# Preparation of Metal–Sulphur–Nitrogen Complexes *via* Photochemical Activation of $S_4N_4$

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Reaction of *cis*-$[PtCl_2(PMe_2Ph)_2]$ with $S_4N_4$, which normally only occurs at temperatures in excess of 100 °C, can be achieved at 0 °C by the use of UV photolysis. Phosphorus-31 NMR studies upon reactions using $S_4N_4$–$S_4{}^{15}N_4$ show the products to contain totally scrambled $^{14}N/^{15}N$ suggesting that the reaction proceeds *via* a reactive sulphur–nitrogen species photochemically generated from $S_4N_4$. Photolysis of $S_4N_4$ alone gives a mixture of $S_8$, $S_4N_2$ and $S_7NH$.

We have recently reported on the preparation of $[Pt(S_2N_2H)Cl(PMe_2Ph)]$ **1** and $[Pt(S_3N)Cl(PMe_2Ph)]$ **2** by reaction of $S_4N_4$ with *cis*-$[PtCl_2(PMe_2Ph)_2]$ at ≈140 °C in xylene.[1] The reaction is inefficient when compared to the other synthetic routes we have developed for **1**[1] and **2**,[2] and is potentially dangerous due to the high temperatures involved, but has the advantage of allowing $^{15}N$-labelled samples to be prepared from $S_4{}^{15}N_4$. In addition, the reaction proved interesting since, by use of mixtures of $S_4N_4$ and $S_4{}^{15}N_4$, we were able to show that at the temperatures involved $S_4N_4$ undergoes rapid nitrogen exchange, presumably *via* an intermediate, short-lived species, which is responsible for the reactivity not observed at room temperature.

Here we report on investigations into the photolysis of $S_4N_4$, which ultimately yields mixtures of $S_8$, $S_4N_2$ and $S_7NH$. In addition we have studied the photochemically activated reaction of $S_4N_4$ with $[PtCl_2(PMe_2Ph)_2]$ **3** at ≤room temperature which rapidly leads to a number of products, including **1** and **2**. The product distribution appears to be identical to that in the high-temperature reaction, hence we deduce that there is great scope for the photolytic activation of $S_4N_4$ in reactions which otherwise require extreme conditions.

## Experimental

Syntheses and reactions of metal complexes were performed at Imperial College. Photolysis was performed using a quartz medium-pressure, 125 W mercury-discharge lamp (Applied Photophysics) with output in the range 265–579 nm, together with a Schlenk-type reaction vessel which allowed the reaction to be performed under an inert atmosphere (Ar). Dichloromethane was dried by and distilled from calcium hydride. Phosphorus-31 NMR spectra were recorded using a JEOL FX90Q spectrometer operating at 36.21 MHz and are referred to 85% $H_3PO_4$. The compound $S_4{}^{15}N_4$ was prepared by reduction of $[S_4{}^{15}N_3]Cl$[3] with KI in MeCN.

A mixture of $S_4N_4$ (40 mg, 0.2 mmol) and *cis*-$[PtCl_2(PMe_2Ph)_2]$ (120 mg, 0.2 mmol) in $CH_2Cl_2$ (100 $cm^3$) was cooled in a salt–ice bath and, with vigorous stirring, photolysed for ≈1 h, during which time the colour of the solution changed from yellow to dark red-brown and some dark solid precipitated. After filtration the volume of the solution was reduced to 10 $cm^3$ *in vacuo* (*without external heating*) and placed on a Bio-Beads gel-permeation column. Elution with $CH_2Cl_2$ resulted in the separation of a red band behind two poorly resolved green and brown bands, together with some unreacted $S_4N_4$ (note: the pattern of bands was identical to that obtained in the previous high-temperature reactions[1]). The red band was collected and the $CH_2Cl_2$ removed *in vacuo*. The $^{31}P$ NMR spectrum of the product revealed the presence of compounds **1** [δ −21.2, $^1J(^{195}Pt–^{31}P)$ 3418 Hz] and **2** (δ −11.8, $^1J$ 3074 Hz) in the ratio 2:1. The presence of the two complexes was also confirmed by their distinctive TLC characteristics: **1**, yellow with $R_f \approx 0.4$; **2**, purple, $R_f \approx 0.8$ in $CH_2Cl_2$. Total yield of the mixture of **1** and **2** 25 mg. No attempt was made to separate the individual components. Reactions involving mixtures of $S_4N_4$ and $S_4{}^{15}N_4$ were performed in an identical manner.

Investigations into the photolysis of $S_4N_4$ alone were performed at the University of Vermont. Cyclohexane was distilled over $LiAlH_4$ through a vacuum stopcock into a quartz reactor tube containing $S_4N_4$, in sufficient amounts to give a saturated solution. The stopcock was closed, the reaction tube rigorously degassed (freeze–thaw method) and photolysed in a Rayonet reactor (253.7 nm) for 24 h after which time a bright red solution and a flocculent precipitate were observed. TLC showed three major bands and two minor ones. Partial separation was achieved using column chromatography (silica, cyclohexane); the first component (and the precipitate) was identified as $S_8$, the second (a red band) as $S_4N_2$ by mass spectrometry whilst the last fraction was shown by IR spectroscopy to contain $S_7NH$.

## Results and Discussion

The rich electronic spectrum of $S_4N_4$ contains at least four transitions covering a broad range of energies. There is evidence that some of these transitions involve the weak sulphur–sulphur bond which closes the $S_4N_4$ cage. If this is so then it would be reasonable to expect $S_4N_4$ to exhibit photochemical activity, possibly through cage activation. Although recent work has developed synthetic routes to metal–sulphur–nitrogen complexes which involve a variety of reagents, such as $S_4N_4H_4$,[4] $[Sn(S_2N_2)Me_2]_2$[5] and $Na(S_3N_3)$,[6] $S_4N_4$ remains the most important single compound pertinent to this field. Its importance stems from its ability to act either as a direct reagent in its own right or as a precursor to other synthons, such as the three mentioned above. Whilst many reactions of $S_4N_4$ with metal species proceed effectively at room temperature, others require the use of elevated temperatures and therefore pose a potential hazard with regard to the explosive capacity of the reagent. In an attempt to devise milder synthetic conditions for this type of reaction we have investigated the effect of UV photolysis upon these systems. While some investigations into the photolysis of norbornene adducts of $S_4N_4$ have been reported,[7] the results herein constitute one of the first attempts to investigate and utilise the photochemical properties of $S_4N_4$.

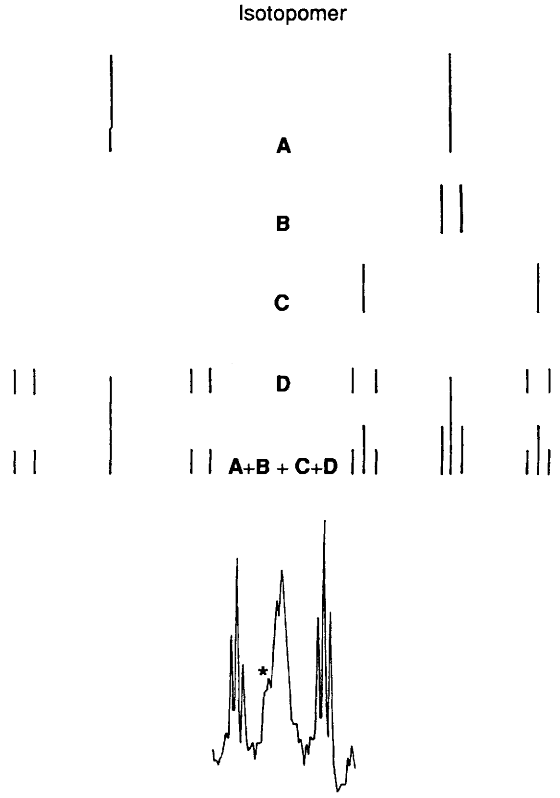
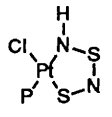


**Fig. 1** Combinations of splitting patterns due to isotopomers present in a 1 : 1 mixture of 100% labelled and unlabelled compound **1** (left-hand side) and fully scrambled 50% labelled **1** (right) together with the observed $^{31}$P-{$^{1}$H} NMR spectrum due to **1** when prepared using a 1 : 1 mixture of $S_4N_4$ and $S_4{}^{15}N_4$

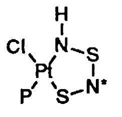
Photolysis of a mixture of *cis*-[$PtCl_2(PMe_2Ph)_2$] and $S_4N_4$ in $CH_2Cl_2$ rapidly results in the formation of [$Pt(S_2N_2H)Cl(PMe_2Ph)$] **1** and [$Pt(S_3N)Cl(PMe_2Ph)$] **2**, which can be detected by $^{31}$P NMR spectroscopy and TLC. The reaction also produces a number of other, as yet unidentified, phosphine–sulphur/nitrogen species, which when separated on a gel-permeation column are identical in appearance and quantity to those produced when the reaction is performed at high temperatures ($\geqslant$ 140 °C) in the absence of UV irradiation. Thus the use of UV photolysis appears to circumvent the high temperatures previously thought necessary and hence greatly reduces the risk of explosion of the $S_4N_4$ (which is always a danger at temperatures in excess of 100 °C).

If a 1 : 1 mixture of $S_4N_4$ and $S_4{}^{15}N_4$ is used to generate compound **1** *via* photolysis, the degree of intermixing of $^{14}$N/$^{15}$N in the product can be determined by NMR spectroscopy and can give an insight into the reaction mechanism. We have previously shown that the spectrum of fully labelled **1** contains $^{15}$N–$^{31}$P couplings ($^{15}$N being spin $\frac{1}{2}$) from both the metal-bound and the far nitrogen, of magnitude 54 and 7 Hz respectively.[1] A simple mixture of labelled and unlabelled **1** would result in a five-line spectrum (Fig. 1); in contrast, intermixing of the nitrogens would result in four isotopomers (**A**–**D**), each making up 25% of the sample.

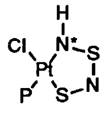
As Fig. 1 shows, the presence of these isotopomers would generate a substantially different splitting pattern to that observed for the simple mixture; the observed spectrum is clearly consistent with such a pattern, although in this case the central triplet is not well resolved due to the presence of an impurity (marked *) and phasing problems. However, line narrowing of the spectrum unequivocably resolves the low-frequency area of the region into a triplet, with identical couplings to those present in the outer two triplets and with twice the area. Hence we can be confident that the product does indeed contain fully intermixed nitrogens.



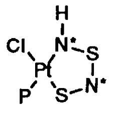
**A**



**B**



**C**



**D**

P = $PMe_2Ph$, N* = $^{15}$N

In view of the fact that it is unlikely that mixtures of [$Pt(S_2N_2H)Cl(PMe_2Ph)$] and [$Pt(S_2{}^{15}N_2H)Cl(PMe_2Ph)$] could exchange nitrogens *after* formation, the only realistic interpretation of this result is that the reaction is proceeding *via* an intermediate formed by photolysis of the $S_4N_4$ and that this intermediate undergoes rapid intermixing of its nitrogens prior to reaction. This conclusion mirrors that reached for the high-temperature reactions, in which we were able to show that at $\geqslant$140 °C $S_4N_4$–$S_4{}^{15}N_4$ mixtures 'scramble' their nitrogens, even in the absence of [$PtCl_2(PMe_2Ph)_2$].

Photolysis of $S_4N_4$ in the absence of metal species results in a mixture of products. This reaction is dependent upon both the concentration and the solvent used; for example, a 1 mmol dm$^{-3}$ solution in $CH_2Cl_2$ is decolourised in *ca.* 30 min. In contrast, photolysis of a saturated solution in cyclohexane is not complete after 24 h. After this time the reaction mixture consists of a flocculent precipitate of sulphur and a red solution. TLC of the solution shows, in addition to unreacted $S_4N_4$, three major products. The major, bright red, fraction was identified as $S_4N_2$ by mass spectrometry: *m*/*z* 156 ($S_4N_2{}^+$), 124 ($S_3N_2{}^+$), 110 ($S_3N^+$), 92 ($S_2N_2{}^+$), 78 ($S_2N^+$) and 46 ($SN^+$). The other fractions were identified as $S_8$ and $S_7NH$ by TLC and IR spectroscopy. Photolysis in MeOH results in complete decolourisation in *ca.* 4 h, with formation of $S_7NH$ and *no* formation of $S_4N_2$. If benzophenone is used as a triplet sensitiser in the cyclohexane photolysis the solution is again rapidly decolourised with no $S_4N_2$ formation. Photolysis in carbon disulphide, which in contrast to the above reactions also occurs with longer-wavelength radiation (*i.e.* using Pyrex rather than quartz reactors), gives $S_4N_2$ as the major product.

The reaction with [$PtCl_2(PMe_2Ph)_2$] is also dependent upon the fact that the phosphine is not bidentate since preliminary studies indicate that [$PtCl_2$(dppe)] [dppe = 1,2-bis(diphenylphosphino)ethane] is inert to $S_4N_4$ under these conditions. This is consistent with the long-established fact that UV irradiation can bring about isomerisation in complexes of the type [$PtCl_2(PR_3)_2$];[8] presumably the labilisation of the phosphine allows the sulphur–nitrogen species to react at the co-ordinatively unsaturated metal centre. This does not mean, however, that the reaction is simply a result of photochemical activation of the dichloride, followed by reaction with unactivated $S_4N_4$. Such a mechanism would provide no pathway for the intermixing of the nitrogens in the system and is clearly at odds with the observation that $S_4N_4$ reacts with UV radiation even in the absence of any metal species. We have yet to assertain the nature of the initial species generated from $S_4N_4$ upon UV irradiation; future work will involve the use of simultaneous combinations of $^{14}$N NMR spectroscopy and photolysis in order to observe the system *in situ*.

The preparation of mixtures of complexes of both the $S_2N_2H^-$ and $S_3N^-$ anions has only previously been observed in high-temperature reactions, such as used in the preparation of [$M(S_2N_2H)_2$], [$M(S_3N)_2$] and [$M(S_2N_2H)(S_3N)$] (where

M = Co, Ni, Pt or Pd) from $MCl_2$.[9] This work promises the possibility of activating such reactions at room temperature; indeed we have found that photolysis of a mixture of $S_4N_4$ and $[CoCl_2(PPh_3)_2]$ in $CH_2Cl_2$ produces traces of the above species. It is likely that many other systems, both organic and inorganic, in which $S_4N_4$ has previously been deemed inert, could well be activated by photolysis, thus providing safe, low-temperature routes to novel sulphur–nitrogen systems.

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## References

1 J. M. Jolliffe, P. F. Kelly and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 1989, 2179.
2 E. Parkes, DIC Thesis, Imperial College, 1986.
3 N. Logan and W. L. Jolly, *Inorg. Chem.*, 1965, **4**, 1508.
4 R. Jones, P. F. Kelly, D. J. Williams and J. D. Woollins, *Polyhedron*, 1987, **6**, 1541.
5 R. Jones, C. P. Warrens, D. J. Williams and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 1987, 907.
6 P. A. Bates, M. B. Hursthouse, P. F. Kelly and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 1986, 2367.
7 M. R. Brinkman and L. H. Sutcliffe, *J. Magn. Reson.*, 1977, **28**, 263.
8 F. R. Hartley, *The Chemistry of Platinum and Palladium*, Applied Science Publishers, London, 1973.
9 J. D. Woollins, R. Grinter, M. K. Johnson and A. J. Thomson, *J. Chem. Soc., Dalton Trans.*, 1980, 1910.

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