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-(Me$_2$N)$_2$C$_2$N$_4$S$_2$](PPh$_3$)$_2$

Tristram Chivers,* Kaveripatnam S. Dhathathreyan, and Tom Ziegler*

Department of Chemistry, The University of Calgary, Calgary T2N 1N4, Alberta, Canada

The reaction of Pt(C$_2$H$_4$)(PPh$_3$)$_2$ with 1,5-E$_2$N$_4$S$_2$ (E = Ph$_2$P, Me$_2$NC) in acetonitrile produces high yields of Pt(1,5-E$_2$N$_4$S$_2$)(PPh$_3$)$_2$ 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(S–S)~ 2.5 Å] in 1,5-dithiatetrazocines E$_2$N$_4$S$_2$, (1a) E = Me$_2$NC;[1] (1b) E = Me$_2$P;[2] (1c) E = Ph$_2$P,[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 isolobal 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(E$_2$N$_4$S$_2$)(PPh$_3$)$_2$, (2a) E = Me$_2$N; (3) E = Ph$_2$P. 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(C$_2$H$_4$)(PPh$_3$)$_2$ with (1a) or (1c) proceed rapidly in toluene under nitrogen at room temperature to give

(1)
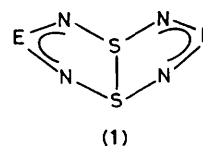
Table 1. Decomposition[a] of calculated D(Pt–L) bond energies (kJ mol^{-1}) in $(PH_3)_2PtL$.

L	$-\Delta E_{prep}$[b]	$-\Delta E_O$	$-\Delta E_D$	$-\Delta E_{BD}$	$-\Delta E_R$	D(Pt–L)
$C_2(CN)_4$	−158.9	−506.4	123.9	561.6	136.4	156.6
$1,5\text{-}(H_2N)_2C_2N_4S_2$	−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[9d] of D(Pt–L) according to equation (2). [b] Contribution from deformation of $(PH_3)_2Pt$ is −50.2 kJ mol^{-1}.

(4)   (5)
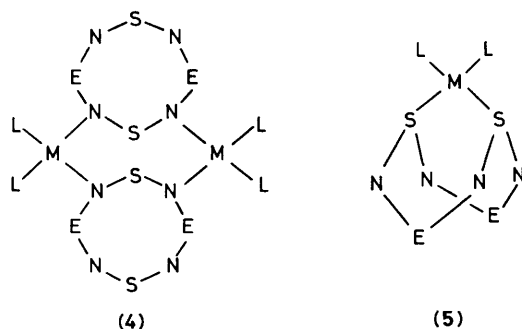
yellow precipitates of 1:1 complexes in which ethylene has been displaced by the heterocyclic ligand [reaction (1)].

$$Pt(C_2H_4)(PPh_3)_2 + E_2N_4S_2 \xrightarrow{-C_2H_4} Pt(E_2N_4S_2)(PPh_3)_2 \quad (1)$$
$$\text{(2a) } E = Me_2NC$$
$$\text{(3) } E = Ph_2P$$
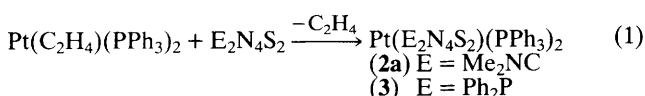
Compound (2a) was obtained in 79% yield as pale yellow, rectangular crystals (m.p. 241 °C) after recrystallization from acetonitrile and (3) was produced in 72% yield as yellow microcrystals (m.p. 197—198 °C) after recrystallization from CH_2Cl_2–C_6H_6.† The ^1H n.m.r. spectrum of (2a) in $CDCl_3$ exhibits a singlet at δ 2.91 [cf. δ 3.15 for (1) (E = Me_2NC)][1] and the $^{31}P\{^1H\}$ n.m.r. spectrum shows a singlet at +19.9 p.p.m. (ref. external 85% H_3PO_4) with $^1J_{Pt-P}$ 3225 Hz. The $^{31}P\{^1H\}$ n.m.r. spectrum of (3) in $CDCl_3$ at 25 °C exhibits singlets at +15.3 (Ph_3P) ($^1J_{Pt-P}$ 2850 Hz) and +39.0 (Ph_2P) (J_{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)‡ {cf. S_4N_4·CuX_2 (X = Br, Cl) and α-[$TiCl_4(S_4N_4)]_2$} and (5).[8]

We have carried out relativistic[9a] density functional calculations[9b] on the complexes $(PH_3)_2PtL$, (2b) L = 1,5-$(H_2N)_2C_2N_4S_2$; (6) L = $C_2(CN)_4$; and (7) L = C_2H_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(Pt–L) bond energies for the three systems [(2b), (6) and (7)] are given in Table 1 decomposed[9d] according to equation (2).

$$D(\text{Pt–L}) = -[\Delta E_{prep} + \Delta E_O + \Delta E_D + \Delta E_{BD} + \Delta E_R] \quad (2)$$

† 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 η^2-S,S' structure (5), with approximately square planar co-ordination at Pt: $\angle PPtP$ = 101.3(3), $\angle SPtS$ = 79.2(5)°, d(Pt–S) = 2.36(1), d(Pt–P) = 2.32(1), d(S–S) = 3.01(2) Å [cf. d(S–S) = 2.43 Å in (1) E = Me_2NC].[1] Problems have been encountered with the refinement and further structural details will be given in the full paper (J. Fait, personal communication).
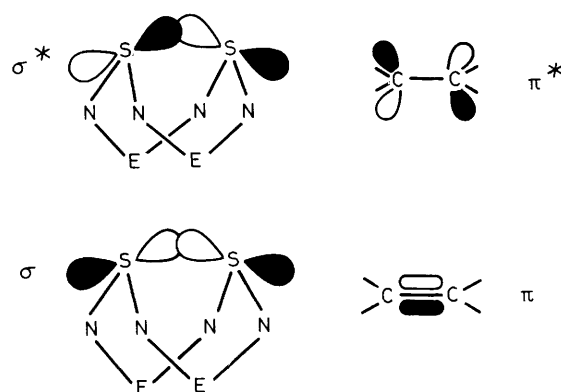

Figure 1. Schematic representation of the S–S σ and σ* orbitals in (1) (S–N antibonding components are not shown) and the π and π* orbitals of alkene.

In equation (2) ΔE_{prep} represents the energy required to deform $(PH_3)_2Pt$ and L into the structures of the two fragments in the combined complex, ΔE_O is the steric interaction energy between $(PH_3)_2Pt$ and L in $(PH_3)_2PtL$, $-\Delta E_D$ is the stabilization of the Pt–L bond due to the donation from σ(S–S) (2b) or π(alkene) (6) and (7), $-\Delta E_{BD}$ is the corresponding stabilization due to the back-donation to σ*(S–S) (2b) or π* (alkene) (6) and (7), and $-\Delta E_R$ represents contributions to D(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 $-\Delta E_{BD}$ is calculated as (6) > (2b) > (7). This order can be related to the energies of the acceptor orbitals, σ*(S–S) or π*(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 $C_2(CN)_4$ in (6) and that to the more electron-rich alkene C_2H_4 in (7).

Numerous adducts of S_4N_4 (1) E = 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 $IrCl(CO)(PPh_3)(S_4N_4)$ in which the Ir atom is inserted into an S–N bond of S_4N_4 which functions as a tridentate (N,S,N) 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 $Pt(S_4N_4)(PPh_3)_2$[13] prior to decomposition to give mono- and di-nuclear complexes containing PtS_2N_2 rings.[14—16] It seems reasonable to propose that η^2-S,S' bonding is also involved in this adduct and that co-ordination of another Pt atom to the

References

1 I. Ernest, W. Holick, G. Rihs, D. Schomburg, G. Shoham, D. Wenkert, and R. B. Woodward, *J. Am. Chem. Soc.*, 1981, **103**, 1540.
2 N. Burford, T. Chivers, P. W. Codding, and R. T. Oakley, *Inorg. Chem.*, 1982, **21**, 982.
3 N. Burford, T. Chivers, and J. F. Richardson, *Inorg. Chem.*, 1983, **22**, 1482.
4 T. Chivers, *Chem. Rev.*, 1985, **85**, 341.
5 R. T. Boeré, A. W. Cordes, S. L. Craig, T. T. Oakley, and R. W. Reed, *J. Am. Chem. Soc.*, 1987, **109**, 868.
6 N. Burford, T. Chivers, M. N. S. Rao, and J. F. Richardson, *Inorg. Chem.*, 1984, **23**, 1946.
7 M. J. S. Dewar, *Bull. Soc. Chim. Fr.*, 1953, **18**, C79; J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 1953, 2939.
8 U. Thewalt, *Angew. Chem., Int. Ed. Engl.*, 1976, **15**, 765; U. Thewalt and B. Muller, *Z. Naturforsch., Teil B*, 1988, **37**, 828; U. Thewalt and K. Holl, *ibid.*, 1988, **43**, 467.
9 (a) J. G. Snijders, E. J. Baerends, and P. Ros, *Mol. Phys.*, 1979, **33**, 1909; (b) A. Becke, *J. Chem. Phys.*, 1986, **84**, 4524; (c) E. J. Baerends, D. E. Ellis, and P. Ros, *Chem. Phys.*, 1973, **2**, 71; (d) T. Ziegler and A. Rauk, *Inorg. Chem.*, 1979, **18**, 1588.
10 T. Chivers and F. Edelmann, *Polyhedron*, 1986, **5**, 1661.
11 P. F. Kelly and J. D. Woollins, *Polyhedron*, 1986, **5**, 607.
12 F. Edelmann, H. W. Roesky, C. Spang, M. Noltemeyer, and G. M. Sheldrick, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 931.
13 A. A. Bhattacharyya, J. A. McLean, Jr., and A. G. Turner, *Inorg. Chim. Acta*, 1979, **34**, L199.
14 C. A. Ghilardi, S. Midollini, S. Moneti, and A. Orlandini, *J. Organomet. Chem.*, 1985, **286**, 419.
15 R. Jones, P. F. Kelly, D. J. Williams, and J. D. Woollins, *J. Chem. Soc., Chem. Commun.*, 1985, 1325.
16 T. Chivers, F. Edelmann, U. Behrens, and R. Drews, *Inorg. Chim. Acta*, 1986, **116**, 145.