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

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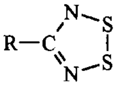
The open-shell complexes, (PhCNEEN)Pt(dppe) (E = S or Se) decompose *via* a chalcogen abstraction process coupled with N-protonation to yield the novel 10π metalla-heterocyclic cations {[PhCN(H)N(H)E]Pt(dppe)}$^+$: the selenium complex is characterised by X-ray crystallography as its chloride salt.

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$_4$]$_2$.



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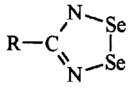

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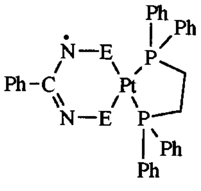
The coordination chemistry of the selenium analogue, **2**, has only recently begun to be investigated, but preliminary results[4,5] indicate that the coordination chemistries of **1** and **2** are similar. Now we report a new decomposition pathway for the monometallic platinum dppe complexes, **3** (E = S or Se), which involves the unexpected extrusion of chalcogen and subsequent ring contraction to form a novel five-membered metallaheterocycle, **4**$^+$.



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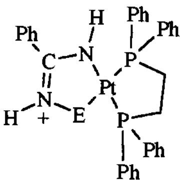

4$^+$

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

$$2\,(\text{PhCNSSN})\text{Pt(dppe)} + \text{dppe} \xrightarrow{2\text{H}/2\text{H}^+} 2\,\{[\text{PhCN(H)SN(H)}]\text{Pt(dppe)}\}^+ + \text{dppeS}_2 \quad (2)$$

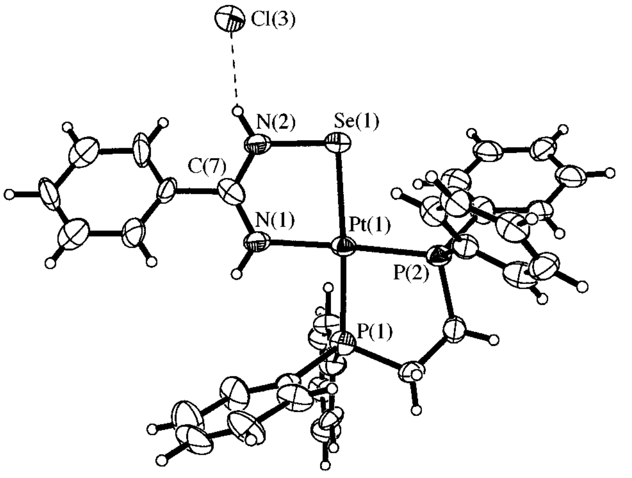

Fig. 1 Crystal structure of [**4**]Cl (E = Se) with heteroatom labelling and with 50% probability ellipsoids.

rigorously dry conditions. Attempts to grow crystals of $\mathbf{4}^+$ (E = S) salts from CH_2Cl_2 by slow evaporation or layering with hexane or Et_2O 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_6H_5Me): $g = 2.058$, $a_{Pt} = 5.4$ 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 $(PhCNSeSeN)_2$ [EPR (C_6H_5Me): $g = 2.03$] 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; δ_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 (δ_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 $[\mathbf{4}]^+$ (E = Se), analogous to $[\mathbf{4}]^+$ (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_2NSe 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_2SePt 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 $\mathbf{2}^+$ 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 $\mathbf{2}^+$ 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_2Cl_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_2Cl_2 solvate molecule (N · · · Cl at 3.78 Å).

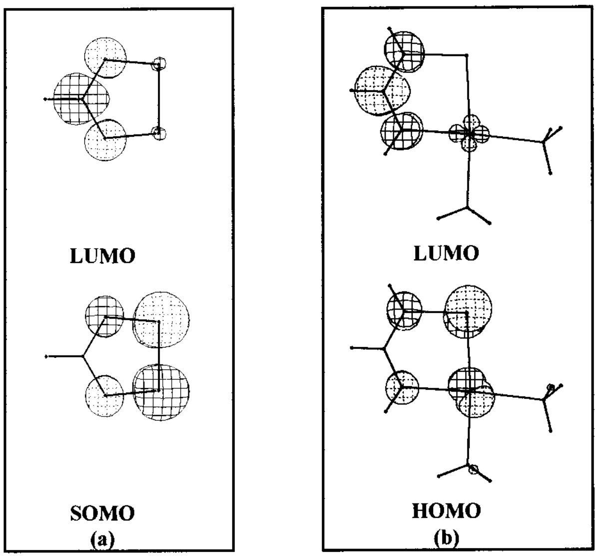

Fig. 2 Frontier molecular orbitals of (a) [HCNSeSeN] and (b) $\{[HCN(H)SeN(H)]Pt(PH_3)_2\}^+$.

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_2SePt unit. These π molecular orbitals are closely related to those observed for the parent heterocycle, $\mathbf{2}^+$; 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 $\mathbf{2}^+$ and **2**, there are 6π and 7π electrons respectively. In $\mathbf{4}^+$ 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 $\mathbf{4}^+$. The HOMOs of both **2** and $\mathbf{4}^+$ are non-bonding with respect to C–N and antibonding with respect to N–Se. The difference in the Se–N bond lengths between $\mathbf{2}^+$, **2** and $\mathbf{4}^+$, described above, can then be rationalised in terms of the sequential addition of electrons into an N–Se antibonding orbital.

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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_2Cl_2: $C_{34}H_{33}Cl_3N_2P_2PtSe$, $M_r = 911.96$, 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 ($2\theta < 50.58°$, $R_{int} = 0.153$). 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_2Cl_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.

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