Novel Bonding Modes in Metallo–Dithiadiazolyl Complexes: Preparation and Crystal Structures of [Pt(SNCPhNS-*S,S*)(PPh$_3$)$_2$]·MeCN and [Pt$_3$(μ-SNCPhNS-*S,S*)$_2$(PPh$_3$)$_4$]·2PhMe

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Reaction of [Pt(PPh$_3$)$_3$] with (PhCNSSN)$_2$ in MeCN leads to [Pt(SNCPhNS-*S,S*)(PPh$_3$)$_2$]·MeCN, which decomposes in toluene to give a novel trimetallic species, [Pt$_3$(μ-SNCPhNS-*S,S*)$_2$(PPh$_3$)$_4$]·2PhMe; the structures of both compounds are reported.

Our previous studies of dithiadiazolyl coordination chemistry[1,2] have shown that in the known complexes [Fe$_2$(CO)$_6$(μSNCPhNS-*S,S*)][1] and [Ni$_2$(C$_5$H$_5$)(μ-SNCPhNS-*S,S*)][2] the dithiadiazolyl ring takes up a bridging position between two metal centres, with each sulfur bonding to both metals in a μ fashion. We have recently been exploring the reactivity of the dithiadiazolyl radicals with platinum phosphine complexes, and have found a new bonding mode in which the dithiadiazolyl ring bonds exclusively to one metal centre: we describe herein the synthesis, structure and ESR spectrum of the metallo-heterocycle, [Pt(SNCPhNS-*S,S*)(PPh$_3$)$_2$] **1** (characterised as its MeCN solvate) and describe its subsequent decomposition to form a trimetallic complex, [Pt$_3$(μ-SNCPhNS-*S,S*)]$_2$(PPh$_3$)$_4$], **2** (characterised as its bis-toluene solvate) of a highly unusual structural type.

Addition of MeCN to a mixture of [Pt(PPh$_3$)$_3$] and (PhCNSSN)$_2$ led to the immediate formation of a dark blue–green microcrystalline precipitate under a blue–green solution. The soluble fraction was filtered off and the precipitate was washed with MeCN. Analysis of the precipitate (with satisfactory elemental analyses, ^{31}P NMR, ESR and FAB mass spectra) indicated the formulation of [Pt(SNCPhNS-*S,S*)(PPh$_3$)$_2$]·MeCN. Crystals of **1** MeCN suitable for X-ray diffraction were grown by slow diffusion of a solution of PhCNSSN in MeCN over excess (PhCNSSN)$_2$ through a grade 3 sinter into a saturated MeCN solution of [Pt(PPh$_3$)$_3$] over excess solid [Pt(PPh$_3$)$_3$].

The structure of **1**† (Fig. 1) shows an unprecedented monometallic dithiadiazolyl complex in which the metal of a Pt(PPh$_3$)$_2$ unit inserts into the S–S bond of the dithiadiazolyl ring forming a six-membered metalloheterocycle. The S–S separation increases from 2.089(5) Å[3] in (PhCNSSN)$_2$ to 3.168(4) Å in **1**, *cf.* d_{SS} in [Ni$_2$(C$_5$H$_5$)$_2$(μ-SNCPhNS-*S,S*)] and [Fe$_2$(CO)$_6$(μ-SNCPhNS-*S,S*] are 2.905(2) and 2.930(2) Å respectively. This indicates an S–S bond order closer to zero than one; the effective radii of sulfur, perpendicular to and along the bond, have been estimated[4] at 2.03 and 1.60 Å respectively. When the S–S bond order is so low it becomes appropriate to write the ligand as SNCPhNS rather than PhCNSSN.

The mean Pt–S bond distance of 2.301(2) Å is slightly shorter than those observed in other sulfide-bound Pt complexes (2.32–2.36 Å).[5] The other changes in ring parameters,most notably bond angles, are consistent with this ring expansion and with the expected decrease in S–S and N–S bond orders. The Pt centre takes up a four-coordinate planar geometry but the PtP$_2$S$_2$ and CN$_2$S$_2$ planes form an angle of 24°, due to the ring buckling that occurs to accommodate, with minimum strain, the extra Pt atom in the ring. The solvent molecule does not appear to interact with the complex.

Each S atom appears to act as a single electron donor, leading to a 16e-Pt^{II} centre (see Fig. 2). However d_{NS} [1.648(7), 1.628(7) Å] is rather shorter than a single bond (typically 1.68 Å)[6] and theoretical calculations[1,2] on metallo–dithiadiazolyl complexes have indicated that the unpaired electron resides in a molecular orbital delocalised over the whole of the M/C/N/S framework. It is therefore a 16/17e-complex. Room-temperature ESR spectra of **1** in CH$_2$Cl$_2$ (Fig. 2) are in agreement with this. It is interesting that there is little change in magnitude of the coupling to the dithiadiazolyl nitrogen nuclei (a_N for the PhCNSSN· radical[7] is 0.52 mT, a_N for **1** = 0.55 mT). We assume that the slight gain in spin density at N despite spin delocalisation on to Pt and two P atoms occurs at the expense of the spin density at the sulfur atoms (**A**).

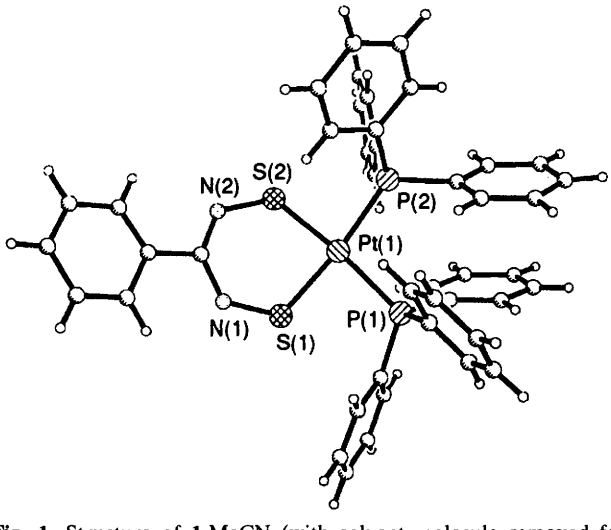


Fig. 1. Structure of **1**·MeCN (with solvent molecule removed for clarity). Selected bond distances (Å) and angles (°) are: Pt(1)–P(1) 2.311(2), Pt(1)–P(2) 2.322(2), Pt(1)–S(1) 2.294(2), Pt(1)–S(2) 2.309(2), S(1)–N(1) 1.628(7), S(2)–N(2) 1.648(7), S(1)–Pt(1)–S(2) 86.78(8), S(1)–Pt(1)–P(1) 87.82(7), P(1)–Pt(1)–P(2) 100.01(7), P(2)–Pt(1)–S(2) 85.43(7), N(1)–S(1)–Pt(1) 115.2(2), N(2)–S(2)–Pt(1) 115.09, C(1)–N(1)–S(1) 128.4(5), C(1)–N(2)–S(2) 128.0(6), N(1)–C(1)–N(2) 129.0(7)

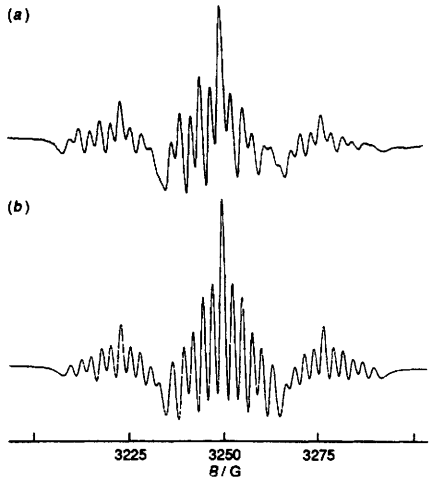


Fig. 2 Experimental (*a*) and simulated (*b*) second-derivative X-band ESR spectrum of **1** in CH$_2$Cl$_2$ at room temperature; g = 2.0485, a_{Pt} = 5.30 mT, a_N = 0.55 mT, a_P = 0.26 mT (ΔH_{pp} = 0.2 mT)

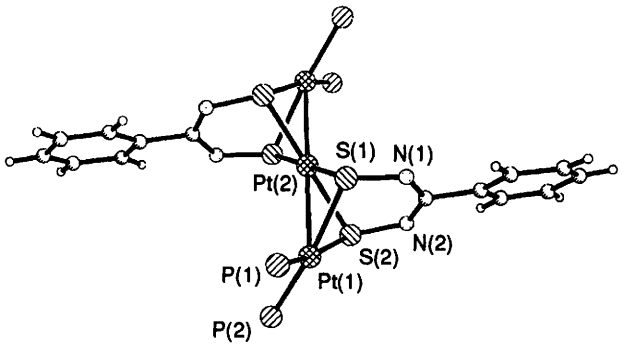
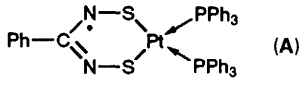


Fig. 3 Structure of **2** (with both toluene solvent molecules and triphenylphosphine phenyl groups removed for clarity). Selected bond distances (Å) and angles (°) are: Pt(1)–P(1) 2.300(5), Pt(1)–P(2) 2.301(5), Pt(1)–S(1) 2.387(4), Pt(1)–S(2) 2.367(4), Pt(1)–Pt(2) 2.865(1), Pt(2)–S(1) 2.344(4), Pt(2)–S(2) 2.332(5), S(1)–N(1) 1.638(14), S(2)–N(2)–1.655(13) P(1)–Pt(1)–P(2) 103.3(2), S(1)–Pt(1)–P(2) 87.8(2), S(1)–Pt(1)–S(2) 78.8(2), S(1)–Pt(2)–S(2) 80.4(2)



(A)

Toluene, CH_2Cl_2 and thf solutions of **1** slowly lose their intense blue colouration, forming a brown solution containing PhCNSSN (according to ESR spectra) over an (ESR inactive) orange precipitate. Crystals of this solid material were grown by slow diffusion of PhCNSSN in solution above solid $(PhCNSSN)_2$ into a saturated solution of $[Pt(PPh_3)_3]$ in toluene. The crystals were found to be of $[Pt_3(\mu\text{-SNCPhNS-}S,S)]_2(PPh_3)]_4\cdot 2PhMe$, *i.e.* **2**·2PhMe, by X-ray diffraction studies.† The structure of **2** is shown in Fig. 3. It is composed of a linear Pt_3 chain bridged by two SNCPhNS ligands in which the terminal Pt atoms are related through a crystallographic inversion centre at Pt(2). Both Pt(1) and Pt(2) atoms possess planar geometries; the terminal Pt atoms have a PtP_2S_2 environment whereas the central Pt is bound only to dithiadiazolyl S atoms, thus producing a PtS_4 coordination geometry. This structure is analogous to the structure of $[Pd_3(\mu\text{-SNCPhNS-}S,S)]_2(PPh_3)_4]$ reported previously.[8] As in **1**, the S–S bond is partially broken [$(d_{SS}$ = 3.046(8) Å] but in **2** dithiadiazolyl ligand takes up a bridging mode between Pt(1) and Pt(2) leading to a Pt···Pt bonding interaction at 2.865(1) Å {*cf.* M···M in $[Ni_2(C_5H_5)_2(\mu\text{-SNCPhNS-}S,S)]$ of 2.441(1) Å and $[Fe_2(CO)_6(\mu\text{-SNCPhNS-}S,S)]$ of 2.533(2) Å}. The square-planar environment at each metal centre is consistent with 16e- Pt^{II}. For the terminal Pt centres the 16e- are made up as follows: 10e- from the metal, 2e- from each phosphine donor and 2e- from each dithiadiazolyl ligand. For the central Pt, the 16e- are composed of 10e- from the metal plus 3e- from each dithiadiazolyl ligand. Thus both SNCPhNS ligands can be thought of as a 5e- donors. However, bridging sulfurs each donate 3e- to the bonding making a total of 6e- for each SNCPhNS. Presumably the remaining 1e- remains delocalised within the ring system pairing up with the free radical electron. As this occurs in both the dithiadiazolyl components the complex is rendered diamagnetic. This was indicated previously by a loss of ESR activity and also by preliminary magnetic measurements. The net 16e/16e/16e M_3 system and $5d_{z2}$, $6p_z$ orbital overlap between the three M atoms in both Pt_3 and Pd_3 structures would thus appear to rationalise the remarkable stability of the complex and may thus explain the absence of any polymeric materials [commonly formed as byproducts in the reacton of $(PhCNSSN)_2$ with metal carbonyls].[9]

Decomposition of **1** to form **2** would appear to involve substitution of phosphine ligands by sulfur lone pairs, and **2** can be thought of as being built up of a naked Pt atom, sandwiched by two molecules of **1**. We are presently investigating the mechanism by which **1** is converted to **2**, the physical properties of **1** and its potential synthetic utility in the formation of mixed-metal complexes.

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Footnote

† *Crystal Data* for **1**·MeCN: $C_{45}H_{38}N_3P_2S_2Pt$, M = 941.63, triclinic, space group $P\bar{1}$, a = 13.240(6), b = 13.366(6), c = 14.090(8) Å, α = 63.57(1), β = 76.38(2), γ = 60.71(2)°, V = 1947 Å^3, [from 2θ values of 46 reflections measured at ±ω (30 ≤ 2θ ≤ 32), λ = 0.71073 Å], Z = 2, D_c = 1.607 g cm^{-3}, T = 150 K, dark green–blue lath, crystal size 0.5 × 0.25 × 0.1 mm, μ = 3.83 mm^{-1}.

For **2**·2PhMe: $C_{100}H_{86}N_4S_4P_4Pt_3$, M = 2181.12, monoclinic, space group $P2_1/c$, a = 12.704(6), b = 24.99(1), c = 13.888(6) Å, β = 101.94(3)°, V = 4313 Å, [from 2θ values of 23 reflections measured at ±ω (26 ≤ 2θ ≤ 28), λ = 0.71073 Å], Z = 2 (molecule lies on an inversion centre), D_c = 1.679 g cm^{-3}, T = 150 K, orange column, crystal size 0.78 × 0.15 × 0.08 mm, μ = 5.08 mm^{-1}.

Data Collection and Processing: Stoë Stadi-4 four-circle diffractometer with Oxford Cryosystems low-temperature device (J. Cosier and A. M. Glazier, *J. Appl. Crystallogr.*, 1986, **19**, 105), graphite-monochromated Mo-Kα radiation, ω–2θ scans. The data were corrected for absorption by means of psi-scans (A. C. T. North, D. C. Phillips and F. S. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24** 351) and a subsequent empirical absorption correction (DIFABS, N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983 **39** 158). Both structures were solved by Patterson methods using SHELXS 86 (G. M. Sheldrick, *Acta. Crystallogr., Sect. A*, 1990, **46**, 467) and refined using full-matrix least-squares techniques (G. M. Sheldrick, SHELXL93, *J. Appl. Crystallogr.*, 1994 in the press). All non-H atoms were refined anisotropically except for the solvate molecule in **2**·2PhMe. H atoms were fixed at calculated position. For **1**, convergence was obtained at $R_1[F_o > 4\sigma(F)]$ = 0.0353, wR_2 = 0.0946 $\{w = 1/[\sigma^2(F_o^2) + 0.0611P^2 + 9.4422P]\}$ where $P = (F_o^2 + 2F_c^2)/3$, S = 1.084 for 4493 independent observed reflections (5 ≤ 2θ < 45°). For **2**, convergence was obtained at $R_1[F_o > 4\sigma(F)]$ = 0.0481, wR_2 = 0.1162 $\{w = 1/[\sigma^2(F_o^2) + 0.0401P^2 + 152.708P]\}$, S = 0.978 for 3408 independent observed reflections (5 ≤ 2θ < 45°). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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