Formation of the bidentate [$Ph_2SNC(Me)N(H)$] ligand by metal-assisted sulfimide addition to acetonitrile; X-ray crystal structure of [$Pt(Ph_2SNH)(Ph_2SNC(Me)NH)Cl$]$Cl\cdot MeCN$

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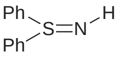
In contrast to similar reactions of Cu, Co and Pd species, the platinum(II) complex [$Pt(MeCN)_2Cl_2$] reacts with Ph_2SNH (ratio 1 : 2) in MeCN *via* a metal assisted addition of the sulfimide to the acetonitrile to give [$Pt(Ph_2SNH)(Ph_2SNC(Me)NH)Cl$]$Cl\cdot MeCN$, the first example of a complex of the bidentate [$Ph_2SNC(Me)N(H)$] ligand.

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. For example, during investigations into its reactivity towards $CuCl_2$ we showed that the N-bound 2 : 1 complex, *trans*-[$CuCl_2(Ph_2SNH)_2$], forms readily *via* reaction in MeCN. Though such a product was not unexpected, it proved to be unusual in its ability to crystallise in either square-planar or pseudo-tetrahedral geometries.[2] Such isomerism appears to be unique for a neutral Cu(II) species, indicating that the ligand properties of **1** are not as simple as one might imagine. This conclusion is backed up by the observation that [$Co(Ph_2SNH_2)_6$]Cl_2 exhibits strong, concerted, directed hydrogen bonding between both sets of triple N–H units on either side of the coordination octahedron and the chloride counter ions.[3] These results, backed up by the obvious potential of the sulfimides in general as functionalised ligands, prompted us to investigate the coordination chemistry of **1** further by addressing its ability to coordinate to Pt and Pd centers.



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Many aspects of the latter chemistry prove to be quite straightforward;[4] thus salts of [Pd_2X_6]$^{2-}$ (X = Cl or Br) form [$PdX_3(Ph_2SNH)$]$^-$ or [$Pd(Ph_2SNH)_4$]X_2 depending upon reaction stoichiometry while 4 equivalents of **1** react slowly with [PPh_4]$_2$[$PtCl_4$] in CH_2Cl_2 to give [$Pt(Ph_2SNH)_4$]Cl_2. There is no evidence from either X-ray crystallographic or IR spectroscopic studies that such products contain **1** as anything other than simple N-bound ligands. During such work, however, we noted that the product of the reaction of **1** with [$Pt(MeCN)_2Cl_2$] (ratio 2 : 1) in acetonitrile† generated crystalline material the IR spectrum of which was unusual in that it exhibited a very strong, broad N–H peak at 3071 cm^{-1} (of the type we have more usually seen associated with cationic sulfimide complexes) and extra bands not normally associated with the Ph_2SNH ligand (at 1540, 1249 and 807 cm^{-1}). As such data were not consistent with the simple formulation [$Pt(Ph_2SNH)_2Cl_2$] we investigated the complex by X-ray crystallography.‡

The structure obtained for **2** (which includes an acetonitrile of solvation) is shown in Fig. 1. Although two of the four coordination sites on the platinum contain expected ligands (N-bound **1** and a chloride) the other two sites are taken up by the nitrogen and sulfur atoms of a chelating [$Ph_2SNC(Me)N(H)$] ligand. Close inspection of the latter and the overall metallocycle of which it is part reveals a number of important points about the reaction and its product. First of all it is clear that during the course of the reaction one of the sulfimide units has added to an acetonitrile and completed the metallocycle by binding to the platinum through a sulfur. Within this metallocycle the S–N distance appears to be virtually identical to that in the unreacted, coordinated sulfimide ligand (1.625 *cf.* 1.618 Å) indicating that this may be best represented as a double bond. Of the two C–N bonds one, N(14)–C(13), is significantly shorter than the other (1.302 *cf.* 1.358 Å) indicating a higher bond order. Thus we can approximate the bonding within the neutral ligand to N(H)=C(Me)N=SPh_2 though as with most sulfimide systems this obviously constitutes something of an over simplification. Bond distances and angles within the coordinated unreacted sulfimide unit are not significantly different to those noted in other complexes of **1**. A point of note about the structure comes with the fact that there are significant H-bonding interactions between the two N–H bonds and the free chloride (average of the two H···Cl distances being 2.26 Å). It is possible that this is a contributory factor in the significant deviation of the N(2)–Pt–S(1) angle from linear (167.6°). In the light of this structure the unexpected IR spectrum may be explained; the strong N–H band comes about thanks to the hydrogen bonding in the system, while the other bands may be assigned to C–N stretches and deformations. The structure is also backed up by the ^{1}H and ^{13}C NMR data (the latter, for example, showing the CH_3–C carbons at δ 19.0 and 183.6 respectively). One final important feature of the structure comes from the fact that it constitutes the first example of a sulfimide unit binding through the sulfur atom as opposed to the nitrogen.

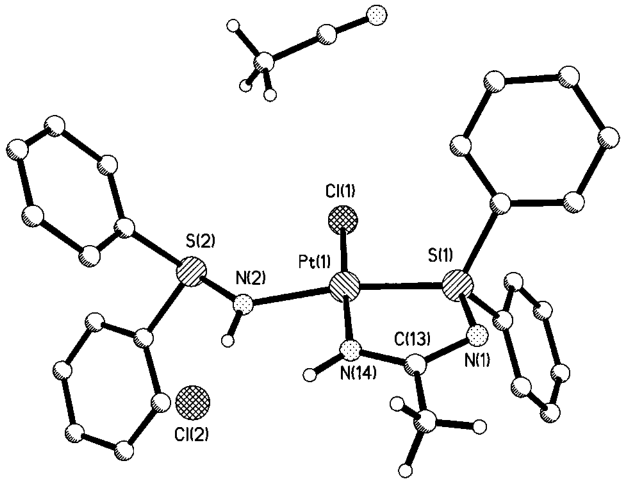

Fig. 1 X-Ray crystal structure of **2**·MeCN. Selected bond distances (Å) and angles (°): Pt–S(1) 2.1876(12), S(1)–N(1) 1.625(4), N(1)–C(13) 1.358(6), C(13)–N(14) 1.302(6), N(14)–Pt 1.989(4), Pt–Cl(1) 2.3191(14), Pt–N(2) 2.012(4), N(2)–S(2) 1.618(4); Pt–S(1)–N(1) 106.7(2), S(1)–N(1)–C(13) 110.8(3), C(13)–N(14)–Pt 119.1(3), N(2)–Pt–S(1) 167.56(14), N(2)–Pt–Cl(1) 94.36(14), Cl(1)–Pt–S(1) 97.84(5), N(2)–Pt–N(14) 87.8(2), Pt–N(2)–S(2) 127.5(3).

A number of aspects of this reaction are noteworthy. One important feature is that it can be repeated using $Pt(MeCN)_2Cl_2$ in CH_2Cl_2; in this case it is clear that coordinated MeCN ligands must be reacting as we no longer have the excess of the ligand in the form of the solvent. Additionally, it should be noted that **1** does not react with MeCN in the absence of the metal centre. Thus the solid retrieved after removal of the solvent from a solution of **1** in MeCN after stirring for 1 h at either ambient temperature, or indeed at reflux temperature, has an identical IR spectrum to the starting material. The choice of metal is also crucial; as we have already noted we have seen no evidence of this type of reaction occurring during reactions involving Co and Cu and attempts to observe analogous reactions using $Pd(MeCN)_2Cl_2$ or $[Pd(MeCN)_4][BF_4]_2$ also fail. Thus the reaction would appear to be specific to Pt, at least amongst the aforementioned metals. This brings us to the question of the reaction mechanism. It is possible that the first stage of the reaction involves coordination of one **1** ligand followed by reaction with the remaining coordinated MeCN. At present we regard this as a less likely option as it implies that coordination to the metal is activating the sulfimide towards attack by MeCN. If this were the case one might suspect that $[Pt(Ph_2SNH)_4]Cl_2$ (from **1** + $[PPh_4]_2[PtCl_4]$ in CH_2Cl_2) would be prone to reaction with this solvent; in fact it can be dissolved in boiling MeCN and, after precipitation by cooling, shows no change in its IR spectrum. In addition it should be remembered that **2** exhibits one unreacted sulfimide ligand. The other possible route involves nucleophilic addition of the sulfimide to the nitrilic carbon followed by proton transfer and coordination of the sulfur *via* loss of the remaining MeCN. This is conceptually a very simple route, the only drawback coming from the fact that it would require the sulfimide/acetonitrile addition to be faster or more efficient than simple substitution. Some justification for this comes with the observation that platinum appears to be less effective (or at least slower) at binding **1** than lighter metals. Thus while conversion of $[Pd_2X_6]^{2-}$ to $[Pd(Ph_2SNH)_4]X_2$ takes place in a matter of minutes, $[Pt(Ph_2SNH)_4]Cl_2$ only forms from $[PPh_4]_2[PtCl_4]$ over the course of many days. In addition, the $[Pt(PMe_2Ph)_2(Ph_2SNH)Cl]^+$ cation forms a solution equilibrium with $Pt(PMe_2Ph)_2Cl_2$ upon addition of Cl^-.[4] We thus favour the second of the two reaction mechanisms; this conclusion is backed up by the fact that nucleophilic addition to coordinated nitriles is well documented.[5] It should also be noted that preliminary work indicates that this reaction can be mirrored for other nitriles such as propionitrile and benzonitrile.

The metallocycle formed in this reaction is a very rare example of a transition metal based MNCNS cyclic system; indeed there would only appear to be one other example of such a unit characterised by X-ray crystallography, namely that found in $[Pt\{PhSNC(MeC_6H_4)NNC(MeC_6H_4)NSPh\}(PPh_3)]$,[6] though here it is a part of a tridentate ligand system (the X-ray structure of recently formed $[Pt\{N(H)C(Ph)N(H)S\}(dppe)]^+$ was not reported, though the species does indeed contain the cyclic PtNCNS unit[7]). In fact we can extend this further and say that with the exception of cases where X = S (the very well known and much studied dithiadiazolyls) the *only* other structure of the type *cyclo*-XNCNS to be found in a search of the Cambridge Structural Database[8] is one in which X = O.[9]

To conclude, we can say that the reaction of $Pt(MeCN)_2Cl_2$ with **1** provides an efficient, high yield route to a very rare structural system, *via* a metal-assisted activation unprecedented for a sulfimide. It is quite feasible that the neutral ligand thus formed will prove to be labile, providing an efficient route to new imine-substituted sulfimide systems; work towards this end is underway.

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Notes and references

† A solution of $[PtCl_2(MeCN)_2]$ (61 mg, 0.18 mmol) in MeCN (20 ml) was treated with a solution of **1** (71 mg, 0.35 mmol) in the same solvent (5 ml) added over a period of 2 min with stirring. Upon continuous stirring the resulting yellow solution suddenly precipitated a pale yellow solid (time required for precipitation to start varied from experiment to experiment, ranging from < 1 to 10 min; in all cases, however, once started precipitation was very rapid). The mixture was stirred for a further 30 min then allowed to settle whereupon the solvent was decanted, the solid washed with cold MeCN (10 ml) and then Et_2O (10 ml) and dried *in vacuo* to give a pale yellow product. Yield 92 mg, 74%.

Recrystallisation from hot MeCN gave 60 mg (48% based upon original amount of Pd used) of well formed crystalline material, though the solution retained a significant yellow colour even after cooling indicating that some reaction/decomposition had occurred during the heating process, hence the lowering of yield. There was no significant difference in the IR spectra of the crude and recrystallised material. X-Ray crystallography confirmed the formulation as $[Pt(Ph_2SNH)(Ph_2SNC(Me)NH)Cl]Cl$ with no solvated MeCN present, though this X-ray data is not presented in full here. Found: C, 42.6; H, 3.3; N, 5.9%. Calc. for $C_{26}H_{25}Cl_2N_3PtS_2$: C, 44.0; H, 3.6; N, 5.9%. ^1H NMR ($CDCl_3$) δ 10.4 (1H, s, NH), 7.99 (8H, m, CH), 7.63 (2H, m, CH), 7.59 (4H, m, CH), 7.50 (6H, m, CH), 2.50 (3H, s, CH_3); ^{13}C NMR ($CDCl_3$) δ 183.6 (NCN), 138.2, 135.7, 134.0, 132.1, 130.0, 129.9, 128.0 (phenyl groups), 19.0 (CH_3).

A similar reaction occurred when $PtCl_2$ was dissolved in hot MeCN (effectively forming the same starting material *in situ*) and then **1** added. In this case recrystallisation gave product with one MeCN of crystallisation {*i.e.* $[Pt(Ph_2SNH)(Ph_2SNC(Me)NH)Cl]Cl\cdot MeCN$} as shown by X-ray crystallography and microanalysis (Found: C, 44.5; H, 3.9; N, 7.6%; Calc. for $C_{28}H_{28}Cl_2N_4PtS_2$: C, 44.8; H, 3.8; N, 7.5%). It is not clear why the two recrystallisations gave solvated and unsolvated materials.

IR spectroscopy confirmed that an identical product is formed if the $Pt(MeCN)_2Cl_2$ reaction is performed in CH_2Cl_2.

‡ *Crystal data* for **2**: all measurements were made on a Siemens SMART diffractometer with graphite monochromated Mo-Kα radiation. Data were collected using small slices: 12830 data collected. $C_{28}H_{28}Cl_2N_4PtS_2$, M = 750.65, monoclinic, space group $P2_1/n$, a = 13.223(1), b = 10.941(1), c = 20.912(1) Å, β = 100.302(1)°, U = 2976.5(1) Å^3, Z = 4, T = 293 K. μ(Mo-Kα) = 5.11 mm^{-1}, λ = 0.71073 Å, $F(000)$ = 1472. R_1 = 0.0268, wR_2 = 0.0486 [$I > 2\sigma(I)$], 4267 independent reflections (4217 observed).

CCDC 182/1247. See http://www.rsc.org/suppdata/cc/1999/1081/ for crystallographic files in .cif format.

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