Chalcogen abstraction from dithiadiazolyl and diselenadiazolyl platinum complexes: crystal structure of a novel metalla-heterocycle

Neil Feeder, Robert J. Less, Jeremy M. Rawson* and J. Nicholas B. Smith

*Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, UK CB2 1EW*

The open-shell complexes, (PhCNEEN)Pt(dppe) (E = S or Se) decompose *via* a chalcogen abstraction process coupled with N-protonation to yield the novel 10π metalla-heterocyclic cations {[PhCN(H)N(H)E]Pt(dppe)}$^+$: the selenium complex is characterised by X-ray crystallography as its chloride salt.

The dithiadiazolyl radical RCNSSN, **1**, has an extremely varied coordination chemistry;[1] it undergoes oxidative addition reactions with a number of low-valent metal species to give mono-, di- or tri-metallic complexes in which the dithiadiazolyl radical ring-opens, with cleavage of the S–S bond. The diversity of the structural types is matched by the variable number of electrons which can be used for ligand–metal bonding (between 2 and 6 e$^-$ depending on the coordination mode).[1] The series of monometallic complexes of general formula (RCNSSN)M(P$_2$) [where M = Pt, Pd and P = PPh$_3$ or $\frac{1}{2}$ dppe] in which the unpaired electron associated with **1** is retained in the complex exhibit an unusual reactivity. For example, (PhCNSSN)Pt-(PPh$_3$)$_2$ disproportionates[2] to form the trimetallic complex Pt$_3$(PhCNSSN)$_2$(PPh$_3$)$_4$ and oxidation of (PhCNSSN)Pd-(dppe) with [NO][BF$_4$] proceeds *via* ring protonation[3] with the formation of [Pd$_2$(PhCNSSNH)(dppe)$_2$][BF$_4$]$_2$.
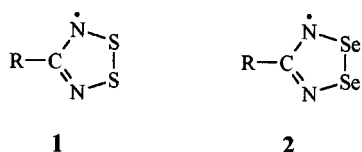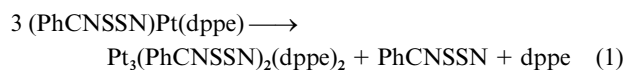

The coordination chemistry of the selenium analogue, **2**, has only recently begun to be investigated, but preliminary results[4,5] indicate that the coordination chemistries of **1** and **2** are similar. Now we report a new decomposition pathway for the mono-metallic platinum dppe complexes, **3** (E = S or Se), which involves the unexpected extrusion of chalcogen and subsequent ring contraction to form a novel five-membered metalla-heterocycle, **4**$^+$.
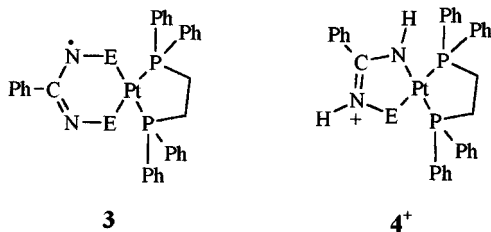
The blue complex, (PhCNSSN)Pt(dppe), **3** (E = S),† was prepared by reaction of Pt(dppe)$_2$ with (PhCNSSN)$_2$ in an analogous fashion to (PhCNSSN)Pd(dppe).[3] The solution EPR spectrum of pure **3** (E = S) [EPR (CH$_2$Cl$_2$, 298 K): g = 2.046, a_N = 0.55, a_P = 0.35 and a_{Pt} = 5.48 mT) exhibited well-resolved coupling to N, P and Pt, consistent with extensive
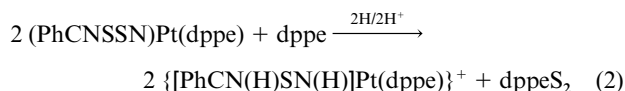
π-delocalisation of the unpaired electron. The intensity of the EPR signal of **3** (E = S) slowly decreased over time and a five-line spectrum [EPR (CH$_2$Cl$_2$, 298 K): g = 2.010, a_N = 0.50 mT] typical[6] of free **1** became observed. Subsequent ^{31}P NMR spectra (CDCl$_3$) of the reaction mixture indicated three major P-containing products which were separated by TLC (silica support, 50 : 50 acetone–acetonitrile eluent).

An orange band was isolated ($R_f \approx 0.65$) which was assigned to the trimetallic complex, Pt$_3$(PhCNSSN)$_2$(dppe)$_2$ on the basis of the singlet ^{31}P NMR resonance with Pt satellites (δ_P +49.8, $^1J_{Pt}$ = 2299 Hz), UV–VIS spectrum and microanalytical data. This observation, coupled with the identification of **1** (by EPR) are consistent with disproportionation of **3** (E = S) [eqn. (1)] in an entirely analogous fashion to the PPh$_3$ derivative.[2]

$$3\ (\text{PhCNSSN})\text{Pt(dppe)} \longrightarrow$$
$$\text{Pt}_3(\text{PhCNSSN})_2(\text{dppe})_2 + \text{PhCNSSN} + \text{dppe} \quad (1)$$

A pale pink band ($R_f \approx 0.5$) was characterised by NMR (MeCN, δ_P +44.8) and a subsequent X-ray diffraction study[7] as 1,2-bis(diphenylphosphino)ethane disulfide, Ph$_2$P(S)CH$_2$-CH$_2$P(S)Ph$_2$ (dppeS$_2$). The dppe, arising as a by-product during the primary decomposition pathway [eqn. (1)] abstracts sulfur (presumably from **3**, see below) to form dppeS$_2$.

The third, yellow, band ($R_f \approx 0.2$) exhibited two ^{31}P resonances with ^2J_P couplings and $^1J_{Pt}$ satellites (δ_P +40.9, ^2J_P = 9, $^1J_{Pt}$ = 3051 Hz; δ_P +44.7, ^2J_P = 9, $^1J_{Pt}$ = 2631 Hz), corresponding to two chemically distinct P environments, *i.e.* PPtP′. The FIB mass spectrum exhibited a molecular ion peak at m/z = 744.1 indicative of S-extrusion from **3** (E = S) and protonation of both N atoms, *i.e.* the cation [**4**]$^+$ (E = S). By comparison with other N,S-bound sulfur–nitrogen ligands[8] such as SNSN^{2-} and SNSNH$^-$, the two ^{31}P NMR resonances (at δ_P +40.9 and δ_P +44.7) can be assigned as P *trans* to N and S respectively. Abstraction of sulfur from organic sulfides and chelating sulfide ligands by nucleophiles such as CN$^-$ or PPh$_3$ is not uncommon,[9] *e.g.* (NH$_4$)$_2$Pt(S$_5$)$_3$ is attacked by PPh$_3$ to give (Ph$_3$P)$_2$PtS$_4$. In this case, the S-abstraction from **3** is carried out by dppe formed by disproportionation of **3** itself [eqn. (1)]. Since no free dppe was observed in the product mixture, the overall reaction can be considered to generate 2 moles of **4**$^+$ from 5 moles of **3**. On this basis, recovered yields of [**4**]Cl were *ca.* 50%. The source of protonation is not entirely clear, although the presence of the Cl$^-$ anion in the product indicates that the chlorinated solvents (CH$_2$Cl$_2$ and CDCl$_3$) are intimately involved in the reaction. Similar N-protonation reactions have previously been observed.[3,10] Although the formation of [**4**]$^+$ (E = S) is accelerated in the presence of a source of H$^+$ ions (*e.g.* carrying out the reaction in wet solvents, with the mixture exposed to the air, or by the addition of silica to the reaction solution) [eqn. (2)], ring-protonation is still observed under
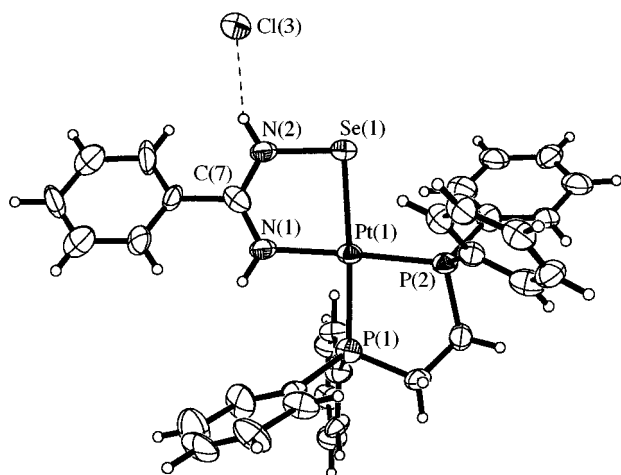
$$2\ (\text{PhCNSSN})\text{Pt(dppe)} + \text{dppe} \xrightarrow{\text{2H/2H}^+}$$
$$2\ \{[\text{PhCN(H)SN(H)}]\text{Pt(dppe)}\}^+ + \text{dppeS}_2 \quad (2)$$

Fig. 1 Crystal structure of [**4**]Cl (E = Se) with heteroatom labelling and with 50% probability ellipsoids.

Fig. 2 Frontier molecular orbitals of (a) [HCNSeSeN] and (b) {[HCN(H)SeN(H)]Pt(PH$_3$)$_2$}$^+$.

rigorously dry conditions. Attempts to grow crystals of **4**$^+$ (E = S) salts from CH$_2$Cl$_2$ by slow evaporation or layering with hexane or Et$_2$O proved unsuccessful.

In a similar manner, addition of excess Pt(dppe)$_2$ to (PhCNSeSeN)$_2$ yielded a green complex which exhibited a broad singlet EPR spectrum with ^{195}Pt satellites [EPR (C$_6$H$_5$Me): $g = 2.058$, $a_{Pt} = 5.4$ mT], which was assigned to **3** (E = Se). Replacement of S by Se leads to line broadening and poorly resolved EPR spectra,[4] and in this instance hyperfine coupling to N could not be resolved. The green colouration was rapidly dissipated to produce a yellow solution containing (PhCNSe-SeN)$_2$ [EPR (C$_6$H$_5$Me): $g = 2.03$] and a small quantity of yellow precipitate. The reaction was repeated on a preparative scale, and a ^{31}P NMR of the yellow precipitate indicated a mixture of two Pt-containing products, with chemical shifts and coupling constants analogous to the sulfur system. The major product, [**4**]Cl (E = Se) obtained in 20% yield, exhibited two P environments ($\delta_P = +41.9$, $^2J_P = 9$, $^1J_{Pt} = 3019$ Hz; $\delta_P +44.7$, $^2J_P = 9$, $^1J_{Pt} = 2691$ Hz), analogous to [**4**]Cl (E = S) whilst the minor product exhibited a single ^{31}P NMR resonance ($\delta_P +47.6$, $^1J_{Pt} = 2363$ Hz), consistent with Pt$_3$(PhCNSeSeN)$_2$(dppe)$_2$. The low solubility of both products precluded the observation of Se satellites. The mass spectrum (FAB) exhibited a molecular ion peak at m/z 791.9, consistent with [**4**]$^+$ (E = Se), analogous to [**4**]$^+$ (E = S) and also a $\nu_{NH} = 3350$ cm^{-1} absorption in the IR. Crystals of [**4**]Cl (E = Se) suitable for X-ray diffraction ‡ were grown by slow diffusion methods (dichloromethane–hexane).

The structure of [**4**]Cl (E = Se) is shown in Fig. 1. The central Pt atom takes up an approximately square-planar geometry with a P$_2$NSe donor set. The chelate nature of both rings leads to some deviation from ideality with both PPtP and NPtSe angles a little less than 90° [84.98(16) and 83.8(4)° respectively]. The Pt–P bonds are unexceptional [averaging 2.255(5) Å] and the Pt–Se and Pt–N bond lengths are 2.4085(19) and 2.043(15) Å respectively. Whilst derivatives of **3** (E = S) typically exhibit a puckering of the metalla-heterocyclic framework to accomodate the ring strain induced at Pt, the structure of [**4**]Cl (E = Se) has an almost planar CN$_2$SePt ring (mean deviation < 0.03 Å). The mean C–N bond length [1.31(2) Å] is the same as those observed [12] in both **2**$^+$ and **2** (R = Ph) which average at 1.36(3) and 1.32(2) Å respectively. In comparison, the Se–N bond length at 1.890(15) Å is longer than that observed [12] in **2**$^+$ and **2** (R = Ph) [averaging 1.76(2) Å and 1.78(1) Å respectively]. This can be rationalised in terms of the addition of an extra electron into an N–Se antibonding orbital (described below). The H atom attached to N(2) is hydrogen–bonded to the chloride anion (N ⋯ Cl 3.07 Å) and the structure can be considered as (PhCNSeNH)Pt(dppe)·HCl (the HCl presumably arises from the CH$_2$Cl$_2$ used during recrystallisation). The second H atom is sterically more protected and does not appear to exhibit any H-bonding, although there is a long intermolecular contact to a Cl atom of a CH$_2$Cl$_2$ solvate molecule (N ⋯ Cl at 3.78 Å).

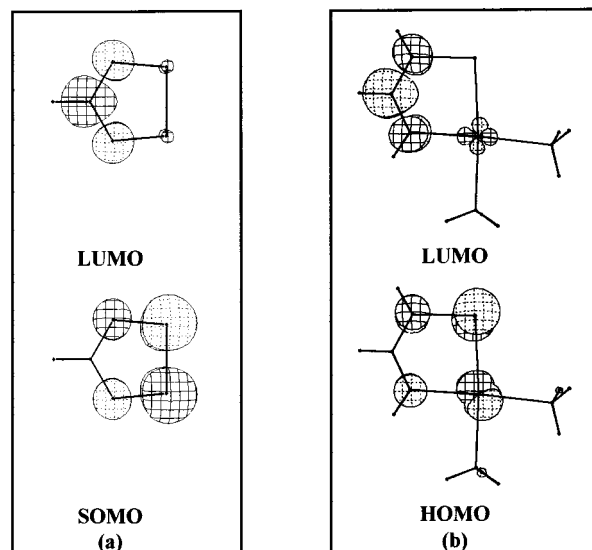Extended Hückel calculations [13] on the parent {[HCN(H)-SeN(H)]Pt(PH$_3$)$_2$}$^+$ cation indicate that the frontier molecular orbitals are both of π-character (Fig. 2) with the LUMO based predominantly on the NCN fragment and the HOMO on the N$_2$SePt unit. These π molecular orbitals are closely related to those observed for the parent heterocycle, **2**$^+$; the two structures being related by replacement of a Se atom in **2** by a Pt(PH$_3$)$_2$ unit and addition of two H atoms on the N atoms. In **2**$^+$ and **2**, there are 6π and 7π electrons respectively. In **4**$^+$ the RC(NH)-(NH)Se$^+$ fragment provides 6π electrons and the Pt centre contributes two orbitals (d$_{xz}$ and d$_{yz}$) and a further 4e$^-$ for π-bonding, producing a formally 10π aromatic system; the d$_{yz}$ orbital contributing to the HOMO of **4**$^+$. The HOMOs of both **2** and **4**$^+$ are non-bonding with respect to C–N and antibonding with respect to N–Se. The difference in the Se–N bond lengths between **2**$^+$, **2** and **4**$^+$, described above, can then be rationalised in terms of the sequential addition of electrons into an N–Se antibonding orbital.

Acknowledgements

Notes and references

† **3** (E = S): yield = 92%, mp 218 °C (decomp.), UV–VIS $\lambda_{max} = 680$ nm (Found: C, 51.3; H, 3.7; N, 3.9. Calc.: C, 51.2; H, 3.8; N, 3.6%).

‡ Crystal data: [**4**]Cl·CH$_2$Cl$_2$: C$_{34}$H$_{33}$Cl$_3$N$_2$P$_2$PtSe, $M_r = 911.96$, monoclinic, $P2_1/c$, $a = 15.000(5)$, $b = 16.426(5)$, $c = 14.722(5)$ Å, $\beta = 103.11(2)°$, $V = 3533(2)$ Å^3, $Z = 4$, $\rho_{calc} = 1.715$ g cm^{-3}, $F(000) = 1776$, graphite-monochromated Mo-Kα radiation, $\lambda = 0.71069$ Å, $\mu = 5.346$ mm^{-1}, $T = 180(2)$ K. Of 11324 reflections collected on a Rigaku R-Axis IIc image plate diffractometer, 6221 were unique data (2θ <50.58°, $R_{int} = 0.153$). The structure was solved by direct methods and refined by full-matrix methods on F^2 values for all reflections [11] with anisotropic displacement parameters for all non-hydrogen atoms, except the CH$_2$Cl$_2$ solvent molecule which was refined isotropically. H atoms, including N–H, were added at calculated postions and refined using a riding model. The refinement of 329 parameters on F^2 using all 6221 unique reflections converged at $wR_2 = 0.144$, $R_1 = 0.071$ [for $F_o > 2\sigma(F_o)$] and goodness of fit $S = 0.85$. Largest residual electron densities were within $+1.03/–1.37$ e Å^{-3}. CCDC reference number 186/1240. See http://www.rsc.org/suppdata/dt/1998/4091 for crystallographic files in .cif format.

1 A. J. Banister, I. May, J. M. Rawson and J. N. B. Smith, *J. Organomet. Chem.*, 1998, **550**, 241.

2 A. J. Banister, I. B. Gorrell, J. A. K. Howard, S. E. Lawrence, C. W. Lehman, 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.

3 A. J. Banister, J. A. K. Howard, I. May and J. M. Rawson, *Chem. Commun.*, 1997, 1763.

4 J. M. Rawson, A. J. Banister and I. May, *Magn. Reson. Chem.*, 1994, **32**, 487.

5 J. E. Davies, R. J. Less, I. May and J. M. Rawson, *New. J. Chem.*, 1998, 763.

6 J. M. Rawson, A. J. Banister and I. Lavender, *Adv. Heterocycl. Chem.*, 1995, **62**, 137.

7 J. A. K. Howard, A. S. Batsanov and J. N. B. Smith, unpublished work.

8 I. P. Parkin and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 1990, 925; C. A. Mahoney, I. P. Parkin, D. J. Williams and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 1989, 1179; (*c*) R. Jones, P. F. Kelly, D. J. Williams and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 1988, 803.

9 See for example: B. Kreutzer, P. Kreutzer and W. Beck, *Z. Naturforsch., Teil B*, 1972, **27**, 461; D. Dudis and J. P. Fackler Jr., *Inorg. Chem.*, 1982, **21**, 3577; J. P. Fackler, Jr., J. A. Fetchin and D. C. Fries, *J. Am. Chem. Soc.*, 1972, **94**, 7332.

10 R. T. Boeré, K. H. Moock, V. Klassen, J. Weaver, D. Lentz and H. Michael-Schulz, *Can. J. Chem.*, 1995, **73**, 1444.

11 G. M. Sheldrick, *SHELXTL Manual*, Siemens Analytical X-Ray Instruments Inc., Madison, WI, 1990; G. M. Sheldrick, SHELXL 93, Program for crystal structure determination, University of Göttingen, 1993.

12 P. D. B. Belluz, A. W. Cordes, E. M. Kristof, P. V. Kristof, S. W. Liblong and R. T. Oakley, *J. Am. Chem. Soc.*, 1989, **111**, 9276.

13 C. Mealli and D. M. Proserpio, *J. Chem. Educ.*, 1990, **67**, 399 (PC version 4.0, 1994, using in-laid parameters).