Further Investigation into the Platinum-Activated Addition of Diphenylsulfimide to Acetonitrile; the X-ray Crystal Structure of $[PPh_4][PtCl_2(Ph_2SNC(Me)NH)]_2Cl$

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Reaction of Ph_2SNH (**1**) with $[PtCl_2(MeCN)_2]$ (1:1 ratio) in MeCN at 50 °C results in the formation of $[PtCl_2\{Ph_2SNC(Me)NH\}]$ (**3**); without heating $[Pt(Ph_2SNH)\{Ph_2SNC(Me)NH\}Cl]Cl$ (**2**) is the primary product. Attempts to grow X-ray quality crystals of **3** have not succeeded; it does, however, form a crystalline 2:1 adduct with $[PPh_4]Cl$ (**3a**), the structure of which confirms the presence of the bidentate $Ph_2SNC(Me)NH$ ligand hydrogen-bonded to the chloride anion. Reaction of **3** with three equivalents of **1** and two of $Tl[PF_6]$ results in the formation of $[Pt(Ph_2SNH)_2\{Ph_2SNC(Me)NH\}_2][PF_6]_2$ (**4**), the first example of a complex containing the $[Ph_2SNC(Me)N(H)]$ unit acting as a monodentate ligand, bound through the nitrogen atom.

Introduction

As part of our continuing interest in the coordination chemistry of sulfur−nitrogen species[1] we have recently reported on the reactivity of *S*,*S*′-diphenylsulfimide, Ph_2SNH (**1**), towards a number of metal centres, including copper (resulting in *trans*-$[CuCl_2(Ph_2SNH_2)]$ which, uniquely for a neutral Cu^{II} species exhibits square-planar and pseudo-tetrahedral allogons),[2] cobalt,[3] and platinum.[4] During investigations into reactions involving the latter metal we discovered that the reaction of two equivalents of **1** with $PtCl_2(MeCN)_2$ resulted in the formation of $[Pt(Ph_2SNH)\{Ph_2SNC(Me)NH\}Cl]Cl$ (**2**) rather than the expected simple substitution product. In effect one of the incoming sulfimide units had added to a metal-bound acetonitrile − an addition that does not take place in the absence of the metal centre (or indeed in the presence of a metal other than platinum, at least amongst those we have investigated so far). The resulting nitrile/sulfimide ligand binds in a bidentate fashion through a nitrogen and a sulfur atom; indeed, one of the most interesting aspects of this reaction was the fact that **2** constitutes the first example of a sulfimide unit binding to a metal centre through a sulfur atom. Here we present the results of further investigations into this reaction.

Results and Discussion

Upon first isolating **2** from the 2:1 reaction of **1** with $PtCl_2(MeCN)_2$ we made preliminary, tentative assumptions about the reaction mechanism. Given that nucleophilic attack upon coordinated nitriles is well known[5] we anticipated that this would be the first stage, with the resulting *N*-bound monodenate ligand then chelating by removal of the other nitrile (and S−Pt bond formation). Then the second sulfimide would displace a chloride to give the final product. In order to go some way to confirming this suggestion we have now analysed the analogous equimolar reaction, which should, on the basis of the latter mechanism, generate $[PtCl_2\{Ph_2SNC(Me)NH\}]$ (**3**). The latter does indeed form, though not in as straightforward a manner as we had anticipated. Within a short time of complete addition of the reagents a crystalline material starts to form; rather than being **3**, however, IR spectroscopy indicates that this material is in fact **2**. If, however, the crude mixture at this stage is heated to ca. 50 °C for two hours any solids present redissolve and the colour of the solution gradually changes from pale yellow to a bright lemon colour. After precipitation of a small amount of impurity with Et_2O, the main reaction product can be retrieved by evaporation of the solvent and trituration of the oily residue with cold ether. Although, unfortunately, we have yet to grow crystals suitable for single crystal diffraction, the resulting bright yellow material may be formulated as **3** by a combination of IR, NMR, and microanalysis.

Further confirmation of its nature comes when crystallisation is attempted in the presence of $[PPh_4]Cl$. We initially performed this in the hope that the chloride would break the Pt−S bond thus giving a monodentate $[Ph_2SNC(Me)NH]$ ligand. In fact this does not happen (though, as we will see, we can achieve this in other ways); rather, the chloride binds through hydrogen bonds to two units of **3** to give the adduct **3a** (Figure 1).

Within the Pt−S−N−C−N metallacycle of **3a** there appears to be minimal difference in geometry between the two independent units and indeed between them and the previously reported values for **2**. While the planes of the two metallacycles are inclined at an angle of 53° to each other,

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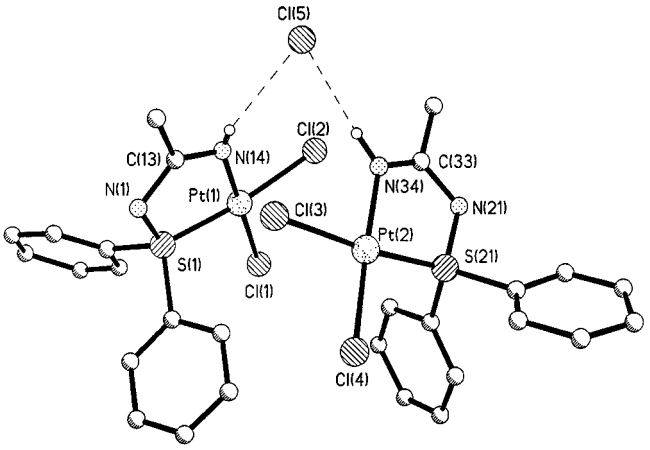
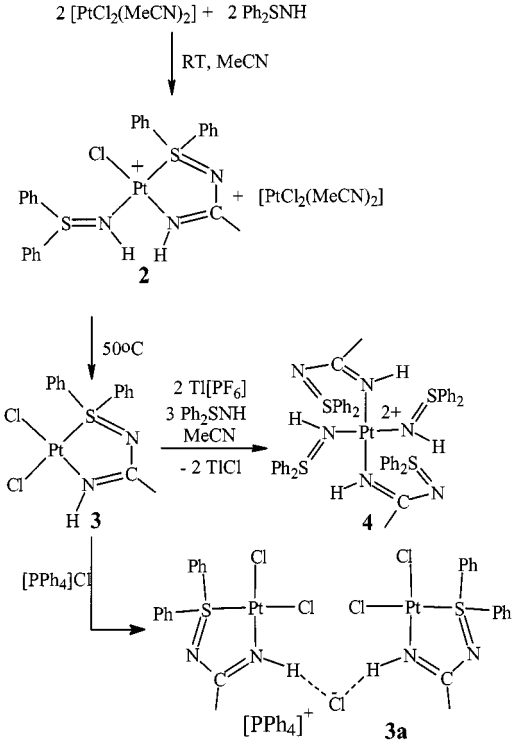


Figure 1. The X-ray crystal structure of **3a** (omitting the $[PPh_4]^+$ cation)

the average H···Cl interaction distance is 2.33 Å, and the average N−H−Cl angle 160°. The resulting structure is interesting for a number of reasons. Firstly it confirms the tendency of the N−H bonds of coordinated sulfimide units to get involved in significant hydrogen bonding interactions. In the case of previously noted examples, the formation of such bonds was undoubtedly aided by the fact that they were part of cation−anion interactions;[3,6] here this is obviously not the case, though the significant interactions are present nonetheless.

In addition, of course, it confirms the basic structure of **3**; further confirmation, and of the original mechanism we put forward, comes when **3** is treated with **1**. Within a few minutes of addition in MeCN crystals of **2** (confirmed by IR) begin to form. We can thus be confident that the kind of mechanism shown in Scheme 1 applies to the system as a whole. As **1** is slowly added to the system during the 1:1 reaction **3** starts to form; once formed it then acts as a competitor to the $PtCl_2(MeCN)_2$. Unreacted **1** can thus either undergo nitrile addition to give more **3** or substitution on the **3** that has been formed in order to give **2**. The latter appears to be preferred, meaning that by the end of addition of **1** the mixture consists of **2** and, presumably, unchanged $PtCl_2(MeCN)_2$. This mixture can, however, be driven through to **3** by heating, suggesting that the unchanged sulfimide ligand in **2** is actually quite labile.



Scheme 1. Summary of the reactions to form **2**, **3**, **3a**, and **4**

An important feature of **3** is its obvious potential as a reagent with which to probe the properties of the bidentate ligand − in particular its lability. A significant result in this area is obtained when **3** (formed in situ) is treated with $Tl[PF_6]$ and three equivalents of **1**. The thallium salt displaces chloride from **3** with, presumably, MeCN taking up the vacant site. This intermediate then reacts with three equivalents of **1** to produce a new species, **4**, which may be isolated in crude form by centrifugation of the mixture (in order to separate the bulk of the finely divided TlCl generated in the reaction) followed by filtration and removal of the solvent. Trituration of the oily product with Et_2O yields an off-white solid from which crystalline material may be grown by slow diffusion of Et_2O into a solution in MeCN.

We can formulate **4** as $[Pt(Ph_2SNH)_2\{Ph_2SNC(Me)NH\}_2][PF_6]_2$ by a combination of microanalysis, IR, NMR. X-ray crystallography also backs this up, though we do not formally present the results here as the structure suffers from poor quality [unit cell: triclinic, space group $P\bar{1}$; a = 10.4943(2), b = 11.0252(3), c = 14.1772(4) Å; α = 107.45(1), β = 100.295(1), γ = 110.441(1)°]. Its does, however, confirm that the Pt centre now exhibits two unchanged sulfimide ligands and two sulfimide/nitrile addition ligands both bound in monodentate fashion as shown in Scheme 1. As for the mechanism of formation of **4**, we can reasonably assume that the initial reaction of $Tl[PF_6]$ with **3** replaces at least one of the halides with MeCN which can then react with **1**, possibly giving $[Pt(Ph_2SNC(Me)NH)_2]$ as an intermediate. Additional molecules of **1** then substitute into this by breaking Pt−S bonds.

In conclusion, the isolation of **3** in good yield will allow us to probe the substitution properties of this new class of chelating ligand. The isolation of **4** is important insofar as it indicates that the new ligands formed in the platinum-assisted sulfimide/nitrile reactions are not constrained to chelation and thus may ultimately prove to be labile. The displacement and isolation of such addition products as free species would provide us with interesting new (and undoubtedly reactive) systems that cannot be generated by direct sulfimide/nitrile reactions. It would also raise the intriguing possibility of adjusting the reaction system to allow the platinum to act catalytically. Work towards this end is currently underway.

Experimental Section

All reactions were carried out under dry nitrogen; MeCN was dried and distilled from calcium hydride, diethyl ether from sodium. −

IR spectra were run with a Perkin−Elmer PE2000 spectrometer; NMR with a Bruker AC250 spectrometer; microanalysis was performed by Loughborough's Departmental service. − Ph_2SNH (**1**) was prepared by our previously reported variation upon the literature route.[6]

3: A solution of $[PtCl_2(MeCN)_2]$ (61 mg, 0.18 mmol) in MeCN (10 mL) was treated with a solution of **1** (36 mg, 0.18 mmol) in the same solvent (10 mL) added over a period of 1 min, with stirring. The resulting mixture was then heated to 50 °C and stirred at this temperature for 2 h during which time the solution colour changed from pale yellow to a bright lemon. At this point the volume of the solvent was reduced to ca. 5 mL in vacuo and Et_2O (50 mL) added with stirring. This resulted in the formation of a small amount of a flocculant white precipitate which was filtered off and the solution reduced to dryness in vacuo then triturated with Et_2O to give a bright yellow product. Yield 60 mg, 67%. − IR (key bands, i.e. non-phenyl): $\tilde{\nu}$ = 3296 cm^{-1} (ms, νN−H), 1529 (s, νC−N), 808 (m, νN−S), 356 (mw, νPt−Cl), 331 (m, νPt−Cl). − ^1H NMR ($CDCl_3$): δ = 8.13 (m, 4 H, phenyl), 7.65 (m, 6 H, phenyl), 2.43 (s, 3 H, CH_3). − $C_{14}H_{14}Cl_2N_2PtS$ (508.3): calcd. C 33.1, H 2.8, N 5.5; found C 32.9, H 2.8, N 5.7. − Crystallisation by slow diffusion of Et_2O into a CH_2Cl_2 solution to which $[PPh_4]Cl$ had been added resulted in well-formed yellow crystals of the adduct $[PPh_4][PtCl_2(Ph_2SNC(Me)NH)]_2Cl$ (**3a**).

4: A crude solution of **3** in MeCN was generated as above from $[PtCl_2(MeCN)_2]$ (43 mg, 0.12 mmol) and **1** (25 mg, 0.12 mmol) (with heating for2 h followed by cooling to room temperature) and treated with $Tl[PF_6]$ (86 mg, 0.25 mmol). This resulted in the immediate production of a finely divided white solid within a pale brown/red solution; the mixture thus formed was stirred for 1 min then solid **1** (73 mg, 0.36 mmol) added. After stirring for 1 h at 60 °C, the mixture was cooled to room temperature and stirred overnight. At this stage it was centrifuged to separate out the bulk of the very finely divided solid present and then filtered through Celite, the solvent volume reduced to a few mL and Et_2O (50 mL) added with stirring. The resulting brown/orange oil was triturated with Et_2O to give the crude product as an off-white solid. Yield 116 mg. Microanalysis reveals this material to be contaminated with variable amounts of a CHN-free impurity, presumably TlCl, which proves surprisingly difficult to remove; the IR spectrum is, however, identical to that of pure crystalline material generated by slow diffusion of Et_2O into an MeCN solution. Yield of the crystalline material is typically half that of the crude material; however, we believe that the bulk of this shortfall reflects decomposition in solution over the time taken for crystallisation (the solution darkens appreciably over a period of days, even in an inert atmosphere) rather than there being a high impurity level in the crude material. − IR (key bands, i.e. non-phenyl): 3366 cm^{-1} (ms), 3320 (m) (both ν N−H), 1542 (s,ν C−N), 918 (m, ν N−S), 842 (vs, br., ν P−F). − ^1H NMR (CD_3CN): δ = 7.74 (m, 2 H, phenyl), 7.62 (m, 4 H, phenyl), 7.36 (m, 14 H, phenyl), 2.41 (s, 3 H, CH_3). − $C_{52}H_{50}F_{12}N_6P_2PtS_4$ (1372.3): C 45.5, H 3.7, N 6.1; found C 45.3, H 3.9, N 6.2.

Crystal Data for 3a: $C_{52}H_{48}Cl_5N_4PPt_2S_2$, M = 1391; triclinic, space group $P\bar{1}$; a = 11.96(1), b = 22.83(1), c = 10.703(6) Å, α = 92.00(5), β = 111.51(6) γ = 77.48(6)°; V = 2651(3) $Å^3$, Z = 2, calculated density: 1.743 gcm^{-3}. Yellow prism, dimensions 0.3 × 0.1 × 0.08 mm, μ (Mo-K_α) = 56.50 cm^{-1}, λ = 0.71069 Å, F(000) = 1352. − 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 50.0°. Of 9820 measured reflections 9333 were unique. An empirical absorption correction was applied resulting in transmission factors ranging from 0.66 to 1.00. − Structure analysis and refinement: The structure was solved by direct methods and refined by full-matrix least squares against F. Non-hydrogen atoms were refined anisotropically; hydrogen atoms were included but not refined. Refinement against F led to R = 0.042 [$R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$], Rw = 0.045. The maximum/minimum residual electron densities in the final ΔF map were 1.33 and −1.96 $e^-/Å^3$; calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation.[7] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-143676. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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