

# Preparation and characterisation of a dithiadiazolyline complex: X-ray crystal structure of $[\text{Pd}_2\{\mu\text{-SNC}(\text{Ph})\text{N}(\text{H})\text{S}\text{-S,S}'\}(\text{dppe})_2][\text{BF}_4]_2 \cdot 3\text{CDCl}_3$

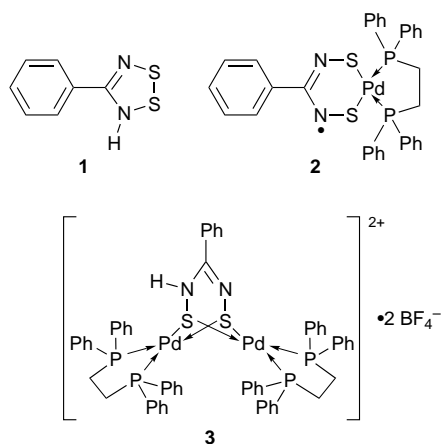
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While the protonated dithiadiazolyl compound,  $\text{PhCNSSNH}$  **1** is unknown, oxidation of  $[\text{Pd}(\text{dppe})_2]$  with  $[\text{PhCNSSN}]_2$  yields the monometallic complex  $[\text{Pd}\{\text{SNC}(\text{Ph})\text{NS}\text{-S,S}'\}(\text{dppe})]$  **2** which can be oxidized with  $[\text{NO}][\text{BF}_4]$  in the presence of moisture to yield the dimetallic complex  $[\text{Pd}_2\{\mu\text{-SNC}(\text{Ph})\text{N}(\text{H})\text{S}\text{-S,S}'\}(\text{dppe})_2][\text{BF}_4]_2$  **3** which contains coordinated **1**; the X-ray crystal structure of **3** is reported as its solvate  $3 \cdot 3\text{CDCl}_3$ .

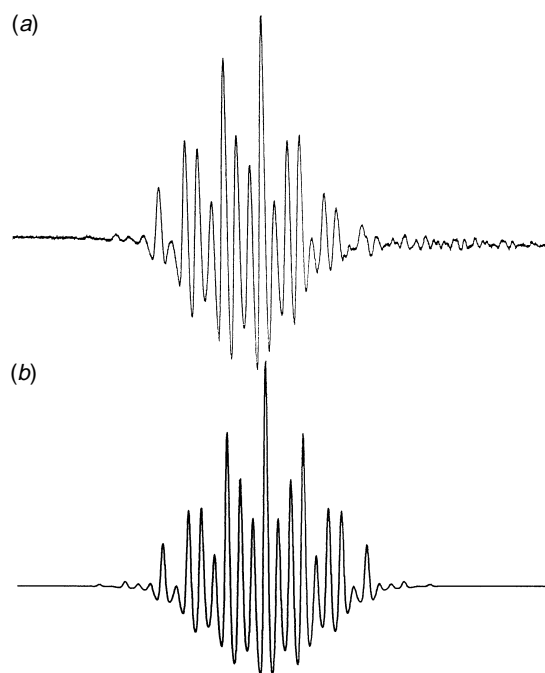
Previously we have reported a series of dithiadiazolyl metal complexes<sup>1–6</sup> containing one, two or three metal centres. In the monometallic compounds, the dithiadiazolyl ligand ring-opens at the S–S bond and chelates the metal, *e.g.*  $[\text{Pt}\{\text{SNC}(\text{Ph})\text{NS}\text{-S,S}'\}(\text{PPh}_3)_2]$ , whereas in the di- and tri-metallic complexes the dithiadiazolyl ligand bridges two metal centres, *e.g.* as in  $[\text{Ni}_2(\eta\text{-C}_5\text{H}_5)_2\{\mu\text{-SNC}(\text{Ph})\text{NS}\text{-S,S}'\}]$  and  $[\text{Pt}_3\{\mu\text{-SNC}(\text{Ph})\text{NS}\text{-S,S}'\}_2(\text{PPh}_3)_4]$ . The versatility of this ligand is exemplified by the number of electrons which it can utilise for metal bonding; two to three electrons in the chelate mode and five or six electrons in the  $\mu,\mu$ -bridging mode. Recent NMR and IR studies (coupled with the absence of an EPR signal)<sup>7,8</sup> on the related complex  $[\text{Fe}_2(\text{CO})_6\{\mu\text{-SNC}(\text{Ph})\text{NS}\text{-S,S}'\}]$  indicated that this complex had been protonated on the ring N and should be more correctly formulated as  $[\text{Fe}_2(\text{CO})_6\{\mu\text{-SNC}(\text{Ph})\text{N}(\text{H})\text{S}\text{-S,S}'\}]$ . The free ligand,  $\text{PhCNSSNH}$  **1**, itself is unknown and we have been intrigued by the possibility of forming other complexes containing this species. We now report the synthesis of the first monometallic palladium dithiadiazolyl compound,  $[\text{Pd}\{\text{SNC}(\text{Ph})\text{NS}\text{-S,S}'\}(\text{dppe})]$  **2** in which the monometallic structure is stabilised through the presence of the chelating diphosphine dppe, and describe its reaction with  $[\text{NO}][\text{BF}_4]$ , in the presence of adventitious moisture, to yield the dimetallic palladium dithiadiazolyline complex,  $[\text{Pd}_2\{\mu\text{-SNC}(\text{Ph})\text{N}(\text{H})\text{S}\text{-S,S}'\}(\text{dppe})_2][\text{BF}_4]_2$  **3**.



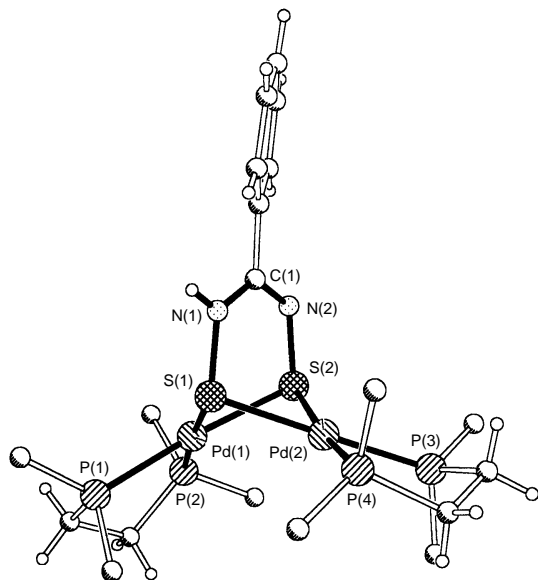
Oxidative addition<sup>3</sup> of  $(\text{PhCNSSN})_2$  to  $[\text{M}(\text{PPh}_3)_4]$  ( $\text{M} = \text{Pt}, \text{Pd}$ ) yielded the trimetallic complexes,  $[\text{M}_3\{\mu\text{-SNC}(\text{Ph})\text{NS}\text{-S,S}'\}_2(\text{PPh}_3)_4]$ .

When  $\text{M} = \text{Pt}$ , this was shown to proceed *via* the monometallic complex  $[\text{M}\{\text{SNC}(\text{Ph})\text{NS}\text{-S,S}'\}(\text{PPh}_3)_2]$ , but the analogous Pd complex could not be detected. We have now found that the chelating phosphine, dppe [1,2-bis(diphenylphosphino)ethane] stabilises the monometallic Pd complex and  $[\text{Pd}\{\text{SNC}(\text{Ph})\text{NS}\text{-S,S}'\}(\text{dppe})]$  **2** can be prepared† in excellent yield by direct reaction of  $(\text{PhCNSSN})_2$  with freshly prepared  $[\text{Pd}(\text{dppe})_2]$ . The unpaired electron in **2** occupies an antibonding orbital based on the metalloheterocyclic framework, of the same symmetry<sup>5</sup> as  $[\text{Pt}\{\mu\text{-SNC}(\text{Ph})\text{NS}\}(\text{PPh}_3)_2]$  and the solution EPR spectrum of **2** (Fig. 1) exhibits hyperfine coupling to two equivalent N and two equivalent P nuclei, plus satellites for the low-abundance <sup>105</sup>Pd isotope (22%,  $I = 5/2$ ).

The antibonding character of the singly occupied molecular orbital,<sup>5</sup> and the electron-rich (16/17e<sup>-</sup>) nature of the metal centre, indicated that one-electron oxidation of **2** should be facile. Preliminary electrochemical investigations on **2** showed three irreversible oxidations with half-wave potentials at -0.10, +0.30 and +1.12 V (referenced to the SSCE). Chemical oxidation‡ of **2** with 1 equiv. of  $[\text{NO}][\text{BF}_4]$  in acetonitrile produced two products, by <sup>31</sup>P NMR, of which the major product [two doublets at  $\delta$  56.6 and  $\delta$  52.9 ( $J_{\text{PP}}$  28 Hz)] fortuitously crystallised from  $\text{CDCl}_3$  and was found to be the dithiadiazolyline complex,  $[\text{Pd}_2\{\mu\text{-SNC}(\text{Ph})\text{N}(\text{H})\text{S}\text{-S,S}'\}(\text{dppe})_2][\text{BF}_4]_2$  **3**. Protonation at the heterocyclic nitrogen due to reaction with moisture renders the phosphorus environments inequivalent, resulting in a pair of doublets in the <sup>31</sup>P NMR



**Fig. 1** Solution EPR spectra of **2** in  $\text{CH}_2\text{Cl}_2$  at room temp; (a) experimental, (b) simulation;  $g = 2.031$ ,  $a_{\text{N}} = 5.7$  G,  $a_{\text{P}} = 3.8$  G,  $a_{\text{Pd}} = 37.2$  G,  $\Delta B_{\text{PP}} = 1.0$  G



**Fig. 2** Structure of the dication in **3** (phosphine phenyl C atoms not bonded to P are removed for clarity). Further selected bond lengths (Å): Pd(1)–P(1) 2.305(2), Pd(1)–P(2) 2.283(2), Pd(2)–P(3) 2.283(2), Pd(2)–P(4) 2.297(2), Pd(1)–S(1) 2.351(2), Pd(1)–S(2) 2.352(2), Pd(2)–S(1) 2.354(2), Pd(2)–S(2) 2.384(2), N(1)–S(1) 1.690(6), N(2)–S(2) 1.683(6).

spectrum. The mass spectrum (FAB) shows a molecular ion peak at  $m/z$  1191.6 consistent with ring-protonation  $\{[\text{Pd}_2\{\mu\text{-SNC(Ph)N(H)S-S,S'}\}(\text{dppe})_2]^{2+}$  has a formula mass of 1191.8}. Compound **3** gave satisfactory microanalytical data, an N–H absorption in the IR ( $3205\text{ cm}^{-1}$ ) and was EPR inactive. The minor product, observed as a singlet at  $\delta$  59.6 in the  $^{31}\text{P}$  NMR, has not been characterised.

The structure§ of the salt **3** was determined by X-ray crystallography and was found to crystallise as a  $\text{CDCl}_3$  solvate,  $3 \cdot 3\text{CDCl}_3$ . The structure of the dication in **3** is shown in Fig. 2. It consists of two approximately square-planar Pd atoms bridged by the two sulfur atoms of a protonated dithiadiazolyl ligand, with each Pd chelated by a dppe ligand. The bidentate nature of both  $\text{P}_2$  and  $\text{S}_2$  donor sets induces  $\text{SPdS}$  and  $\text{PPdP}$  bond angles to be less than the idealised  $90^\circ$  and the strain is accommodated by the Pd atoms which sit approximately  $0.1\text{ \AA}$  above the  $\text{P}_2\text{S}_2$  mean plane. The Pd...Pd contact [ $3.0687(8)\text{ \AA}$ ] is longer than the sum of the metallic radii ( $2.76\text{ \AA}$ ) and is unsurprising since no Pd–Pd bond is necessary to satisfy the bonding requirements of either metal (see below). Within the heterocyclic ring, the S–S bond is formally broken to accommodate the two metal ions [cf.  $3.106(2)$  in **3** and  $2.089(5)\text{ \AA}$  in the free ligand<sup>9</sup> ( $\text{PhCNSSN}$ )<sub>2</sub>]. This ring-opening is accompanied by marked increases in the bond angles at C and N  $\{128.8(7), 129.3(5)$  and  $125.7(5)^\circ$  at C(1), N(1) and N(2), respectively, cf.  $121$  and  $116^\circ$  for the free ligand ( $\text{PhCNSSN}$ )<sub>2</sub>}. Although the location of the N–H proton could not be unambiguously determined from the X-ray data, an analysis of the heterocyclic bond lengths and angles clearly supports a more localised structure with protonation at N(1); within **3** the bond angle at N(1) is notably larger than that at N(2) and the C(1)–N(1) bond length is marginally (3 esds) longer than C(1)–N(2). In addition, the close approach of one of the  $\text{BF}_4^-$  counter ions to N(1) [ $\text{N}(1)\cdots\text{F}(21)$  at  $2.82\text{ \AA}$ ] can be rationalised in terms of an N–H...F hydrogen bond.

The combined crystallographic and spectroscopic evidence, clearly support the presence of a protonated dithiadiazolyl ligand. Electronically, the protonated dithiadiazolyl ligand acts as a six-electron donor, each sulfur forming a  $\sigma$  bond to one Pd and a dative bond to the second Pd. Thus each Pd formally has a 16-electron configuration (ten valence electrons, four from the

chelating phosphine, three from the dithiadiazolyl ligand, less one to accommodate the doubly positive charge on the ion) which is consistent with the observed square-planar geometry.

These results provide the first example of a monometallic Pd dithiadiazolyl complex (**2**) and also provide conclusive spectroscopic and structural evidence for the existence of dithiadiazolyl complexes. Compound **3** provides the first experimental evidence for a dimetallic intermediate in the formation of the trimetallic Pt and Pd complexes from the corresponding monometallic dithiadiazolyl derivatives. The exact source of protonation of the dithiadiazolyl ligand in **3** is presently unclear, although it is evident that the presence of adventitious moisture, as in the synthesis of  $[\text{Fe}_2(\text{CO})_6\{\mu\text{-SNC(Ph)NS-S,S}\}]$  could also play a role here. The  $^{31}\text{P}$  NMR spectrum clearly indicates the protonation occurs readily at an early stage in the reaction and not during the slow recrystallisation process.

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## Footnotes and References

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† Reaction of freshly prepared  $[\text{Pd}(\text{dppe})_2]$  [ $0.500\text{ g}$ ,  $0.55\text{ mmol}$ ] with a slight excess of  $(\text{PhCNSSN})_2$  [ $0.11\text{ g}$ ,  $0.30\text{ mmol}$ ] in toluene ( $20\text{ ml}$ ) yielded an immediate deep green precipitate of  $[\text{Pd}\{\text{SNC(Ph)NS-S,S'}\}(\text{dppe})_2]$  **2** under a light green solution. The product was filtered, washed with PhMe ( $3 \times 10\text{ ml}$ ) and dried *in vacuo*. Yield  $0.37\text{ g}$ ,  $97\%$ . Found: C,  $58.0$ ; H,  $3.7$ ; N,  $4.4$ . Calc. for **2** C,  $57.8$ ; H,  $4.08$ ; N,  $4.3\%$ . Compound **2** slowly decomposes, even in the solid state, and was freshly prepared for all reactions.

‡ A solution of  $[\text{NO}][\text{BF}_4]$  ( $0.039\text{ g}$ ,  $0.33\text{ mmol}$ ) in MeCN was added dropwise to a suspension of **2** ( $0.228\text{ g}$ ,  $0.33\text{ mmol}$ ) in MeCN. An immediate evolution of gas was observed and the solution turned red. After stirring for  $3\text{ h}$  the resultant yellow solution was filtered and evaporated to yield crude **3** ( $0.17\text{ g}$ ,  $75\%$ ). Crystals suitable for X-ray diffraction were grown by slow evaporation of a  $\text{CDCl}_3$  solution over 1 week. Found: C,  $50.6$ ; H,  $3.8$ ; N,  $2.4$ ; Calc. for **3** C,  $51.9$ ; H,  $4.0$ ; N,  $2.1\%$ .

§ Crystal data for  $3 \cdot 3\text{CDCl}_3$ :  $\text{C}_{62}\text{H}_{57}\text{B}_2\text{Cl}_9\text{F}_8\text{N}_2\text{P}_4\text{Pd}_2\text{S}_2$ ,  $M = 1723.57$ , monoclinic, space group  $P2_1/c$ ,  $a = 11.0729(7)$ ,  $b = 23.3848(14)$ ,  $c = 27.300(2)\text{ \AA}$ ,  $\beta = 94.718(1)^\circ$ ,  $U = 7045.1(8)\text{ \AA}^3$ ,  $\mu = 1.064\text{ mm}^{-1}$ ,  $Z = 4$ ,  $D_c = 1.63\text{ g cm}^{-3}$ ,  $T = 150(2)\text{ K}$ . A red crystal ( $0.48 \times 0.34 \times 0.18\text{ mm}$ ) was examined on a Siemens SMART CCD three-circle diffractometer with graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073\text{ \AA}$ ), 29647 reflections were measured ( $2.30 < 2\theta < 50.78^\circ$ ) of which 11549 were unique ( $R_{\text{int}} = 0.449$ ). The structure was solved by direct methods and refinement was carried out on  $F^2$  values using SHELXTL software.<sup>10</sup> At convergence  $R_1 [F > 2\sigma(F)] = 0.070$  and  $wR_2$  (all data) =  $0.148$  with a goodness of fit of 1.25. Max. and min. residual electron densities were within  $\pm 1.8\text{ e \AA}^{-3}$ . All elements heavier than C were refined anisotropically except for the three disordered F atoms in one of the  $\text{BF}_4^-$  anions. H atoms were added at calculated positions with a fixed thermal parameter. CCDC 182/562.

- 1 A. J. Banister, I. B. Gorrell, W. Clegg and K. A. Jørgensen, *J. Chem. Soc., Dalton Trans.*, 1989, 229.
- 2 A. J. Banister, I. B. Gorrell, W. Clegg and K. A. Jørgensen, *J. Chem. Soc., Dalton Trans.*, 1991, 1105.
- 3 A. J. Banister, I. B. Gorrell, S. E. Lawrence, C. W. Lehmann, I. May, G. Tate, A. J. Blake and J. M. Rawson, *J. Chem. Soc., Chem. Commun.*, 1994, 1779.
- 4 A. J. Banister and I. May, *Phosphorus, Sulfur, Silicon*, 1994, **93–94**, 447.
- 5 A. J. Banister, I. B. Gorrell, J. A. K. Howard, S. E. Lawrence, C. W. Lehmann, I. May, J. M. Rawson, B. K. Tanner, C. I. Gregory, A. J. Blake and S. P. Fricker, *J. Chem. Soc., Dalton Trans.*, 1997, 377.
- 6 A. J. Banister, I. May, J. M. Rawson and J. N. B. Smith, *J. Organomet. Chem.*, 1997, in the press.
- 7 V. Klassen, K. Preuss, K. H. Moock and R. T. Boéré, *Phosphorus, Sulfur, Silicon*, 1994, **93–94**, 449.
- 8 R. T. Boéré, K. H. Moock, V. Klassen, J. Weaver, D. Lentz and H. Michael-Schulz, *Can. J. Chem.*, 1995, **73**, 1444.
- 9 A. Vegas, A. Perez-Salazar, A. J. Banister and R. G. Hey, *J. Chem. Soc., Dalton Trans.*, 1979, 1812.
- 10 G. M. Sheldrick, SHELXTL, version 5.0, Siemens Analytical X-Ray Instruments Inc., Madison, WI, 1995.

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