixture was poured onto 3 M hydrochloric acid and then the organic solvent was evaporated. The mixture was extracted with chloroform (3 × 30 ml), and the organic layer was dried over anhydrous $MgSO_4$. After removal of the solvent, the crude product was purified by column chromatography ($SiO_2$, $CHCl_3$/EtOAc (2:1)) to afford **6a** as a pale yellow oil (5.029 g, 94%). $^1$H NMR (400 MHz, $CDCl_3$) *d* 2.41 (s, 6H), 2.61 (t, *J* = 6.6 Hz, 4H), 3.67 (t, *J* = 6.6 Hz, 4H), 3.72 (s, 4H), 3.74-3.79 (m, 12H), 4.06 (t, *J* = 4.4 Hz, 4H), 4.12 (t, *J* = 5.0 Hz, 4H), 4.17 (t, *J* =

4.8 Hz, 4H), 6.85-6.91 (m, 8H), 7.15-7.26 (m, 4H), 7.29 (d, *J* = 8.2 Hz, 4H), 7.79 (d, *J* = 8.2 Hz, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$) *d* 21.62 ($CH_3$), 30.81, 36.50, 68.77, 68.90 (×2), 69.38, 69.46, 69.90, 70.95 ($CH_2$), 114.87, 114.93, 121.67, 121.80, 127.64, 127.70, 128.59, 129.48, 129.80 (CH), 133.03, 138.69, 144.73, 148.85, 148.97 (C). Anal. Calcd for $C_{50}H_{62}O_{14}S_4$: C, 59.15; H, 6.16. Found: C, 58.82; H, 6.20.

**Synthesis of ditosylate 6b.** To a solution of diol **5b** (4.090 g, 4.63 mmol) in THF (40 mL) was added a solution of NaOH (0.555 g, 13.8 mmol) in water (40 mL), and the mixture was stirred for 1 h below 0 °C. A solution of *p*-toluenesulfonyl chloride (1.997 g, 10.5 mmol) in THF (20 mL) was then added dropwise to the reaction mixture during 30 min below 0 °C, and the mixture was stirred for further 7 h. The mixture was poured onto 3 M hydrochloric acid and then the organic solvent was evaporated. The mixture was extracted with chloroform (3 × 50 ml), and the organic layer was dried over anhydrous $MgSO_4$. After removal of the solvent, the crude product was purified by column chromatography ($SiO_2$, $CHCl_3$/EtOAc (1:1)) to afford **6b** as a pale yellow oil (4.788 g, 87%). $^1$H NMR (400 MHz, $CDCl_3$) *d* 2.43 (s, 6H), 2.61 (t, *J* = 6.8 Hz, 4H), 3.59-3.63 (m, 12H), 3.66-3.71 (m, 12H), 3.72 (s, 4H), 3.82 (t, *J* = 5.0 Hz, 4H), 3.85 (t, *J* = 5.0 Hz, 4H), 4.12-4.16 (m, 12H), 6.90 (s, 8H), 7.14-7.26 (m, 4H), 7.32 (d, *J* = 8.6 Hz, 4H), 7.79 (d, *J* = 8.6 Hz, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$) *d* 21.62 ($CH_3$), 30.75, 36.50, 68.70, 68.75, 68.77, 69.26, 69.78, 69.80, 70.33, 70.72, 70.76 (×2), 70.78 ($CH_2$), 114.79, 114.82, 121.62, 121.67, 127.63, 127.95, 128.58, 129.39, 129.82 (CH), 132.98, 138.68, 144.78, 148.87, 148.92 (C). Anal. Calcd for $C_{58}H_{78}O_{18}S_4$: C, 58.47; H, 6.60. Found: C, 58.12; H, 6.72.

**Synthesis of 7a.** A solution of ditosylate **6a** (3.407 g, 3.36 mmol) and dithiol (572 mg, 3.36 mmol) in acetonitrile (30 mL) was added dropwise to a refluxing suspension of $K_2CO_3$ (1.422 g, 10.3 mmol) in acetonitrile (300 mL) during 16 h, and then the mixture was refluxed for 20 h. After removal of the solvent, water (50 mL) was added and the mixture was extracted with chloroform (3 × 60 mL). The organic layer was dried over anhydrous $MgSO_4$, and the solvent was removed under reduced pressure. The crude product thus obtained was purified by column chromatography ($SiO_2$, $CHCl_3$/EtOAc (1:1)) to afford **7a** as colorless crystals (1.197 g, 42%), mp 83-85 °C, $^1$H NMR (400 MHz, $CDCl_3$) *d* 2.59 (t, *J* = 6.9 Hz, 8H), 3.65 (t, *J* = 6.9 Hz, 8H), 3.71 (s, 8H), 3.77 (t, *J* = 4.6 Hz, 8H), 4.12 (t, *J* = 4.6 Hz, 8H), 6.90 (s, 8H), 7.15-7.26 (m, 8H). $^{13}$C NMR (400 MHz, $CDCl_3$) *d*30.72, 36.47, 68.87, 69.49, 71.05 ($CH_2$), 114.68, 121.62, 127.65, 128.64, 129.52 (CH), 138.69, 148.94 (C). Anal. Calcd for $C_{44}H_{56}O_8S_4$: C, 62.83; H, 6.71. Found: C, 62.52, H, 6.77.

**Synthesis of 7b.** A solution of ditosylate **6b** (5.767 g, 4.84 mmol) and dithiol (820 mg, 4.82 mmol) in acetonitrile (50 mL) was added dropwise to a refluxing suspension of $K_2CO_3$ (2.004 g, 14.5 mmol) in acetonitrile (200 mL) during 24 h, and then the mixture was refluxed for 36 h. After removal of the solvent, water (50 mL) was added and the mixture was extracted with

chloroform ($3 \times 50$ mL). The organic layer was dried over anhydrous $MgSO_4$, and the solvent was removed under reduced pressure. The crude product thus obtained was purified by column chromatography ($SiO_2$, $CHCl_3$/EtOAc (1:1)) to afford **7b** as colorless oil (2.204 g, 45%). $^1$H NMR (400 MHz, $CDCl_3$) *d* 2.60 (t, *J* = 6.7 Hz, 8H), 3.59 (t, *J* = 6.7 Hz, 8H), 3.59 (t, *J* = 4.8 Hz, 8H), 3.71 (t, *J* = 4.8 Hz, 8H), 3.72 (s, 8H), 3.84 (t, *J* = 4.8 Hz, 8H), 4.14 (t, *J* = 4.8 Hz, 8H), 6.87-6.89 (s, 8H), 7.16-7.26 (m, 8H). $^{13}$C NMR (100 MHz, $CDCl_3$) *d* 30.68, 36.51, 68.92, 69.82, 70.36, 70.81, 70.87 ($CH_2$), 114.80, 121.63, 127.64, 128.64, 129.45 (CH), 138.70, 148.96 (C). Anal. Calcd for $C_{52}H_{72}O_{12}S_4$: C, 61.39; H, 7.13. Found: C, 61.01; H, 6.96.