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Remarkable *S*,*N*,*S′* tridentate chelation to palladium(II) by the monoanion derived from $[Ph_2P(S)NH]_2CO$

Pravat Bhattacharyya, Alexandra M. Z. Slawin and J. Derek Woollins *

Department of Chemistry, University of St Andrews, Fife, UK KY16 9ST.
E-mail: jdw3@st-andrews.ac.uk

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The reaction between $[PdCl_2(PhCN)_2]$ and $[Ph_2P(S)NH]_2C{=}O$ (H_2L) proceeds with monodeprotonation of an amine group in the disulfide ligand to give [Pd(HL)Cl] 1, in which the $(HL)^-$ anion supplies an *S*,*N*,*S′* donor set to palladium(II), leading to disparate *S*,*N* chelate ring sizes at the metal.

We have recently investigated[1] the imidodiphosphinates $[R_2P(E)NP(E')R'_2]^-$ (R, R′ = alkyl, aryl or alkoxy; E, E′ = oxygen, sulfur or selenium) as structural analogues of the more widely known β-diketonates, such as $[CH_3C(O)CHC(O)CH_3]^-$. Despite the ubiquity of the β-diketonates throughout inorganic chemistry, the anions derived from β-triketones $[RC(O)CH_2C(O)CH_2C(O)R]$ have been largely neglected; although *O*,*O′* bidentate and *O*,*O′*,*O″* tridentate chelation modes are observed in organotin(IV) complexes of β-triketonate anions,[2] platinum(II) centres favour *C*,*C′* metallation to form platinacyclobutan-3-one rings.[3] We considered that the presence of weakly acidic amine protons and the potential to offer three chalcogen atoms for co-ordination to metal centres made $[Ph_2P(S)NH]_2C{=}O$ (H_2L)[4] an ideal candidate for study as a structural analogue of β-triketones; here we describe the unusual tridenticity displayed by the monoanion derived from H_2L at palladium(II).

Treatment of $[PdCl_2(PhCN)_2]$ with one molar equivalent of H_2L at room temperature in dichloromethane proceeds with the elimination of HCl and displacement of two molecules of benzonitrile from the palladium(II) co-ordination sphere to give [Pd(HL-*S*,*N*,*S′*)Cl] **1** in good yield (86%).† Compound **1** is moderately soluble in chlorinated solvents and thf, and stable to oxygen and moisture. Crystallographic analysis‡ of **1** reveals monodeprotonation of H_2L and subsequent co-ordination by the $(HL)^-$ anion to Pd(1) in two distinct chelation modes, Fig. 1. The C(25)–O(25) carbonyl vector is directed away from the metal centre, tridentate coordination of the $(HL)^-$ anion occurs through the S(1), N(2) and S(2) atoms producing fused six-membered Pd(1)–S(1)–P(1)–N(1)–C(25)–N(2) and four-membered Pd(1)–S(2)–P(2)–N(2) palladacycles, with completion of the donor set at Pd(1) by a chloro ligand Cl(1) bound *trans* to N(2). The four membered Pd(1)–S(2)–P(2)–N(2) ring is essentially planar (mean deviation from planarity 0.04 Å) while for the six membered chelate ring P(1) lies 0.8 Å from the plane defined by the remaining five atoms of the hexa-atomic ring (mean deviation from planarity 0.03 Å). The phosphorus–sulfur bond lengths are inequivalent in **1**, a feature also seen in the free ligand H_2L,[4] with P(2)–S(2) in the complex, associated with the Pd–S–P–N chelate being the longer within the pair. Co-ordination increases the P–S lengths by *ca.* 0.06 Å compared with H_2L [2.016(3) and 1.991(3) Å in **1**, 1.931(1) and 1.942(1) Å in H_2L]; conversely the phosphorus–nitrogen distances, identical within statistical significance in **1** [N(1)–P(1) 1.661(6), N(2)–P(2) 1.651(5) Å], are slightly shorter than the corresponding lengths in H_2L [1.686(2) and 1.702(2) Å]. In accord with the disparate sizes of the chelate rings the *cis* S–Pd–N angles are markedly different [N(2)–Pd(1)–S(2) 78.3(2)°, N(2)–Pd(1)–S(1) 99.4(2)°], the *trans* N(2)–Pd(1)–Cl(1) vector being restricted to 172.0(2)°. Tetra-atomic M–E–P–N metallacycles (E = chalcogen or NR) remain rare in the literature, the majority of structurally characterised complexes containing this motif being of first row d-block metals.[5] At palladium(II) the unsymmetrical ligand $(PhO)_2P(S)NHP(O)(OPh)_2$ forms four-membered *S*,*N* chelate rings[6] in *trans*-$[Pd\{(PhO)_2P(S)NP(O)(OPh)_2\text{-}S,N\}_2]$ in preference to *S*,*O* chelation, the metallacycle parameters [Pd–N 2.055(3) Å, Pd–S 2.342(1) Å, N–Pd–S 78.53(8)°] show close correspondence to those of **1**; notably *S*-monodentate co-ordination is observed in *trans*-$[PdCl_2\{(EtO)_2P(S)NHC_6H_4NO_2\text{-}2\}_2]$.[7] Strong intermolecular dimer pair hydrogen-bonding interactions seen between adjacent molecules in the crystal structure of H_2L persist in the structure of **1** (Fig. 2), with H(1n)···O(25′) 1.79 Å and N(1)–H(1n)···O(25′) 177°, *cf.* 1.86 Å and 175.3° respectively in the dimer pairs of H_2L.

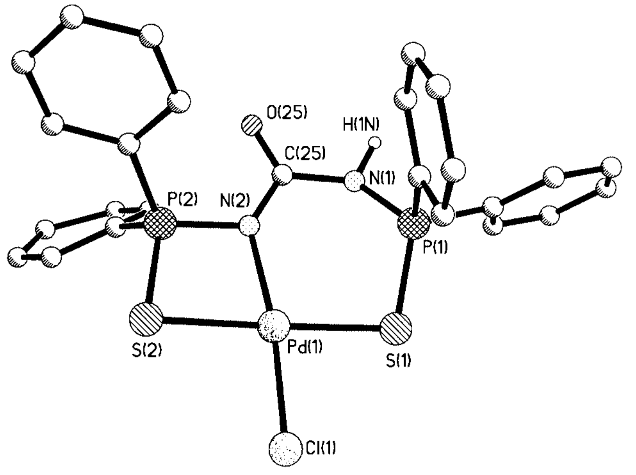

Fig. 1 Molecular structure of **1** (C–H atoms omitted for clarity). Selected bond lengths (Å) and angles (°); Pd(1)–Cl(1) 2.296(2), Pd(1)–S(1) 2.325(2), Pd(1)–S(2) 2.340(2), Pd(1)–N(2) 2.042(5), P(2)–S(2) 2.016(3), P(2)–N(2) 1.651(5), N(2)–C(25) 1.353(8), C(25)–O(25) 1.235(7), C(25)–N(1) 1.389(8), N(1)–P(1) 1.661(6), P(1)–S(1) 1.991(3); S(2)–Pd(1)–S(1) 177.66(7), S(2)–Pd(1)–N(2) 78.3(2), S(1)–Pd(1)–N(2) 99.4(2), S(2)–Pd(1)–Cl(1) 94.20(7), S(1)–Pd(1)–Cl(1) 88.02(7), N(2)–Pd(1)–Cl(1) 172.0(2), Pd(1)–S(2)–P(2) 81.94(8), S(2)–P(2)–N(2) 98.0(2), P(2)–N(2)–Pd(1) 101.3(3), N(1)–P(1)–S(1) 113.6(2), Pd(1)–N(2)–C(25) 137.2(5), N(2)–C(25)–N(1) 117.7(6), C(25)–N(1)–P(1) 126.8(5), P(1)–S(1)–Pd(1) 98.27(9), C(25)–N(2)–P(2) 121.0(5).

The $^{31}P\{^1H\}$ NMR spectrum of **1** comprises two singlets; one signal resembles the free ligand value (δ_P 56.1 *cf.* 52.2 for H_2L) which corresponds to the P(1) atom in the six-membered ring whereas the other phosphorus environment P(2) (δ_P 91.6) experiences substantial deshielding upon *N*-metallation and concomitant formation of the four-membered palladacycle. The characteristic $^{31}P\{^1H\}$ NMR shifts upon ligation provide a powerful diagnostic tool, hence we have been able to recognise similar *E*,*N*,*E′* tridentate co-ordination by the anions of $[Ph_2P(E)NH]_2CO$ (E = sulfur or selenium) at platinum(II) and rhodium(III) centres.[8]

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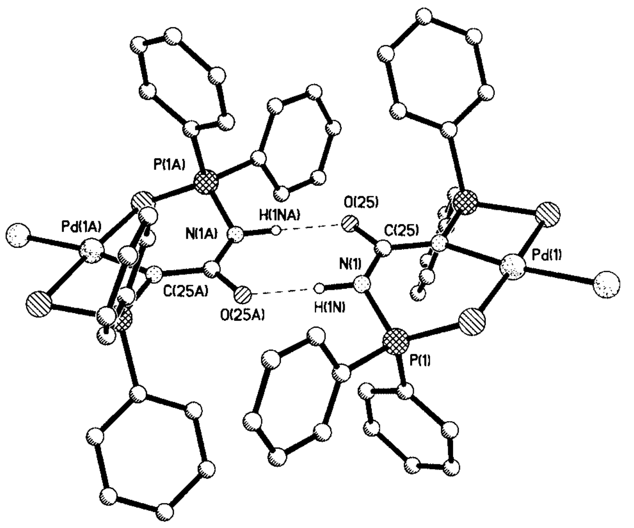

Fig. 2 Dimer pair formation in the solid state structure of **1**.

In conclusion, *N*-metallation of H_2L in the reaction with $[PdCl_2(PhCN)_2]$ produces a complex [Pd(HL)Cl] containing an *S*,*N*,*S′* tridentate $(HL)^-$ anion; the observation of tridenticity in preference to *S*,*S′* or *S*,*O* bidentate co-ordination modes for example, is perhaps rationalised by substantial flexibility in the H_2L backbone in alliance with an ionisable NH proton.

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Notes and references

† [Pd(HL-*S*,*N*,*S′*)Cl] **1**. To a solution of $[PdCl_2(PhCN)_2]$ (43 mg, 0.11 mmol) in dichloromethane (2 cm^3) was added H_2L (55 mg, 0.11 mmol) in dichloromethane (2 cm^3) and the reaction mixture stirred at room temperature for 30 min, during which time an orange precipitate appears. Precipitation of **1** is completed by the addition of hexane (10 cm^3). Yield 60 mg, 86%. Found (Calc. for $PdC_{25}H_{21}N_2P_2OS_2Cl$); C 46.7(47.4), H 3.6(4.4), N 4.6(3.3)%. FAB$^+$ MS; *m/z* 597, $[M^+ - Cl]$. IR (KBr, cm^{-1}); 3052m (ν_{NH}), 1618s (ν_{CO}), 1107s, 802s (ν_{PN}) and 687s (ν_{PS}). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 36.2 MHz); 56.1 (s), 91.6 (s). Needles of **1** suitable for X-ray analysis were grown by vapour diffusion of diethyl ether into a dichloromethane solution of the complex.

‡ Single crystal X-ray diffraction studies on crystals of [Pd(HL-*S*,*N*,*S′*)Cl] **1** were performed using a Bruker SMART diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods, the non-hydrogen atoms were refined with anisotropic displacement parameters; phenyl hydrogen atoms were idealised and fixed (C–H 0.95 Å), $U(H) = 1.2U_{eq}(C)$; the NH proton H(1n) associated with N(1) was located using a ΔF map and allowed to refine isotropically subject to a distance constraint. An attempt to model the slight disorder of the C(19)–C(24) phenyl ring was made, however this proved unsuccessful. This phenyl ring has been refined as an idealised rigid body. Structural refinements were by the full-matrix least-squares method on F^2 using the program SHELXTL.[9] $C_{25}H_{21}ClN_2P_2OPdS_2$, $M = 633.35$, orthorhombic, $a = 12.2320(2)$ Å, $b = 18.5402(2)$ Å, $c = 24.4688(2)$ Å, $U = 5549.13(14)$ Å^3, $T = 293$ K, space group *Pbca*, $Z = 8$, $F(000) = 2544$, μ(Mo-Kα) = 1.052 mm^{-1}. Of 25983 measured data, 3982 were unique (R_{int} 0.0834), to give $R1[I > 2\sigma(I)] = 0.0504$ and $wR2 = 0.1015$. CCDC reference number 186/1932. See http://www.rsc.org/suppdata/dt/b0/b002413i/ for crystallographic files in .cif format.

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