

η^2 -S,S'-1,5-Dithia-2,4,6,8-tetrazocine Analogues of η^2 -Alkene Complexes: Preparation and Electronic Structure of Pt[1,5-(Me₂N)₂C₂N₄S₂](PPh₃)₂

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The reaction of Pt(C₂H₄)(PPh₃)₂ with 1,5-E₂N₄S₂ (E = Ph₂P, Me₂NC) in acetonitrile produces high yields of Pt(1,5-E₂N₄S₂)(PPh₃)₂ in which the η^2 -S,S' bonding between platinum and the heterocyclic ligand is shown by density functional calculations to be analogous to that found in η^2 -alkene–platinum complexes.

The nature of the weak cross-ring S–S interactions [$d(\text{S}–\text{S}) \sim 2.5 \text{ \AA}$] in 1,5-dithiatetrazocines E₂N₄S₂, (**1a**) E = Me₂NC;¹ (**1b**) E = Me₂P;² (**1c**) E = Ph₂P,³ is a fundamental issue in understanding the unusual structures and bonding in sulphur–nitrogen (S–N) rings and cages.⁴ In connection with studies of the stereochemistry of oxidation of (**1a**)⁵ and (**1c**)^{5,6} by polar and radical reagents, Oakley *et al.* have pointed out the isobal correspondence between the σ and σ^* orbitals of these S–S bonds and the π and π^* orbitals of an electron-deficient alkene (Figure 1).⁵ As a test of this analogy we have investigated the reactions of (**1a**) and (**1c**) with zerovalent platinum complexes and we report here the preparation of Pt(E₂N₄S₂)(PPh₃)₂, (**2a**) E = Me₂N; (**3**) E = Ph₂P. These complexes exhibit a novel bonding mode between the

heterocyclic ligand and platinum involving an η^2 -S,S' interaction which, on the basis of relativistic density functional calculations, is comparable to that found in the classic metal–alkene complexes.⁷

The reactions of Pt(C₂H₄)(PPh₃)₂ with (**1a**) or (**1c**) proceed rapidly in toluene under nitrogen at room temperature to give

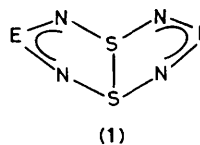
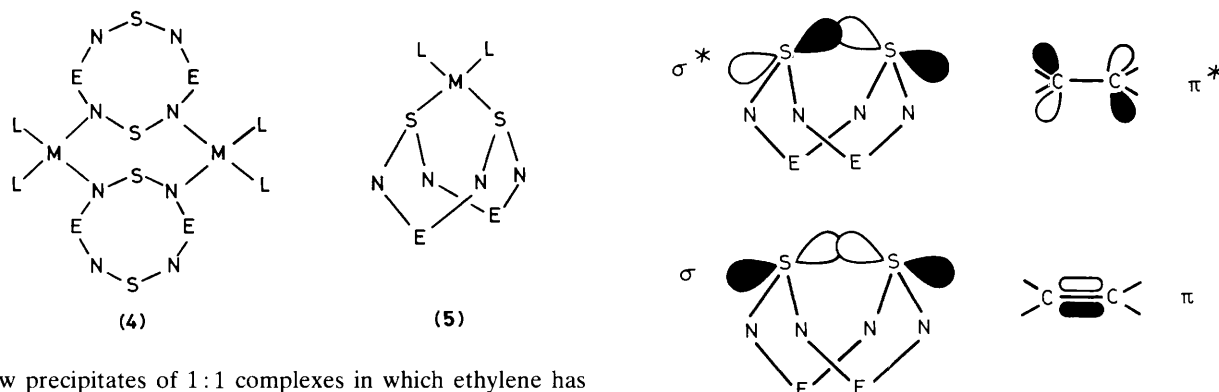


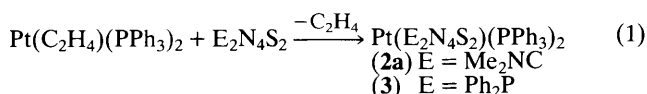
Table 1. Decomposition^a of calculated $D(\text{Pt-L})$ bond energies (kJ mol^{-1}) in $(\text{PH}_3)_2\text{PtL}$.

L	$-\Delta E_{\text{prep}}^b$	$-\Delta E_{\text{O}}$	$-\Delta E_{\text{D}}$	$-\Delta E_{\text{BD}}$	$-\Delta E_{\text{R}}$	$D(\text{Pt-L})$
$\text{C}_2(\text{CN})_4$	-158.9	-506.4	123.9	561.6	136.4	156.6
$1,5\text{-(H}_2\text{N)}_2\text{C}_2\text{N}_4\text{S}_2$	-63.3	-493.5	156.5	376.2	128.1	104.0
C_2H_4	-110.4	-306.7	92.1	266.5	123.4	65.5

^a Decomposition^d of $D(\text{Pt-L})$ according to equation (2). ^b Contribution from deformation of $(\text{PH}_3)_2\text{Pt}$ is $-50.2 \text{ kJ mol}^{-1}$.



yellow precipitates of 1:1 complexes in which ethylene has been displaced by the heterocyclic ligand [reaction (1)].



Compound (2a) was obtained in 79% yield as pale yellow, rectangular crystals (m.p. 241°C) after recrystallization from acetonitrile and (3) was produced in 72% yield as yellow microcrystals (m.p. $197\text{--}198^\circ\text{C}$) after recrystallization from $\text{CH}_2\text{Cl}_2\text{-C}_6\text{H}_6$.[†] The ^1H n.m.r. spectrum of (2a) in CDCl_3 exhibits a singlet at δ 2.91 [cf. δ 3.15 for (1) ($\text{E} = \text{Me}_2\text{NC}$)][‡] and the $^{31}\text{P}\{^1\text{H}\}$ n.m.r. spectrum shows a singlet at +19.9 p.p.m. (ref. external 85% H_3PO_4) with $^1J_{\text{Pt-P}}$ 3225 Hz. The $^{31}\text{P}\{^1\text{H}\}$ n.m.r. spectrum of (3) in CDCl_3 at 25°C exhibits singlets at +15.3 (Ph_3P) ($^1J_{\text{Pt-P}}$ 2850 Hz) and +39.0 (Ph_2P) ($J_{\text{Pt-P}}$ 580 Hz). The ^{31}P n.m.r. spectrum of (3) at -60°C is identical to that obtained at 25°C . The n.m.r. data for (2a) and (3) indicate that the heterocyclic ligand is symmetrically bonded to platinum, but these data do not distinguish between the structural possibilities (4) \ddagger [cf. $\text{S}_4\text{N}_4\cdot\text{CuX}_2$ ($\text{X} = \text{Br}, \text{Cl}$) and $\alpha\text{-[TiCl}_4(\text{S}_4\text{N}_4)]_2$] and (5).[§]

We have carried out relativistic^{9a} density functional calculations^{9b} on the complexes $(\text{PH}_3)_2\text{PtL}$, (2b) $\text{L} = 1,5\text{-(H}_2\text{N)}_2\text{C}_2\text{N}_4\text{S}_2$; (6) $\text{L} = \text{C}_2(\text{CN})_4$; and (7) $\text{L} = \text{C}_2\text{H}_4$, based on the HFS-LCAO program system,^{9c} where (2b) should serve as a realistic model for the title compound (2a); (6) and (7) are representative d^{10} alkene complexes. Calculated $D(\text{Pt-L})$ bond energies for the three systems [(2b), (6) and (7)] are given in Table 1 decomposed^{9d} according to equation (2).

$$D(\text{Pt-L}) = -[\Delta E_{\text{prep}} + \Delta E_{\text{O}} + \Delta E_{\text{D}} + \Delta E_{\text{BD}} + \Delta E_{\text{R}}] \quad (2)$$

[†] Satisfactory C, H, and N analyses were obtained for (2a) and (3).

[‡] Preliminary X-ray structural data for (2a) have established that this complex adopts the $\eta^2\text{-S,S}'$ structure (5), with approximately square planar co-ordination at Pt: $\angle\text{PPtP} = 101.3(3)$, $\angle\text{SPtS} = 79.2(5)^\circ$, $d(\text{Pt-S}) = 2.36(1)$, $d(\text{Pt-P}) = 2.32(1)$, $d(\text{S-S}) = 3.01(2) \text{ \AA}$ [cf. $d(\text{S-S}) = 2.43 \text{ \AA}$ in (1) $\text{E} = \text{Me}_2\text{NC}$].[‡] Problems have been encountered with the refinement and further structural details will be given in the full paper (J. Fait, personal communication).

Figure 1. Schematic representation of the S-S σ and σ^* orbitals in (1) (S-N antibonding components are not shown) and the π and π^* orbitals of alkene.

In equation (2) ΔE_{prep} represents the energy required to deform $(\text{PH}_3)_2\text{Pt}$ and L into the structures of the two fragments in the combined complex, ΔE_{O} is the steric interaction energy between $(\text{PH}_3)_2\text{Pt}$ and L in $(\text{PH}_3)_2\text{PtL}$, $-\Delta E_{\text{D}}$ is the stabilization of the Pt-L bond due to the donation from $\sigma(\text{S-S})$ (2b) or $\pi(\text{alkene})$ (6) and (7), $-\Delta E_{\text{BD}}$ is the corresponding stabilization due to the back-donation to $\sigma^*(\text{S-S})$ (2b) or $\pi^*(\text{alkene})$ (6) and (7), and $-\Delta E_{\text{R}}$ represents contributions to $D(\text{Pt-L})$ from relativistic effects. The results in Table 1 confirm the notion that the bonding in (2b) is analogous to that found in platinum-alkene complexes.⁷ In fact the order for $-\Delta E_{\text{BD}}$ is calculated as (6) > (2b) > (7). This order can be related to the energies of the acceptor orbitals, $\sigma^*(\text{S-S})$ or $\pi^*(\text{alkene})$, calculated (in eV) as -5.4 , -3.3 , and -1.7 , for the free (deformed) ligands of (6), (2b), and (7), respectively. The charges back-donated are 0.92, 0.76, and 0.57 for (6), (2b), and (7), respectively. Thus the back-donation to the heterocyclic ligand in (2b) is seen to fall between that to the electron-deficient alkene $\text{C}_2(\text{CN})_4$ in (6) and that to the more electron-rich alkene C_2H_4 in (7).

Numerous adducts of S_4N_4 (1) $\text{E} = \text{S}$, with transition metal halides, are known and they involve mono- or bi-dentate co-ordination to the metal *via* a nitrogen atom.^{10,11} The only exception is the six-co-ordinate complex $\text{IrCl}(\text{CO})(\text{PPh}_3)(\text{S}_4\text{N}_4)$ in which the Ir atom is inserted into an S-N bond of S_4N_4 which functions as a tridentate (N,S,S) ligand.¹² Thus compound (2a) represents a new structural type and bonding mode for complexes of S-N ligands with metals and presages an interesting co-ordination chemistry for ligands of type (1).

Finally, we note that the reaction of S_4N_4 with zerovalent platinum complexes produces the unstable adduct $\text{Pt}(\text{S}_4\text{N}_4)(\text{PPh}_3)_2$ ¹³ prior to decomposition to give mono- and di-nuclear complexes containing PtS_2N_2 rings.¹⁴⁻¹⁶ It seems reasonable to propose that $\eta^2\text{-S,S}'$ bonding is also involved in this adduct and that co-ordination of another Pt atom to the

second S-S bond in S₄N₄ leads to cleavage of the S-N heterocycle to give the observed cyclometallathiazenes.

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