

## Bifunctional dithiocarbamates: A bridge between coordination chemistry and nanoscale materials

*Edward J. Knight, Andrew. R. Cowley, Graeme Hogarth and James D. E. T. Wilton-Ely*

BTD = 2,1,3-benzothiadiazole, TOAB = *n*-tetraoctylammonium bromide

### Experimental Section

**General Comments** - All experiments were carried out under aerobic conditions and the majority of the complexes appear indefinitely stable towards the atmosphere in solution or in the solid state. The following complexes have been described elsewhere: [PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>],<sup>[S1]</sup> [NiCl<sub>2</sub>(dppf)],<sup>[S2]</sup> [Rh(η<sup>2</sup>-SCNMe<sub>2</sub>)Cl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>],<sup>[S3]</sup> [PtCl<sub>2</sub>(dppf)],<sup>[S4]</sup> [Ru(S<sub>2</sub>CNC<sub>4</sub>H<sub>8</sub>NH<sub>2</sub>)(dppm)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub>.<sup>[S5,S6]</sup> All other reagents were used as obtained from commercial sources. FAB-MS data were obtained using an Autospec Q instrument. Infrared data were obtained using a Perkin Elmer Paragon 1000 FT-IR spectrometer, KBr plates were used for solid state IR spectroscopy, and characteristic triphenylphosphine-associated infrared data are not reported. NMR spectroscopy was performed at 25°C using a Varian Mercury 300 spectrometer in CDCl<sub>3</sub> unless otherwise indicated. All couplings are in Hertz. Resonances in the <sup>31</sup>P NMR spectrum due to the hexafluorophosphate counteranion were observed but are not included below. Elemental analysis data were obtained from London Metropolitan University.

[(dppm)<sub>2</sub>Ru(S<sub>2</sub>CNC<sub>4</sub>H<sub>8</sub>NCS<sub>2</sub>)Pd(PPh<sub>3</sub>)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> (**2**):

[Ru(S<sub>2</sub>CNC<sub>4</sub>H<sub>8</sub>NH<sub>2</sub>)(dppm)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> (**1**, 80 mg, 0.066 mmol) was dissolved in dichloromethane (20 mL) and methanol (20 mL). Treatment with NEt<sub>3</sub> (3 drops, excess) was followed by stirring for 5 mins. Carbon disulfide (3 drops, excess) was added and the reaction stirred for a further 5 mins. A dichloromethane (5 mL) solution of [PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (47 mg, 0.067 mmol) was added and a methanolic solution (10 mL) of NH<sub>4</sub>BF<sub>4</sub> (7 mg, 0.067 mmol). The reaction was stirred for 16 hrs. All solvent was removed and the residue was taken up in a minimum amount of dichloromethane and filtered through celite filter agent. Cold ethanol (30 mL) was added and the pale yellow product precipitated under reduced pressure, washed with cold ethanol (10 mL) and hexane (10 mL) and dried. Yield: 118 mg (94 %). IR (nujol): ν = 1725, 1586, 1573, 1311, 1280, 1227, 1048 (B-F), 841 cm<sup>-1</sup>; <sup>31</sup>P NMR (121.5 MHz, CDCl<sub>3</sub>, 25°C): -18.1, -5.5 (t × 2, J(P,P) = 35 Hz; dppm), 26.9 (s;

PPh<sub>3</sub>) ppm; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25°C): δ = 3.67 (m(br), 8 H; NC<sub>4</sub>H<sub>8</sub>N), 4.60, 4.92 (m × 2, 4 H; PCH<sub>2</sub>P), 6.50, 6.92, 7.01, 7.28, 7.44, 7.67 (m × 6, 40 H + 30 H; C<sub>6</sub>H<sub>5</sub>) ppm; MS (FAB): *m/z* (%): 1823 (28) [M+BF<sub>4</sub>]<sup>+</sup>, 1214 (14) [M-2PPh<sub>3</sub>]<sup>+</sup>; Elemental analysis calcd (%) for C<sub>92</sub>H<sub>82</sub>B<sub>2</sub>F<sub>8</sub>N<sub>2</sub>P<sub>6</sub>PdRuS<sub>4</sub>: C 58.0, H 4.1, N 1.5; found: C 58.0, H 4.0, N 1.5.

[CpCo(S<sub>2</sub>CNC<sub>4</sub>H<sub>8</sub>NH<sub>2</sub>)(PPh<sub>3</sub>)](PF<sub>6</sub>)<sub>2</sub> (**3**):

[CoCpI<sub>2</sub>(CO)] (500 mg, 1.232 mmol) was dissolved in acetone (20 mL) to which the zwitterion S<sub>2</sub>CNC<sub>4</sub>H<sub>8</sub>NH<sub>2</sub> (219 mg, 1.350 mmol) was added as a solution in a mixture of acetone (20 mL) and methanol (20 mL). NH<sub>4</sub>PF<sub>6</sub> (600 mg, 3.681 mmol) was added as a solution in methanol (15 mL). The reaction was stirred for 2 hrs. All solvent was removed and the residue was suspended in ethanol (60 mL) and triphenylphosphine (355 mg, 1.354 mmol) added. The reaction was heated to reflux for 2 hrs, after which all solvent was removed and the residue taken up in a minimum amount of dichloromethane and filtered through diatomaceous earth. The crude product was redissolved in dichloromethane (10 mL) and diethylether (40 mL) added to precipitate the purple product. This was washed with diethylether (10 mL) and dried. Yield: 626 mg (61 %). IR (nujol): ν = 1260, 1145, 1093, 999 (C-S), 839 (P-F) cm<sup>-1</sup>; <sup>31</sup>P NMR (121.5 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25°C): 44.8 (s; PPh<sub>3</sub>) ppm; <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25°C): δ = 2.71, 2.87, 3.24, 3.64 (m × 4, 8 H; NC<sub>4</sub>H<sub>8</sub>N), 5.33 (s, 5 H; C<sub>5</sub>H<sub>5</sub>), 7.49 - 7.64 (m, 15 H; C<sub>6</sub>H<sub>5</sub>) ppm; MS (ES) *m/z* (%): 548 (100) [M]<sup>+</sup>, 285 (35) [M-PPh<sub>3</sub>]<sup>+</sup>. Elemental analysis calcd (%) for C<sub>28</sub>H<sub>30</sub>CoF<sub>12</sub>N<sub>2</sub>P<sub>3</sub>S<sub>2</sub>: C 40.1, H 3.6, N 3.3; found: C 40.2, H 3.5, N, 3.4.

[(dppf)Ni(S<sub>2</sub>CNC<sub>4</sub>H<sub>8</sub>NCS<sub>2</sub>)Co(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(PPh<sub>3</sub>)](PF<sub>6</sub>)<sub>2</sub> (**4**):

Procedure as for **2**, using compound **3** (60 mg, 0.072 mmol), excess NEt<sub>3</sub> and carbon disulfide, [NiCl<sub>2</sub>(dppf)] (49 mg, 0.072 mmol) and NH<sub>4</sub>PF<sub>6</sub> (12 mg, 0.074 mmol) to give a purple product in 67 % yield (74 mg). IR (nujol): ν = 1231, 1160, 1093, 1028, 999 (C-S), 838 (P-F) cm<sup>-1</sup>; <sup>31</sup>P NMR (121.5 MHz, CDCl<sub>3</sub>, 25°C): 31.4 (s; dppf), 45.0 (s; PPh<sub>3</sub>) ppm; <sup>1</sup>H NMR (121.5 MHz, CDCl<sub>3</sub>, 25°C): δ = 3.47 - 3.77 (m, 8 H; NC<sub>4</sub>H<sub>8</sub>N), 4.39, 4.51 (s(br) × 2, 8 H; C<sub>5</sub>H<sub>4</sub>), 5.28 (s, 5 H; C<sub>5</sub>H<sub>5</sub>), 7.31 - 7.82 (m, 35 H; C<sub>6</sub>H<sub>5</sub>) ppm; MS (FAB) *m/z* (%): 1380 (1) [M+PF<sub>6</sub>]<sup>+</sup>, 972 (5) [M-PPh<sub>3</sub>]<sup>+</sup>. Elemental analysis calcd (%) for C<sub>63</sub>H<sub>56</sub>CoF<sub>12</sub>FeN<sub>2</sub>NiP<sub>5</sub>S<sub>4</sub>: C 49.6, H 3.7, N 1.8; found: C 49.8, H 3.7, N 1.9.

[Rh(η<sup>2</sup>-SCNMe<sub>2</sub>)(S<sub>2</sub>CNC<sub>4</sub>H<sub>8</sub>NH<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>](Cl)(PF<sub>6</sub>) (**5**):

[Rh(η<sup>2</sup>-SCNMe<sub>2</sub>)Cl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (300 mg, 0.381 mmol) was dissolved in THF (40 mL) and methanol (40 mL). The zwitterion S<sub>2</sub>CNC<sub>4</sub>H<sub>8</sub>NH<sub>2</sub> (124 mg, 0.765 mmol) was added as a solution in a mixture of THF (15 mL) and methanol (15 mL). NH<sub>4</sub>PF<sub>6</sub> (124 mg, 0.762 mmol) was added as a solution in

methanol (20 ml). The reaction was heated to reflux for 3 hrs. All solvent was removed and the residue was taken up in a minimum amount of dichloromethane and filtered through diatomaceous earth. Ethanol (20 mL) was added and the orange product precipitated under reduced pressure. This was washed with ethanol (10 mL), hexane (10 mL) and dried. Yield: 250 mg (82 %). IR (KBr/nujol):  $\nu = 1604, 1256, 1221, 1160$  (C-S),  $999$  (C-S),  $918$  (C-S),  $839$  (P-F),  $748$   $\text{cm}^{-1}$ ;  $^{31}\text{P}$  NMR (121.5 MHz,  $[\text{d}_6]$ acetone,  $25^\circ\text{C}$ ): 25.2 (d,  $J(\text{P,Rh}) = 92$  Hz;  $\text{PPh}_3$ ), 25.6 (d,  $J(\text{P,Rh}) = 91$  Hz;  $\text{PPh}_3$ ), 156.1 (hp,  $J(\text{P,F}) = 708$  Hz;  $\text{PF}_6^-$ ) ppm;  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ ,  $25^\circ\text{C}$ ):  $\delta = 2.56$  (s, 3 H;  $\text{NCH}_3$ ), 2.66 (m, 4 H;  $\text{NC}_4\text{H}_8\text{N}$ ), 2.71 (s, 3 H;  $\text{NCH}_3$ ), 3.01, 3.18 (m  $\times$  2, 4 H;  $\text{NC}_4\text{H}_8\text{N}$ ), 7.20 - 7.69 (m, 30 H;  $\text{C}_6\text{H}_5$ ) ppm; MS (FAB)  $m/z$  (%): 877 (25)  $[\text{M}]^+$ , 614 (100)  $[\text{M}-\text{PPh}_3]^+$ . Elemental analysis calcd (%) for  $\text{C}_{44}\text{H}_{46}\text{ClF}_6\text{N}_3\text{P}_3\text{RhS}_3$ : C 49.9, H 4.4, N 4.0; found: C 49.7, H 4.5, N 4.2.

$[(\text{dppf})\text{Pt}(\text{S}_2\text{CNC}_4\text{H}_8\text{NCS}_2)\text{Rh}(\eta^2\text{-SCNMe}_2)(\text{PPh}_3)_2](\text{PF}_6)_2$  (**6**):

Procedure as for **2**, using compound **5** (100 mg, 0.126 mmol), excess  $\text{NEt}_3$  and carbon disulfide,  $[\text{PtCl}_2(\text{dppf})]$  (103 mg, 0.126 mmol) and  $\text{NH}_4\text{PF}_6$  (21 mg, 0.129 mmol) to give a yellow product in 96 % yield (197 mg). IR (nujol):  $\nu = 1603, 1227, 1160, 1095, 1028, 999$  (C-S), 918, 839 (P-F)  $\text{cm}^{-1}$ ;  $^{31}\text{P}$  NMR (121.5 MHz,  $[\text{d}_6]$ acetone,  $25^\circ\text{C}$ ): 15.4 (s,  $J(\text{P,Pt}) = 3374$  Hz; dppf), 25.6 (d,  $J(\text{P,Rh}) = 91$  Hz;  $\text{PPh}_3$ ) ppm;  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ ,  $25^\circ\text{C}$ ):  $\delta = 2.81, 2.98$  (s  $\times$  2, 6 H;  $\text{CH}_3$ ), 3.17, 3.45 (m  $\times$  2, 8 H;  $\text{NC}_4\text{H}_8\text{N}$ ), 4.51, 4.68 (s(br)  $\times$  2, 8 H;  $\text{C}_5\text{H}_4$ ), 7.40 - 7.58 (m, 50 H;  $\text{C}_6\text{H}_5$ ) ppm; MS (FAB)  $m/z$  (%): 1737 (1)  $[\text{M}]^+$ , 1474 (1)  $[\text{M}-\text{PPh}_3]^+$ , 1438 (2)  $[\text{M}-\text{Cl}-\text{PPh}_3]^+$ . Elemental analysis calcd (%) for  $\text{C}_{79}\text{H}_{72}\text{F}_{12}\text{FeN}_3\text{P}_6\text{PtRhS}_5$ : C 47.7, H 3.6, N 2.1; found: C 47.4, H 3.5, N 2.2.

### NP1:

An aqueous solution (7 mL) of  $\text{HAuCl}_4$  (18.6 mg, 0.055 mmol) was rapidly stirred with a chloroform solution (7 mL) of the phase transfer reagent TOAB (89.9 mg, 0.164 mmol) until complete transfer of the  $\text{AuCl}_4^-$  anion had occurred. The organic layer was collected and to which was added a chloroform solution (7 mL) of  $[\text{Ru}(\text{S}_2\text{CNC}_4\text{H}_8\text{NCS}_2)(\text{dppm})_2]$  (152 mg, 0.137 mmol), freshly prepared in situ from  $[\text{Ru}(\text{S}_2\text{CNC}_4\text{H}_8\text{NH}_2)(\text{dppm})_2](\text{BF}_4)_2$  (165 mg, 0.137 mmol),  $\text{NEt}_3$  (5 drops, excess) and carbon disulfide (4 drops, excess). The orange solution was stirred at  $4^\circ\text{C}$  for 10 mins. An aqueous solution (15 mL) of  $\text{NaBH}_4$  (116 mg, 3.07 mmol) was added dropwise over 10 mins to the stirred solution at  $4^\circ\text{C}$ , causing a colour change from orange to dark brown. The solution was stirred for a further 2 hrs with the temperature under  $10^\circ\text{C}$ . The organic layer was isolated and washed with water (3  $\times$  5 mL) and then concentrated ( $\sim$  5 mL) under reduced pressure. Water was added to precipitate the dark brown product and the mixture stored at  $-18^\circ\text{C}$  for 18 hrs. The supernatant liquid was decanted and the product washed with water (5  $\times$  10 mL), warm ethanol (3  $\times$  10 mL) and dried.

**NP2:**

HAuCl<sub>4</sub> (11.2 mg, 0.033 mmol) in water (35 mL) was brought to the boil with vigorous stirring. To this solution was added trisodium citrate (37.8 mg, 0.129 mmol) in water (4 mL) and boiling continued for 10 mins. The heating source was removed and the reaction stirred for a further 15 mins. In a separate reaction flask, compound **1** (100 mg, 0.083 mmol) was dissolved in methanol (10 mL), treated with NEt<sub>3</sub> (5 drops, excess) and the reaction stirred for 5 mins. Carbon disulfide (4 drops, excess) was added and the reaction stirred for 5 mins. This solution was added dropwise to the previously prepared citrate stabilized nanoparticles resulting in precipitation of a fine blue solid. The reaction was stirred for a further 3 hrs, stored at – 18°C for 18 hrs, and the blue precipitate collected by filtration and washed with water (5 x 10 mL), warm ethanol (3 x 10 mL) and air dried.

**Crystallography**

Crystals of [(dppm)<sub>2</sub>Ru(S<sub>2</sub>CNC<sub>4</sub>H<sub>8</sub>NCS<sub>2</sub>)Pd(PPh<sub>3</sub>)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub>·(OEt<sub>2</sub>)(CH<sub>2</sub>Cl<sub>2</sub>)<sub>3</sub> (**2**) were grown by slow diffusion of diethylether into dichloromethane. Single crystal X-ray diffraction data were collected using graphite monochromated Mo-Kα radiation ( $\lambda = 0.71073 \text{ \AA}$ ) on an Enraf-Nonius KappaCCD diffractometer. The diffractometer was equipped with a Cryostream N<sub>2</sub> open-flow cooling device<sup>S7</sup> and the data were collected at 150(2) K. Series of  $\omega$ -scans were performed in such a way as to cover a sphere of data to a maximum resolution of 0.78 Å. Cell parameters and intensity data were processed using the DENZO-SMN package.<sup>S8</sup> The structure was solved by direct methods using SIR92<sup>S9</sup> and refined on F using the CRYSTALS suite.<sup>S10</sup> Intensities were corrected for absorption effects by the multi-scan method, based on multiple scans of identical and Laue equivalent reflections within DENZO-SMN. All non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms were visible in the difference map. Hydrogen atoms were added geometrically and then refined using soft restraints and added to a riding model. A small amount of counterion disorder was modelled and restraints were used to maintain a sensible geometry and thermal ellipsoids. Single Crystal X-ray Diffraction Data: C<sub>99</sub>H<sub>98</sub>B<sub>2</sub>Cl<sub>6</sub>F<sub>8</sub>N<sub>2</sub>OPdRuS<sub>4</sub>,  $M = 2239.78$ , triclinic ( $P-1$ ),  $a = 13.9532(2) \text{ \AA}$ ,  $b = 15.4074(2) \text{ \AA}$ ,  $c = 25.2067(4) \text{ \AA}$ ,  $\alpha = 102.9433(6)^\circ$ ,  $\beta = 92.8485(6)^\circ$ ,  $\gamma = 106.8897(6)^\circ$ ,  $V = 5015.09(13) \text{ \AA}^3$ ,  $Z = 2$ ,  $\mu(\text{Mo-K}\alpha) = 0.732 \text{ mm}^{-1}$   $D_{\text{calcd}} = 1.483 \text{ g/cm}^3$ ,  $T = 150(2) \text{ K}$ , 75176 reflections collected, 22434 independent ( $R_{\text{int}} = 0.044$ ),  $R_1 = 0.0647$ ,  $wR_2 = 0.0650 [I > 2\sigma(I)]$ . Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre, CCDC 677009. Copies of the data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**References**

- S1 J. R. Blackburn, R. Nordberg, F. Stevie, R. G. Albridge and M. M. Jones, *Inorg. Chem.*, 1970, **9**, 2374-2376.
- S2 A. W. Rudie, D. W. Lichtenberg, M. L. Katcher and A. Davison, *Inorg. Chem.*, 1978, **17**, 2859- 2863.
- S3 A. F. Hill, D. A. Tocher, A. J. P. White, D. J. Williams and J. D. E. T. Wilton-Ely, *Organometallics*, 2005, **24**, 5342-5355.
- S4 G. M. Whitesides, J. F. Gaasch and E. R. Stedronsky, *J. Am. Chem. Soc.*, 1972, **94**, 5258-5270.
- S5 J. D. E. T. Wilton-Ely, D. Solanki and G. Hogarth, *Eur. J. Inorg. Chem.*, 2005, 4027-4030.
- S6 E. J. Knight, D. Solanki, G. Hogarth, K. B. Holt, A. L. Thompson and J. D. E. T. Wilton-Ely, *Inorg. Chem.*, in press.
- S7 J. Cosier and A. M. Glazer, *J. Appl. Cryst.*, 1986, **19**, 105.
- S8 Z. Otwinowski and W. Minor, *Processing of X-ray Diffraction Data Collected in Oscillation Mode, Methods Enzymol.*, 1997, 276, Eds C. W. Carter and R. M. Sweet, Academic Press.
- S9 A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori and M. Camalli, *J. Appl. Cryst.*, 1994, **27**, 435.
- S10 P. W. Betteridge, J. R. Cooper, R. I. Cooper, K. Prout and D. J. Watkin, *J. Appl. Cryst.*, 2003, **36**, 1487-1487.