Isolation of the first diselenadiazolyl complex, $Pd_3[PhCNSeSeN]_2[PPh_3]_4 \cdot 2PhMe$

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L e t t e r

The selenium–nitrogen radical PhCNSeSeN is shown to be partially associated in solution; it undergoes an oxidative addition reaction to Pd(PPh₃)₄ *via* Se—Se bond cleavage, and the structure of the first diselenadiazolyl–metal complex, $Pd_3[PhCNSeSeN]_2[PPh_3]_4$ is reported.

The chemistry of the 1,2,3,5-dithiadiazolyl ring system (**1**) is well established.[1] However, it was not until 1989 that the related diselenadiazolyl ring system (**2**) was prepared.[2] Since then a number of derivatives have been reported[3,4] by Oakley and co-workers. These materials have been investigated for their potential as low-dimensional molecular conductors and a number of doped forms show electrical conductivity.[4] In contrast to the extensive chemistry[1] of the sulfur-based ring system, **1**, there has, to our knowledge, been only one report[5] regarding the chemistry of **2** and we were intrigued to investigate whether derivatives of **2** might exhibit similar, or different, physical and chemical properties to **1**. We now report studies on the solution behaviour of **2a** and its reactivity towards the zero-valent group 10 metal complex Pd(PPh₃)₄.

Derivatives of the dithiadiazolyl radical, **1**, are almost exclusively associated in the solid state through a spin-paired dimerisation process at sulfur.[1] Nevertheless, the dimerisation energy is relatively weak (*ca.* 35 kJ mol⁻¹)[6] and the derivatives become almost completely dissociated upon dissolution. The monomer–dimer equilibria exhibited by these radicals can be elegantly studied by UV/VIS spectroscopy; Passmore and Sun[7] have shown that solutions of the isomeric radical **3a** exhibit two distinct absorption bands (250 and 376 nm) and a weaker band at 480 nm; the intensity of the high-energy band is directly proportional to the concentration of monomeric **3a** whereas the intensities of the bands at 376 and 480 nm are proportional to the square of the radical concentration, consistent with the presence of dimers in solution.

Our solution UV/VIS studies (10^{-2} to 10^{-5} M solutions in THF) show that **1a** exhibits absorption maxima at 225, 285, 410 and 580 nm. Variable concentration studies indicate that the absorption at 410 nm corresponds to monomeric **1a**, whereas the absorption at 580 nm corresponds to dimeric $(\mathbf{1a})_2$ and this absorption gives rise to the typical purple colouration observed for concentrated solutions of **1a**. Previous work has shown that 0.04 M solutions of **1a** in CFCl₃ are yellow and essentially completely dissociated.[7]

Solutions of **2a** in THF are EPR active (broad singlet, $g = 2.04$)[5] and **2a** exhibits an intense absorption around 244 nm in its UV/VIS spectrum, corresponding to monomeric **2a**.
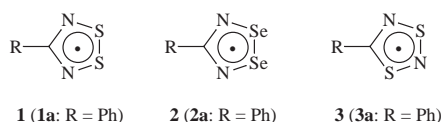
Estimates of the unpaired spin density on selenium (based on EPR studies[5]) indicate that there is a small increase in unpaired electron density at the chalcogen[5] (compared to S) and this might be expected to strengthen this dimerisation process. Even under dilute conditions (10^{-3}–10^{-4} M), two additional absorption maxima can be observed (375 and 487 nm) which exhibit a linear dependence between the square of the radical concentration and the absorption maxima; indicative of incomplete dissociation (*cf.* **1a**). These absorptions (Fig. 1) give rise to the purple colour of **2a** in solution and we infer that the monomer–dimer equilibrium

$$[PhCNSeSeN]_2 \rightleftharpoons 2PhCNSeSeN^{\cdot} \qquad (1)$$

lies further to the left for **2a** in comparison to **1a**. The intensity of the EPR spectrum (relative to a standard DPPH solution) indicates that at room temperature the dissociation process is only *ca.* 70% complete.‡
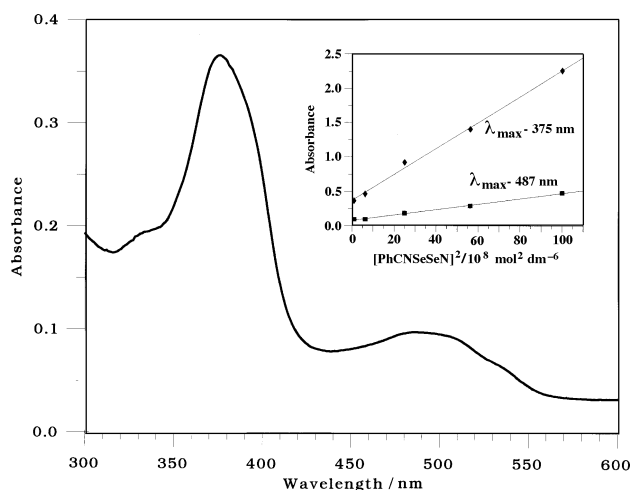
Fig. 1 UV/VIS spectrum of a 10^{-4} M solution of **2a** in THF. Inset: linear relationship between absorbance and the square of **2a** concentration for the absorption maxima observed at 375 and 487 nm
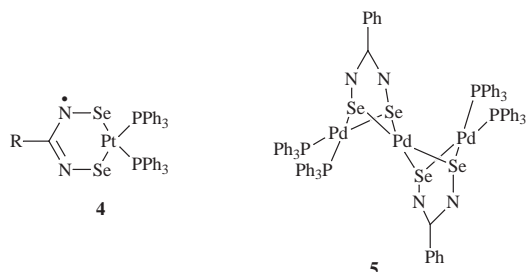
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‡ The width of the solution EPR signal precludes the observation of any hyperfine structure. The peak width broadens markedly on cooling which makes an accurate determination of peak intensity difficult. This has hindered our attempts to extract the thermodynamic ΔH and ΔS parameters for the equilibrium process from variable-temperature EPR studies.

1 (**1a**: R = Ph) **2** (**2a**: R = Ph) **3** (**3a**: R = Ph)

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† Present address: B319.4, British Nuclear Fuels Ltd. UK Group, Sellafield, Seascale, Cumbria, UK, CA20 1PG.
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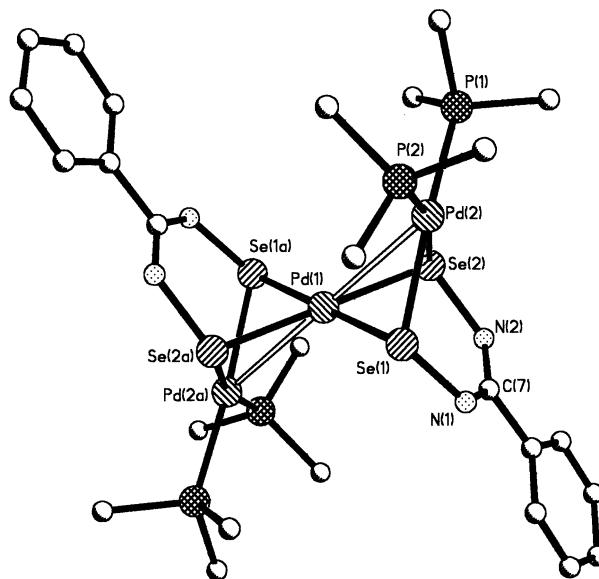One of the most diverse aspects of the chemistry of **1**, is its coordination chemistry,[8] in which it can provide 2e⁻, 3e⁻, 5e⁻ or 6e⁻ for metal–ligand bonding. EPR evidence has supported[5] the transient formation of the diselenadiazolyl–platinum complex, **4**, which rapidly decomposed to EPR inactive products. As a continuation of our work in this area we now provide the first solid-state characterisation of a diselenadiazolyl–metal complex, $Pd_3[PhCNSeSeN]_2[PPh_3]_4$ (**5**).

Reaction of $[PhCNSeSeN]_2$ with $Pd[PPh_3]_4$ in THF yielded $Pd_3[PhCNSeSeN]_2[PPh_3]_4$ (**5**) as a deep-red pre-

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Fig. 2 Structure of **5** (with solvent molecules removed and only P-bound C atoms of PPh_3 groups shown for clarity). Selected bond lengths (Å) and angles (°) are: Pd(1)—Se(1) 2.4481(10), Pd(1)—Se(2) 2.4526(9), Pd(2)—P(1) 2.345(2), Pd(2)—P(2) 2.342(2), Pd(2)—Se(1) 2.4698(11), Pd(2)—Se(2) 2.4903(11), Se(1)—N(1) 1.826(6), Se(2)—N(2) 1.815(6), N(1)—C(7) 1.318(9), N(2)—C(7) 1.326(9), Pd(1)···Pd(2) 2.9657(9), Se(1)Pd(1)Se(2) 81.56(3), Se(1)Pd(1)Se(2a) 98.44(3), Se(1)Pd(2)Se(2) 80.38(3), P(1)Pd(2)P(2) 101.47(7), P(1)Pd(2)Se(1) 168.70(5), P(1)Pd(2)Se(2) 88.53(5), P(2)Pd(2)Se(1) 89.83(6), P(2)Pd(2)Se(2) 166.34(5). Symmetry transformation to generate equivalent (a) atom: $-x, -y, 1-z$

cipitate,§ sparingly soluble in most common organic solvents. The FAB mass spectrum of **5** exhibited a multiplet at 830 amu consistent with the $\{Pd_3[PhCNSeSeN]_2[PPh_3]_3\}^{2+}$ fragment. Crystals of **5** suitable for X-ray diffraction¶ were grown from toluene by slow diffusion techniques.[9] The structure of **5** (Fig. 2) is centrosymmetric and reveals three Pd atoms bridged by two PhCNSeSeN ligands in which the Se—Se bond is formally cleaved, the Se—Se distance increasing from 2.341(3) Å in **2a**[2] to 3.201(1) Å in **5**. The increase in Se···Se distance is accommodated by an increase in the average hinge angles at C and N [from 128(2)° and 116(1)° in **2a** to 134.8(7)° and 124.5(5)° in **5**, respectively]. Heterocyclic Se—Se bond cleavage has previously been reported by Chivers et al.[14] for derivatives of the 1,5-$Ph_4P_2N_4Se_2$ ring system. The terminal Pd atoms take up planar geometries with the PPdP angle [101.47(7)°] somewhat greater than the idealised 90° owing to the strain imposed by the chelating diselenadiazolyl ligand [SePdSe = 80.38(3)°]. The central Pd atom possesses a planar $PdSe_4$ coordination geometry with the corresponding SePdSe bond angles of 81.56(3)°.

The diamagnetic nature of this compound, coupled with the square-planar environment about each Pd is entirely analo-

gous to the sulfur derivative,[9] $Pd_3[PhCNSSN]_2[PPh_3]_4$. Thus, the 16e⁻ associated with terminal Pd atoms are composed of: 10e⁻ from the metal, 2e⁻ from each phosphine donor and 2e⁻ from the diselenadiazolyl ligand. The bonding requirements for the central Pd atom are made up as follows: 10e⁻ from the metal centre and 3e⁻ from each diselenadiazolyl ligand. Thus each diselenadiazolyl ligand provides 5e⁻ for metal–ligand bonding.

These studies illustrate that, in comparison to the sulfur analogue **1a**, the diselenadiazolyl radical, **2a**, is more strongly associated in solution. Despite these differences in physical properties, the chemical reactivity of **2a** towards zero-valent group 10 metal phosphines would appear to be analogous to that observed for dithiadiazolyls, **1**. A more detailed investigation of the monomer–dimer equilibrium and substituent effects on this process are underway. Further experiments are being carried out to compare the reactivities of **1** and **2**.

§ A mixture of **2a** (80 mg, 0.30 mmol) and $Pd(PPh_3)_4$ (500 mg, 0.43 mmol) were stirred in THF (20 ml) for 4 h at room temperature. The resultant red-brown solid was filtered and washed with THF (3 × 20 ml) and dried in vacuo. Yield 205 mg, 72%. ³¹P NMR (CDCl₃), $\delta + 35.6$(s) (the low solubility of **5**, precluded observation of Se satellites). Calcd for **5**, THF: C, 54.25%; H, 3.92%; N, 2.81%; found: C, 54.25%; H, 4.28%; N, 2.46%.

¶ Crystal Data for **5**, 2PhMe: $C_{100}H_{86}N_4P_4Pd_3Se_4$, $M = 2102.65$, triclinic, space group $P\bar{1}$, $a = 14.102(4)$, $b = 14.242(4)$, $c = 11.022(3)$ Å, $\alpha = 98.87(2)$, $\beta = 93.82(2)$, $\gamma = 79.74(2)°$, $V = 2151$ Å³ [from 2θ values of 25 reflections measured at $\pm\omega$ ($15 \leqslant 2\theta \leqslant 20$)], $\lambda = 0.71069$ Å, $Z = 1$ (molecule lies on an inversion centre), $D_e = 1.624$ g cm⁻³, $T = 150$ K, red block, crystal size 0.3 × 0.2 × 0.2 mm, $\mu = 2.44$ mm⁻¹.

Data Collection and Processing: Rigaku AFC 5R diffractometer with Oxford Cryosystems low-temperature device[10] graphite monochromated Mo-Kα radiation, ω-2θ scans. The data were corrected for absorption by means of psi-scans.[11] The structure was solved by direct methods using SHELXS-86[12] and refined using full-matrix least-squares techniques.[13] All non-H atoms were refined anisotropically and H atoms were added at calculated positions with a fixed thermal parameter. Convergence was obtained at $R_1[F_0 > 2\sigma(F)] = 0.051$, wR_2 (all data) $= 0.114$, $S = 1.032$ for 7538 independent reflections ($5 \leqslant 2\theta \leqslant 50$°). Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre, reference number 440/043. See Information for Authors, Issue No. 1.

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