



# Oxidative addition of functional disulfides to platinum(II): Formation of chelating and bridging thiolate–carboxylate complexes of platinum(IV)

Matthew S. McCready, Richard J. Puddephatt \*

Department of Chemistry, University of Western Ontario, London, Canada N6A 5B7

## ARTICLE INFO

### Article history:

Received 1 October 2010

Accepted 25 October 2010

Available online 30 October 2010

### Keywords:

Platinum

Oxidative Addition

Disulfide

Thiolate

Carboxylate

## ABSTRACT

An unusual type of oxidative addition of disulfides containing a carboxylic acid group to platinum(II) is established, giving the first thiolate–carboxylate complexes of platinum(IV). The disulfide  $R_2S_2$  with  $R = CH_2CH_2CO_2H$  reacts with  $[PtMe_2(2,2'-bipyridine)]$  to give RSH and the chelating thiolate–carboxylate complex  $[PtMe_2(\kappa^2-S,O-SCH_2CH_2CO_2)(bipy)]$ . However, the disulfide  $R_2S_2$  with  $R = C_6H_3-4-NO_2-3-CO_2H$  reacts to give first the product of *trans* oxidative addition  $[PtMe_2(SR)_2(bipy)]$ , which slowly reacts further to give RSH and the bridging thiolate–carboxylate complex  $[Pt_2Me_4(\kappa^2-S,O-SC_6H_3-4-NO_2-3-CO_2)_2(bipy)_2]$ .

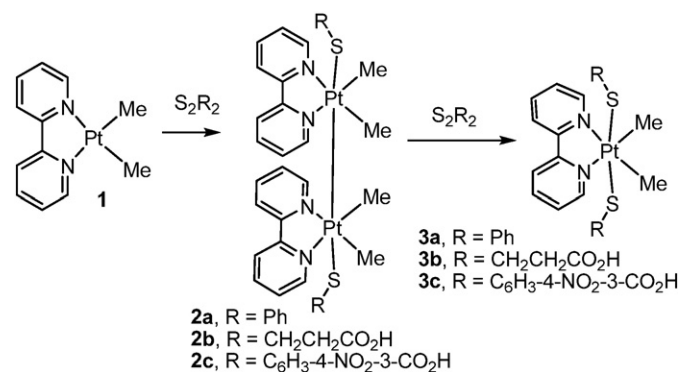
© 2010 Elsevier B.V. All rights reserved.

The reversible cleavage of the S–S bond of a disulfide  $R_2S_2$  by reaction with a transition metal complex, cluster, nanoparticle or surface can have significance in areas ranging from self-assembled monolayers and tribology to catalysis and medicinal chemistry [1–5]. The oxidative addition of the S–S bond to transition metal complexes is one route for activation of disulfides and there have been several studies of such reactions with either platinum(0) or platinum(II) complexes [6–11]. In particular, in an earlier study it was shown that the reaction of  $[PtMe_2(2,2'-bipyridine)]$ , **1**, with diphenyl disulfide occurred according to Scheme 1, with initial formation of a diplatinum(III) complex  $[Pt_2(SPh)_2Me_2(bipy)_2]$ , **2a**, which finally gave the dithiolatoplatinum(IV) complex  $[Pt(SPh)_2Me_2(bipy)]$ , **3a** [9]. This article shows that the disulfides  $R_2S_2$  with  $R = CH_2CH_2CO_2H$  or  $C_6H_3-4-NO_2-3-CO_2H$  can give the first examples of thiolate–carboxylate complexes of platinum(IV) [12,13].

The reaction of complex **1** [9,14] with the disulfide  $R_2S_2$ ,  $R = CH_2CH_2CO_2H$ , in either acetone or dimethylsulfoxide occurred according to Scheme 2 to give the 3-thiolatopropionate complex  $[PtMe_2(SCH_2CH_2CO_2)(bipy)]$ , **4**, which was isolated as a red-brown solid. Complex **4** was characterized in the  $^1H$  NMR by the presence of two methylplatinum resonances at  $\delta = 0.43$  [s, 3 H,  $^2J(PtH) = 73$  Hz, MePt *trans* to O] and  $1.56$  [s, 3 H,  $^2J(PtH) = 69$  Hz, MePt *trans* to N] and by four overlapping multiplet resonances, integrating to a total of four protons, for the  $CH_2CH_2$  protons in the range  $\delta = 2.3$ – $2.6$ . The MALDI MS gave a peak at  $m/z = 486$  (**4** +  $H^+$ ). The reaction occurred slowly over a period of several days at room temperature, so it was

easily monitored by  $^1H$  NMR spectroscopy. Fig. 1 shows that as complex **1** reacts slowly, only the peaks assigned to **4** are observed, with no evidence for formation of **2b** or **3b**, Scheme 1, the expected products of oxidative addition of the S–S bond. If the primary reaction was with the carboxylic acid group, cleavage of a methylplatinum bond would be expected to occur [15,16], so it is likely that the reaction occurs by an  $S_N2$  mechanism at the S–S bond to give an intermediate  $[PtMe_2(SCH_2CH_2CO_2H)(bipy)]^+[SCH_2CH_2CO_2H]^-$ , which then undergoes proton transfer to give  $HSCH_2CH_2CO_2H$  and complex **4** (Scheme 2) rather than simple coordination of the thiolate anion to give **3b**.

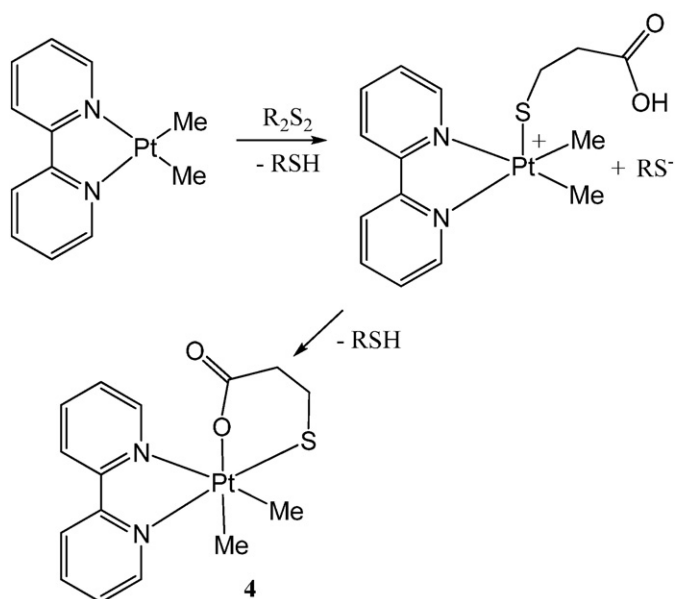
The reaction of complex **1** with the disulfide  $R_2S_2$ ,  $R = C_6H_3-4-NO_2-3-CO_2H$ , occurred much more rapidly and gave complex **3c** as the major product. Fig. 2 shows the NMR spectrum of a 2:1 mixture of



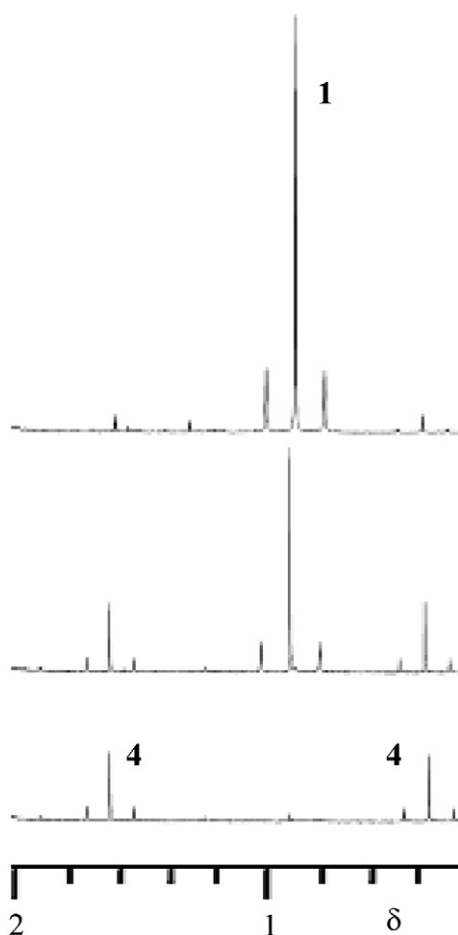
Scheme 1.

\* Corresponding author.

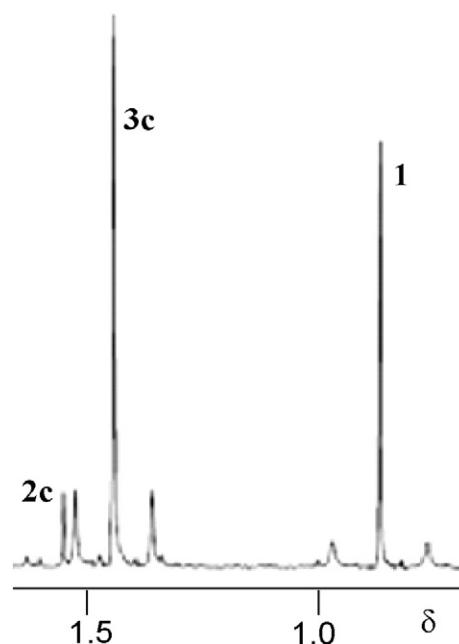
E-mail address: [pudd@uwo.ca](mailto:pudd@uwo.ca) (R.J. Puddephatt).



**1** and  $\text{R}_2\text{S}_2$  in  $\text{dmso-d}_6$  a few minutes after mixing. Complex **3c** is identified by the single methylplatinum resonance at  $\delta = 1.45$ ,  $^2J(\text{PtH}) = 69$  Hz, by comparison to the known complex **3a** [ $\delta(\text{MePt}) = 1.50$ ,  $^2J(\text{PtH}) = 71$  Hz] [9]. Almost half of complex **1** remained and a



**Fig. 1.**  $^1\text{H}$  NMR spectra (400 MHz,  $\text{dmso-d}_6$ ) in the methylplatinum area during the reaction of complex **1** with  $\text{R}_2\text{S}_2$ ,  $R = \text{CH}_2\text{CH}_2\text{CO}_2\text{H}$  to give complex **4**: top, after 10 min.; center, after 5 h.; bottom, after 4 d.

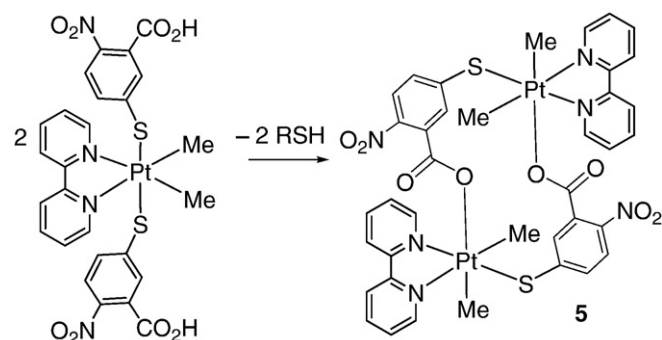


**Fig. 2.**  $^1\text{H}$  NMR spectra (400 MHz,  $\text{dmso-d}_6$ ) in the methylplatinum area during the reaction of complex **1** with  $\text{R}_2\text{S}_2$ ,  $R = \text{C}_6\text{H}_3-4-\text{NO}_2-3-\text{CO}_2\text{H}$ , to give complex **3c**, with **2c** as minor product.

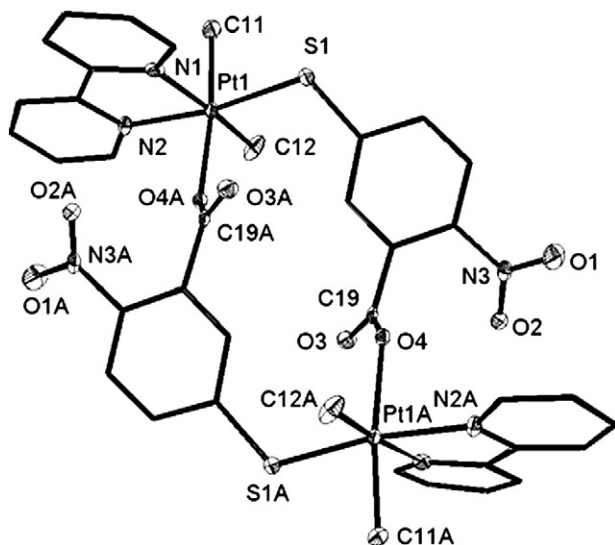
minor product was tentatively identified as **2c** [ $\delta(\text{MePt}) = 1.56$ ,  $^2J(\text{PtH}) = 66$  Hz]. Under similar conditions, complex **1** reacts with  $\text{Ph}_2\text{S}_2$  to give mostly **2a**, so the selectivity is greatly affected by the nature of the aryl group. The reaction was also examined in acetone and in dimethylformamide (dmf) and gave similar results, though the product **3c** is insoluble in acetone.

When the reaction of complex **1** with  $\text{R}_2\text{S}_2$ ,  $R = \text{C}_6\text{H}_3-4-\text{NO}_2-3-\text{CO}_2\text{H}$ , was carried out in dmf, or in a mixture of dmf and chlorobenzene, the initial product **3c** slowly decomposed with precipitation of a yellow crystalline solid which was characterized as the binuclear complex  $[\text{Pt}_2\text{Me}_4(\text{C}_6\text{H}_3-4-\text{NO}_2-3-\text{CO}_2)_2(\text{bipy})_2]$ , **5**, according to Scheme 3. Once formed, this complex was insoluble in all common organic solvents so NMR data could not be obtained.

The structure of complex **5** is shown in Fig. 3 [17]. The complex is binuclear and centrosymmetric. The complex contains two thiolate-carboxylate ligands which bridge between octahedral dimethylplatinum(IV) centers. The low solubility of complex **5** appears to result from a 3-dimensional network structure involving many weak  $\text{CH}\cdots\text{O}$  and  $\text{CH}\cdots\text{S}$  interactions using the oxygen atoms of the nitro and carbonyl groups and the sulphur atoms of the thiolate groups. There are channels in the structure which are occupied by highly disordered dmf molecules, whose electron density was treated by using SQUEEZE.



**Scheme 3.**  $R = \text{C}_6\text{H}_3-4-\text{NO}_2-3-\text{CO}_2\text{H}$ . The decomposition of complex **3c** to give complex **5**.



**Fig. 3.** A view of the structure of complex **5**. Selected bond parameters: Pt(1)–S(1) 2.287(4); Pt(1)–O(4) 2.127(9); Pt(1)–N(1) 2.14(1); Pt(1)–N(2) 2.08(1); Pt(1)–C(11) 2.06(1); Pt(1)–C(12) 2.06(1) Å.

The differences in chemistry between the two disulfides studied evidently arises from the much higher reactivity to oxidative addition of the diaryldisulfide compared to the dialkyldisulfide, and from ability of the ligand  $[\text{SCH}_2\text{CH}_2\text{CO}_2]^{2-}$  to chelate in forming complex **4** compared to inability of the rigid ligand  $[\text{SC}_6\text{H}_3\text{-4-NO}_2\text{-3-CO}_2]^{2-}$  to chelate, thus leading to slow formation of the binuclear complex **5**.

#### Acknowledgements

We thank the NSERC (Canada) for financial support and Dr. G. Popov for the structure determination.

#### Appendix A. Supplementary material

CCDC 795154 contains the crystallographic data for complex **5**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [http://www.ccdc.cam.uk/data\\_request.cif](http://www.ccdc.cam.uk/data_request.cif).

#### References

- [1] J.B. Schlenoff, M. Li, H. Ly, *J. Am. Chem. Soc.* 117 (1995) 12528.
- [2] T. Kondo, T. Mitsudo, *Chem. Rev.* 100 (2000) 3205.
- [3] H. Kuniyasu, F. Yamashita, J. Terao, N. Kambe, *Angew. Chem. Int. Ed.* 46 (2007) 5929.
- [4] S. Fakhri, V.P. Munk, M.A. Shipman, P.D. Murdoch, J.A. Parkinson, P.J. Sadler, *Eur. J. Inorg. Chem.* (2003) 1206.
- [5] H. Wei, X. Wang, Q. Liu, Y. Lu, Z. Guo, *Inorg. Chem.* 44 (2005) 6077.
- [6] U. Siemeling, F. Bretthauer, C. Bruhn, *J. Organomet. Chem.* 695 (2010) 626.
- [7] V.G. Albano, M. Monari, I. Orabona, A. Panunzi, G. Roviello, F. Ruffo, *Organometallics* 22 (2003) 1223.
- [8] A. Ishii, S. Kashiura, Y. Hayashi, W. Weigand, *Chem. Eur. J.* 13 (2007) 4326.
- [9] K.J. Bonnington, M.C. Jennings, R.J. Puddephatt, *Organometallics* 27 (2008) 6521.
- [10] K.-T. Aye, J.J. Vittal, R.J. Puddephatt, *J. Chem. Soc. Dalton* (1993) 1835.
- [11] A.J. Canty, H. Jin, B.W. Skelton, A.H. White, *Inorg. Chem.* 16 (1998) 3975.
- [12] W. Henderson, L.J. McCaffrey, B.K. Nicholson, *J. Chem. Soc. Dalton* (2000) 2753.
- [13] L.J. McCaffrey, W. Henderson, B.K. Nicholson, J.E. Mackey, M.B. Dinger, *J. Chem. Soc. Dalton* (1997) 2577.
- [14] P.K. Monaghan, R.J. Puddephatt, *J. Chem. Soc. Dalton Trans.* (1988) 595.
- [15] U. Belluco, M. Giustini, M. Graziano, *J. Am. Chem. Soc.* 89 (1967) 6494.
- [16] G.S. Hill, L.M. Rendina, R.J. Puddephatt, *Organometallics* 14 (1995) 4966.
- [17] Crystal data for **5**: formula  $\text{C}_{38}\text{H}_{34}\text{N}_6\text{O}_8\text{Pt}_2\text{S}_2$ , fw = 1157.01, triclinic, space group  $P\bar{1}$ ,  $a = 9.5670(4)$ ,  $b = 10.5794(5)$ ,  $c = 11.7181(6)$  Å,  $\alpha = 95.393(3)^\circ$ ,  $\beta = 95.400(3)^\circ$ ,  $\gamma = 93.415(3)^\circ$ ,  $V = 1172.73(10)$  Å<sup>3</sup>,  $Z = 1$ ,  $R_1 = 0.075$ ,  $wR_2 = 0.157$ . The crystals were prepared by slow diffusion of a solution of **5** into  $N,N$ -dimethylformamide into a solution of complex **1** in chlorobenzene. Analytical data: Calcd. for  $\text{C}_{38}\text{H}_{34}\text{N}_6\text{O}_8\text{Pt}_2\text{S}_2$ : C 39.45, H 2.96, N 7.26. Found: C 39.02, H 2.76, N 7.10%.