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A comparison of the coordination chemistry of Ph_2SNH and $Ph_2SNCH_2CH_2CN$; the preparation and X-ray crystal structures of $[PPh_4][PdBr_3(Ph_2SNCH_2CH_2CN)]$ and *trans*-$[PdBr_2(Ph_2SNCH_2CH_2CN)_2]$, the first fully characterised complexes of a N-substituted sulfimide

Paul F. Kelly [a,*], Kevin G. Parker [a], Miguel A. Rodiel [a], Alexandra M.Z. Slawin [b]

[a] *Department of Chemistry, Loughborough University, Loughborough, Leicestershire, LE11 3TU, UK*
[b] *Department of Chemistry, University of St Andrews, St Andrews, KY16 9ST, UK*

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Abstract

Reaction of excess Ph_2SNH (**1**) with $[PPh_4]_2[Pd_2Br_6]$ results in the formation of homoleptic $[Pd(Ph_2SNH)_4]Br_2$. In contrast the analogous reaction of the N-substituted sulfimide $Ph_2SN–CH_2CH_2CN$ (**2**) with $[PPh_4]_2[Pd_2Br_6]$ only results in the formation of *trans*-$[PdBr_2(Ph_2SNCH_2CH_2CN)_2]$ (**3**) even if the ligand is present in large excess. Lowering the reaction ratio to 2:1 (ligand: dimer) allows isolation of $[PPh_4][PdBr_3(Ph_2SNCH_2CH_2CN)]$ (**4**). Compounds **3** and **4** constitute the first examples of fully characterised complexes of N-substituted sulfimides and X-ray crystallography confirm the ligands to be bound to the metal through nitrogen; although the nitrile end groups of the substituents have the potential to bind to metals, no evidence for this is seen in these particular systems. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Complexes; Palladium; Sulfimides; Nitriles

1. Introduction

Our recent reports on the reactivity of *S*,*S*-diphenylsulfimide, Ph_2SNH (**1**), towards a number of metal centres have revealed an unexpectedly rich chemical diversity. Thus we have seen unique product isomerism (with the first examples of square-planar/pseudo-tetrahedral allogonism in a neutral Cu(II) complex [1]), unexpected hydrogen-bonding features (e.g. between cation and anion in $[Co(Ph_2SNH)_6]Cl_2$ [2]) and metal-mediated nitrile activation (with **1** adding to platinum-bound acetonitrile [3]). All such observations serve to confirm the obvious potential of sulfimides as a versatile class of ligand whose chemistry has been essentially ignored until now. This potential is further enhanced by the close structural and electronic relationship they share with sulfoxides. The R_2SNR' unit of the sulfimides is isoelectronic with the R_2SO of the sulfoxides suggesting that the versatile coordination chemistry of the latter [4] should be amenable to the former. The potential of the sulfimides goes further than this, however, thanks to the fact that unlike the sulfoxides they can be derivatised on the nitrogen atom. The contrast of the R_2SNR' unit with that of R_2SO allows the introduction of R' groups with a range of properties. They could, for example, provide steric control over the resulting complex by placing bulky units close to the nitrogen. They could also be chosen to provide an extra coordination site for the ligand by the introduction of an appropriate end group.

The starting point for the development of the latter idea is clearly an assessment of the general coordination chemistry of substituted derivatives of **1**. In this study we have, therefore, chosen to contrast the affinity of **1** towards simple palladium centres with that of $Ph_2SNCH_2CH_2CN$ (**2**), a derivative chosen for its ease of preparation from **1** and for the fact that it possesses potentially coordinating cyano end groups.

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* Corresponding author.
E-mail address: p.f.kelly@lboro.ac.uk (P.F. Kelly).

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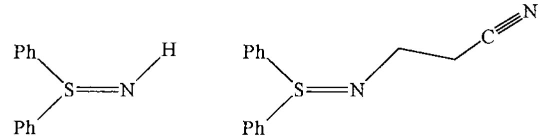
2. Results and discussion

The reaction of an excess of **1** with $[PPh_4]_2[Pd_2Br_6]$ mirrors that with $[PPh_4]_2[PtCl_4]$ [5] insofar as the homoleptic cation $[Pd(Ph_2SNH)_4]^{2+}$ results (Fig. 1). Thus stirring a mixture of the two in CH_2Cl_2 overnight results in gradual deposition of the bright yellow–orange crystalline product. It can be characterised by its distinctive IR spectrum. The latter is very similar to that of its platinum and copper analogues, both of which have had their structure confirmed by X-ray crystallography (though as chloride salts in both cases). Thus a very strong, broad N–H stretch is seen at 3114 cm^{-1} (compared to 3081, 3126 and 3056 cm^{-1} for $[Cu(Ph_2SNH)_4]Cl_2$, $[Cu(Ph_2SNH)_4]Br_2$ and $[Pt(Ph_2SNH)_4]Cl_2$, respectively). The strength and width of this band is distinctive to ionic complexes of **1** (thanks to the strong degree of H-bonding between cation and anion); the S–N stretch in this case (955 cm^{-1}) is also in a similar position to the aforementioned species (940, 936 and 934 cm^{-1}, respectively). When allied to the microanalysis results for this product there can be no doubt that $[Pd(Ph_2SNH)_4]Br_2$ has formed. Thus **1** appears capable of complete substitution of all of the bromides in $[Pd_2Br_6]^{2-}$.



1 **2**

Fig. 1. The structures of **1** and **2**.

Table 1
Selected bond distances (Å) and angles (°) in complex **3**

Bond distances			
Pd–N(1)	2.038(4)	Pd–Br(1)	2.4479(6)
N(1)–S(1)	1.604(5)	C(3)–N(3)	1.159(10)
Bond angles			
N(1)–Pd–Br(1)	92.20(11)	N(1)–Pd–Br(1A)	87.80(11)
Pd–N(1)–S(1)	110.3(2)	C(10)–S(1)–C(4)	101.8(3)

Table 2
Selected bond distances (Å) and angles (°) in complex **4**

Bond distances			
Pd–Br(1)	2.425)(1)	Pd–Br(2)	2.423(2)
Pd–Br(3)	2.430(1)	Pd–N(1) 2.026(7)	
N(1)–S(1)	1.581(7)	C(3)–N(3)	1.10(1)
Bond angles			
Br(1)–Pd–N(1)	88.1(2)	Br(3)–Pd–N(1)	88.8(2)
Pd–N(1)–S(1)	117.4(4)	C(4)–S(1)–C(10)	101.8(5)

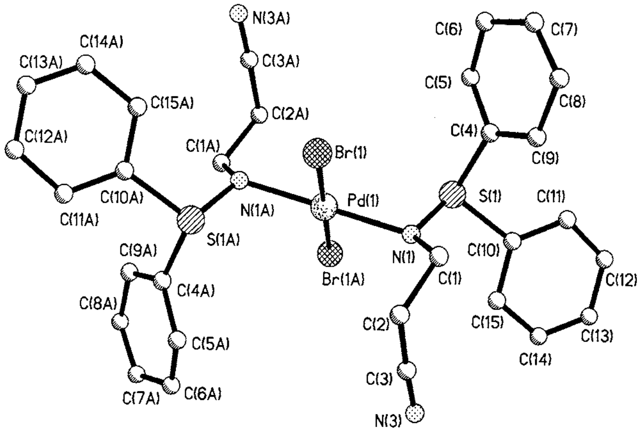


Fig. 2. The molecular structure of **3**.

If we move on to the propionitrile derivative of **1**, $Ph_2SNCH_2CH_2CN$ (**2**), we find a subtle difference in its reactivity towards $[Pd_2Br_6]^{2-}$. In this case reaction of an excess of **2** proceeds quickly but with no production of insoluble material even after stirring for a number of days. Crystallisation of such mixtures only results in the isolation of the orange coloured disubstituted species $[PdBr_2(Ph_2SNCH_2CH_2CN)_2]$ (**3**). X-ray crystallography confirms that, as in complexes of **1**, both the sulfimide ligands are N-bound; it also indicates a *trans* geometry (Fig. 2). The ligands arrange themselves with the CH_2CH_2CN units pointing away from, and on opposite faces of, the $PdBr_2N_2$ coordination plane. Although such an arrangement would leave the cyano groups capable of interactions with neighbouring molecules there are no significant close approaches to be seen. Within the ligand the two most pertinent features for contrast with previously characterised complexes of the free sulfimide **1** are the S–N bond length and the angle at the nitrogen (Table 1). In this case these values are 1.60 Å and 110.3°; although the former compares well to values note for **1** as ligand, the angle is some 12° less than in any complex of **1**. This clearly reflects the extra steric effect of the CH_2 unit bound to the N compared to a simple proton.

Thus **2** appears to be unable to substitute all of the bromide ions in $[Pd_2Br_6]^{2-}$, providing an obvious contrast with **1**. If the molar ratio of the reaction is lowered a salt of the monosubstituted species $[PdBr_3(Ph_2SNCH_2CH_2CN)]^-$ (**4**) may be isolated. Interestingly it appears to be easier to isolate the latter in good yield than it is to generate the corresponding free sulfimide analogue, $[PPh_4][PdBr_3(Ph_2SNH)]$. In the latter case it is likely that the product is contaminated with significant amounts of more highly substituted products; **4** though may be readily isolated and crystallised (Table 2). X-ray crystallography (Fig. 3) confirms the presence of the single sulfimide unit. Within this the S–N bond length is marginally shorter than in **3** (1.58 Å); in contrast the angle at the N is significantly wider at 117.4°, though still far less than in any complex of **1** we have thus far seen.

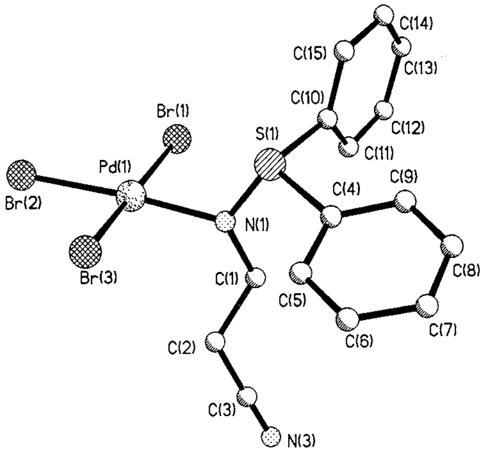


Fig. 3. The molecular structure of the anion in **4**.

Table 3
X-ray data for **3** and **4**

Compound	3	4
Colour, habit	Orange block	Yellow plate
Size (mm)	$0.19 \times 0.11 \times 0.1$	$0.1 \times 0.30 \times 0.30$
Formula	$C_{30}H_{28}Br_2PdN_4S_2 \cdot 0.5\ C_4H_{10}O$	$C_{39}H_{34}Br_3PdN_2S$
M	811.96	939.86
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions		
a (Å)	10.4735(2)	12.860(5)
b (Å)	11.7597(2)	13.33(1)
c (Å)	14.8369(1)	11.883(6)
α (°)	87.391(1)	109.10(6)
β (°)	80.995(1)	98.79(4)
γ (°)	81.437(1)	89.92(6)
V (Å^3)	1784.29(5)	1899(2)
Z	2	2
Difractometer	Bruker SMART	Rigaku AFC7S
λ (Å)	0.71073	0.71073
Collected	10251	7010
Used	5104 [R_{int} 0.0229]	6686 [R_{int} 0.049]
μ (Mo–K$_\alpha$) (mm^{-1})	2.904	3.73
Refined against	F^2	F
R_1	0.0651; wR_2 0.1661 [$I>2\sigma(I)$]	0.030; wR_2 0.038 [$I>3\sigma(I)$]

A key observation in the above reaction comes when less than the correct molar ratio of **2** is used in the reaction. Crystallisation of the products yields **4** together with unreacted $[PPh_4]_2[Pd_2Br_6]$; in other words there is no evidence that the cyano end groups within **4** can themselves coordinate to Pd (note that the starting dimer is susceptible to attack by nitriles and thus reacts with MeCN as solvent, for example). This of course does not absolutely rule out coordination through the cyano groups in the right circumstances, but it does suggest that the latter's nitrogen is a far poorer donor than the sulfimide nitrogen.

To conclude, we have demonstrated that N-substituted sulfimides can coordinate to metals in a similar manner to the free sulfimide **1** (before this study no fully characterised examples of such complexes have been reported [6]). Although **2** is a less powerful ligand than **1** insofar as it cannot (under these mild conditions at least) fully substitute the bromides within $[Pd_2Br_6]^{2-}$, one or two ligands can be added to the palladium in good yield. This result paves the way for the formation of complexes of sulfimides with a range of substituents and suggests that they also have the potential to act as bridging ligands (though in the case of **2** the cyano end groups are not strongly coordinating). Analogy with sulfoxide coordination chemistry suggests there is much worthwhile work to be done in this area.

3. Experimental

$[PPh_4]_2[Pd_2Br_6]$ was prepared as noted previously from $PdCl_2$ [7]; **1** was prepared by our recently reported modification of the literature method (the latter, and indeed other published methods, proving to be unreliable in our hands) [8]. Compound **2** was generated by the reaction of acrylonitrile with **1** using a slight (but, in our experience, important) amendment to the literature method [9] whereby the crude product was extracted into cold Et_2O to separate it from unreacted **1**; removal of the solvent yielded **2** as a pure oil (^{1}H-NMR).

3.1. *trans-[PdBr$_2$(Ph$_2$SNCH$_2$CH$_2$CN)$_2$] (**3**)*

A solution of $[PPh_4]_2[Pd_2Br_6]$ (0.19 g, 0.11 mmol) in CH_2Cl_2 (20 ml) was treated with a solution of **2** (0.25 g, 1 mmol) in the same solvent (10 ml) and the resulting mixture stirred. There was an almost instantaneous lightening of the colour to a bright orange; after stirring for 1 day the volume of the solution was reduced to 3 ml and ether layered upon it. Slow diffusion of the ether yielded a mixture of orange crystals and a dark red oil. This oil–crystal mixture was separated and quickly washed with cold acetone (3 × 3 ml) in order to remove most of the oil. The solid was then redissolved in CH_2Cl_2 and recrystallised by ether diffusion to yield a crop of well-formed orange crystals.

Yield 60 mg (35%); IR 2248 (mw) [ν C–N], 924 cm^{-1} (m) [ν S–N]; ^{1}H-NMR ($CDCl_3$) Phenyl multiplets plus δ 3.12 (t, 8Hz, CH_2), δ 2.69 ppm (t, 8Hz, CH_2). Anal. Found: C, 46.9; H, 4.2; N, 6.6; Calc. for $C_{30}H_{28}Br_2PdN_4S_2 \cdot 0.5\ C_4H_{10}O$ (i.e. half a molecule of ether solvate per molecule — see Table 3): C, 47.3; H, 4.1; N, 6.6%.

3.2. *[PPh$_4$][PdBr$_3$(Ph$_2$SNCH$_2$CH$_2$CN)] (**4**)*

A solution of $[PPh_4]_2[Pd_2Br_6]$ (0.19 g,0.14 mmol) in CH_2Cl_2 (20 ml) was treated with a solution of **2** (73 mg, 0.29 mmol) in the same solvent (10 ml) added dropwise over the course of a minute with stirring. After stirring for a further 1 h the volume of the solvent was reduced to 2 ml in vacuo and the product precipitated with Et_2O (50 ml); a dark maroon coloured micro-crystalline product was obtained by recrystallisation from CH_2Cl_2–toluene while X-ray quality crystals were grown by slow diffusion of ether into a CH_2Cl_2 solution.

Yield of recrystallised material 120 mg (46%). IR 2224 (mw) [ν C–N], 913 cm^{-1} (m) [ν S–N]. ^1H-NMR ($CDCl_3$) Phenyl multiplets plus δ 3.10 (t, 8Hz, CH_2), δ 2.86 ppm (t, 8Hz, CH_2). Anal. Found: C, 49.0; H, 3.4; N, 2.4; Calc. for $C_{39}H_{34}Br_3PdN_2S$: C, 49.8; H, 3.6; N, 3.0%.

3.3. $[Pd(Ph_2SNH)_4]Br_2$

A solution of $[PPh_4]_2[Pd_2Br_6]$ (78 mg, 0.06 mmol) in CH_2Cl_2 (20 ml) was treated with solid **1** (0.1 g, 0.5 mmol) and the mixture stirred. After all the solid had dissolved the colour of the mixture lightened to yellow–orange; it was allowed to stand overnight during which time an orange crystalline material was deposited. This was filtered, washed with CH_2Cl_2 and dried in vacuo.

Yield 72 mg (61%). IR 3114 (s, br) [ν N–H], 955 cm^{-1} (s) [ν S–N]. Anal. Found: C, 53.9; H, 4.0; N, 5.0; Calc. for $C_{48}H_{44}Br_2PdN_4S_4$: C, 53.8; H, 4.1; N, 5.2%.

3.4. X-ray crystal structure of **3**

Crystals of **3** were grown by slow diffusion of ether into a dichloromethane solution. Data were collected (using a Bruker SMART diffractometer with graphite monochromated Mo–K_α radiation) using small slices: 10 251 data collected, 5104 data used ($R_{int} = 0.0229$). Data were corrected for Lorentz and polarisation effects and an empirical absorption correction was applied resulting in transmission factors ranging from 0.496 to 0.693. The structures were solved (with one unit of Et_2O of crystallisation for every pair of molecules of **3**) by direct methods and refined by full-matrix least-squares against F^2 leading to $R_1 = 0.0651$, $wR_2 = 0.1661$ with $I > 2\sigma(I)$. The maximum/minimum residual electron densities in the final ΔF map were 1.365 and -1.034 e $Å^{-3}$; calculations were performed using SHELXTL [10].

3.5. X-ray crystal structure of **4**

Crystals of **4** were grown by slow diffusion of ether into a dichloromethane solution. Data were collected (using a Rigaku AFC7S diffractometer with graphite monochromated Mo–K_α radiation) by the ω–2θ scan technique to a maximum 2θ value of 50.1°. Of 7010 measured reflections 6686 were unique. Data were corrected for Lorentz and polarisation effects and an empirical absorption correction was applied resulting in transmission factors ranging from 0.601 to 1.00. Non-hydrogen atoms were refined anisotropically; hydrogen atoms were included but not refined. The structure was solved by direct methods and refined by full-matrix least-squares against F leading to $R = 0.030$ [$R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$], $R_w = 0.038$. The maximum/minimum residual electron densities in the final ΔF map were 0.38 and -0.35 e $Å^{-3}$; calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Corporation [11].

4. Supplementary material

Supplementary data have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 146754 (**3**) and CCDC no. 146755 (**4**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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