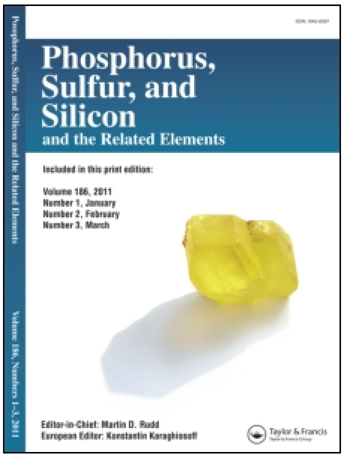

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

REACTION OF Pt(Se_2N_2)(DPPE) WITH HALOGENS: A NEW ROUTE TO Se_4N_4. THE X-RAY CRYSTAL STRUCTURE OF 3[PtI_2(DPPE)]·I_2·2[CH_2C_2]

Ivan P. Parkin[a]; Alexandra M. Z. Slawin[a]; David J. Williams[a]; J. Derek Woollins[a]
[a] Department of Chemistry, Imperial College, South Kensington, London

To cite this Article Parkin, Ivan P. , Slawin, Alexandra M. Z. , Williams, David J. and Woollins, J. Derek(1991) 'REACTION OF Pt(Se_2N_2)(DPPE) WITH HALOGENS: A NEW ROUTE TO Se_4N_4. THE X-RAY CRYSTAL STRUCTURE OF 3[PtI_2(DPPE)]·I_2·2[CH_2C_2]', Phosphorus, Sulfur, and Silicon and the Related Elements, 57: 3, 273 — 277

To link to this Article: DOI: 10.1080/10426509108038859

URL: http://dx.doi.org/10.1080/10426509108038859

Phosphorus, Sulfur, and Silicon, 1991, Vol. 57, pp. 273–277
Reprints available directly from the publisher
Photocopying permitted by license only

REACTION OF $Pt(Se_2N_2)(dppe)$ WITH HALOGENS: A NEW ROUTE TO Se_4N_4. THE X-RAY CRYSTAL STRUCTURE OF $3[PtI_2(dppe)]\cdot I_2\cdot 2[CH_2C\ell_2]$

IVAN P. PARKIN, ALEXANDRA M. Z. SLAWIN, DAVID J. WILLIAMS
and J. DEREK WOOLLINS

Department of Chemistry, Imperial College,
South Kensington, London, SW7 2AY

(Received March 25, 1990; in final form July 1, 1990)

The reaction of $Pt(Se_2N_2)(dppe)$ (**1**) with stoichiometric quantities of halogen (Cl_2, Br_2 or I_2) in CH_2Cl_2 yields $PtX_2(dppe)$ and Se_4N_4. In the case of iodine the rate of reaction was much slower than for the other halogens and ^{31}P n.m.r. evidence suggests that the reaction proceeds *via* the protonated complex $[Pt(Se_2N_2H)(dppe)]I$. The crystal structure of $3[PtI_2(dppe)]\cdot I_2\cdot 2[CH_2C\ell_2]$ is reported.

INTRODUCTION

There have been a few reports of metalla-selenium-nitrogen heterocycles. Dehnicke and co-workers have synthesized the tungsten and molybdenum compounds $[WCl_4(NSeCl)]_2$ and $[MoCl_4(NSeCl)]_2$ from the reaction of Se_4N_4 in refluxing solvents with the corresponding metal chloride.[1,2] We have found that reaction of $[PtCl_2(PMe_2Ph)]_2$ with Se_4N_4 in refluxing chloroform gives low yields of $Pt(Se_3N)(PMe_2Ph)_2$ and $Pt(Se_2N_2)(PMe_2Ph)_2$.[3,4] Se_4N_4 is dangerously explosive, much more so than the well known sulphur analogue[5] S_4N_4, and the slightest shock or friction applied to this substance is extremely hazardous. The synthesis of Se_4N_4 *via* liquid ammonia and $SeCl_4$ at high pressure is difficult and dangerous,[6] thus a convenient method of making small quantities of Se_4N_4 would be advantageous.

On continuing our studies into the synthesis of metalla-selenium-nitrogen heterocycles we have found that reaction of $PtCl_2(PR_3)_2$ with $SeCl_4$ in liquid ammonia[4,7] gives $Pt(Se_2N_2)(PR_3)_2$ in *ca* 25–75% yield. The best yield in the reaction is for PR_3 = ½dppe (**1**). Because of the large amounts of material available *via* this pathway we attempted reaction of (**1**) with halogens. Surprisingly, rather than oxidative addition (seen for the analogous M—S—N complex[8]) reaction of (**1**) with halogens give $PtX_2(dppe)$ and Se_4N_4 and thus represents a good route for the safe synthesis of small amounts of Se_4N_4. Here, we provide details of these reactions and report the X-ray structure of $3[PtI_2(dppe)]\cdot I_2\cdot 2[CH_2C\ell_2]$ (**2**).

RESULTS AND DISCUSSION

Reaction of $Pt(Se_2N_2)(dppe)$ (**1**) with chlorine or bromine in CH_2Cl_2 produces $PtX_2(PR_3)_2$ and Se_4N_4, Equation (1)

---

*Author to whom correspondence should be addressed.

$$2Pt(Se_2N_2)(dppe) + 2X_2 \rightarrow 2PtX_2(dppe) + Se_4N_4 \qquad (1)$$

The reaction proceeds extremely rapidly and the Se_4N_4 is immediately precipitated on addition of the halogen. This reaction is not analogous to that of $Pt(S_2N_2)(PR_3)_2$ (**2**) or $[Pt(S_2N_2H)(PR_3)_2]BF_4$ (**3**) which undergo oxidative addition of the halogens to form an isolable Pt(IV) compound[8] $[Pt(S_2N_2H)X_2(PR_3)_2]BF_4$.

When iodine reacts with (**1**) there is an immediate darkening of the solution from orange to red. Monitoring of the reaction by ^{31}P n.m.r. showed that 3 hours after mixing about 20% PtI_2(dppe) and 80% of what can be assigned to $[Pt(Se_2N_2H)(dppe)]I$ (^{31}P n.m.r. $\delta_A = 48.8$, $\delta_X = 36.4$ ppm, $^1J_A = 2683$, $^1J_X = 3094$ Hz[7]) was present in solution (Figure 1). A small amount of Se_4N_4 was also precipitated. This indicates that the reaction was slower for iodine compared to the other halogens and suggested that the reaction proceeds by protonation of (**1**) prior to addition of halogen and expulsion of Se_4N_4. The ^{31}P n.m.r. of the reactive solution showed only $PtI_2(PR_3)_2$ after 3 days and an almost quantitative amount of Se_4N_4 was isolated.

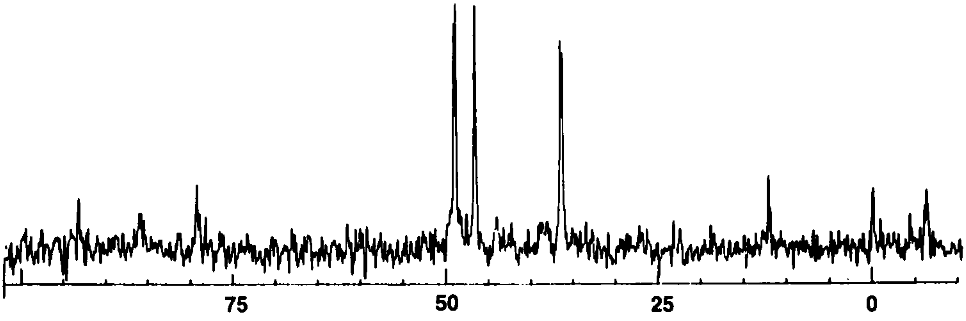

FIGURE 1 ^{31}P-{^1H} n.m.r. ($CH_2Cl_2/CDCl_3$) of the reaction between $Pt(Se_2N_2)$(dppe) and I_2 after 3 hours.

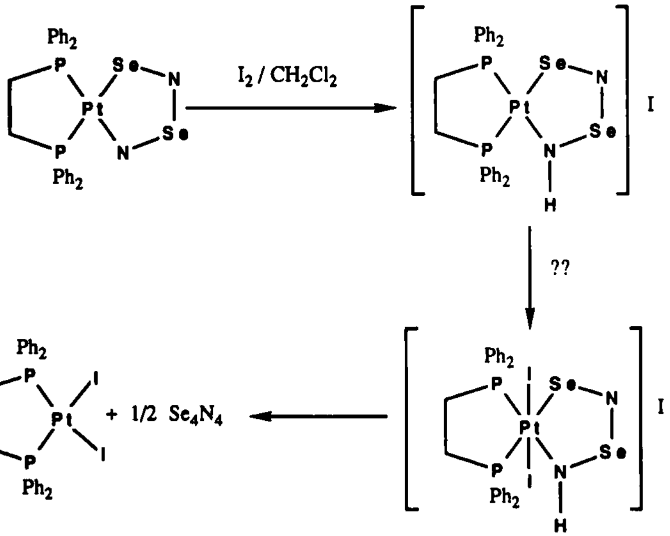

FIGURE 2 Proposed mechanism for the reaction between $PtSe_2N_2$(dppe) and I_2.

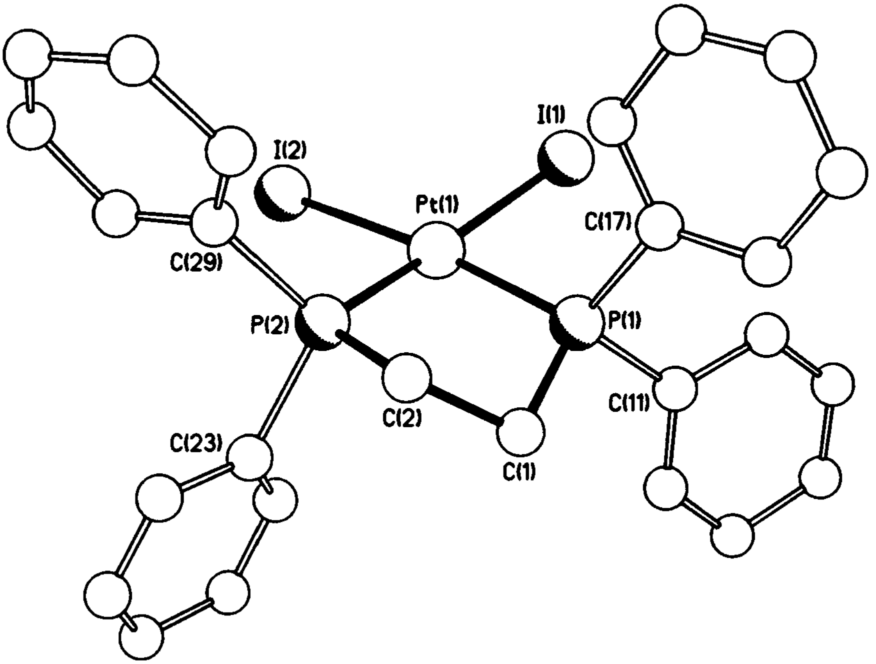

FIGURE 3 X-ray crystal structure of one of the $PtI_2(dppe)$ molecules in $3[PtI_2(dppe)]\cdot I_2\cdot 2[CH_2Cl_2]$.

The proposed reaction mechanism is shown in Figure 2. The most significant feature is the ready oxidation of $[Se_2N_2]^{2-}$ to give Se_4N_4. This suggests that reaction of (**1**) with halogens provides a good *in situ* source of the very explosive Se_4N_4 and should render investigation of the chemistry of this cage viable.

The three crystallographically independent $PtI_2(dppe)$ molecules in (**2**) all have essentially the same conformation; each possessing approximiate non-crystallographic C_2 symmetry about an axis bisecting the I—Pt—I angle (Figure 1, Table I). The platinum coordination geometry differs slightly between the three molecules. Molecule (i) exhibiting a small twist of 9° between the P_2Pt and I_2Pt planes; molecule (ii) is essentially square planar with a maximum deviation from the PtP_2I_2 least squares plane of 0.01 Å (for P(4)); the coordination geometry of molecule (iii) is slightly folded with I(5) and I(6) lying 0.12 Å from the PtP_2 plane. There are however no major departures from orthogonal geometries at the three independent platinum centres. All of the Pt—I distances are within statistical significance equivalent (average 2.658 Å) as are the Pt—P distances (average 2.238 Å). Similarly the P—C distances are equivalent and normal. The included iodine molecule (I(7)–I(8) = 2.751 Å) has close intermolecular I . . . I contacts (I(8) . . . I(6) 3.45 Å, I(7) . . . I(4′) 3.55 Å); these distances are comparable with the intramolecular *cis* P . . . I distances in each independent $PtI_2(dppe)$ molecule (range 3.48–3.60 Å).

EXPERIMENTAL

All reactions were performed under an inert atmosphere using standard Schlenk line techniques (N_2, Ar). CH_2Cl_2 was distilled from CaH_2; *n*-hexane from Na/benzophenone and both were degassed prior

TABLE I

Selected bond lengths (Å) and angles (°) for the three independent PtI_2(dppe) molecules and the included I_2 molecule in (**2**). The numbering scheme for molecules (i) is shown in Figure 3 whilst the atoms in molecules (ii) and (iii) are numbered sequentially.

	(i)	(ii)	(iii)
Pt—I(1)	2.651(3)	2.650(3)	2.662(3)
Pt—I(2)	2.655(3)	2.674(3)	2.659(3)
Pt—P(1)	2.246(9)	2.250(9)	2.243(9)
Pt—P(2)	2.238(9)	2.215(9)	2.237(10)
P(1)—C(1)	1.802(34)	1.773(37)	1.841(33)
P(1)—C(11)	1.754(31)	1.844(33)	1.789(32)
P(1)—C(17)	1.806(34)	1.769(36)	1.792(31)
P(2)—C(2)	1.824(30)	1.863(33)	1.843(34)
P(2)—C(23)	1.891(37)	1.838(33)	1.828(33)
P(2)—C(29)	1.809(35)	1.758(33)	1.823(33)
I(7)—I(8)	2.751(5)		
I(1)—Pt—I(2)	90.7(1)	91.2(1)	89.8(1)
P(1)—Pt—P(2)	86.0(3)	86.1(3)	85.9(3)
Pt—P(1)—C(1)	107.0(11)	107.6(11)	108.1(11)
Pt—P(1)—C(11)	118.0(11)	118.3(11)	116.1(11)
Pt—P(1)—C(17)	104.4(15)	112.5(11)	112.5(10)
Pt—P(2)—C(2)	109.0(11)	107.5(11)	107.6(12)
Pt—P(2)—C(23)	119.0(11)	112.3(11)	116.1(11)
Pt—P(2)—C(29)	107.4(15)	116.1(12)	118.0(11)

to use. $CDCl_3$ was used as supplied (Aldrich). $MCl_2(PR_3)_2$ were prepared by the slow addition of stoichiometric amounts of the appropriate phosphine to MCl_2(cod) [cod = 1,5 cyclo-octadiene]. $Pt(Se_2N_2)$(dppe) was prepared from reaction of $SeCl_4$ (Fluka) and $PtCl_2$(dppe) in liquid ammonia and recrystallized from CH_2Cl_2/ *n*-hexane prior to use.[7] The halogens I_2, Br_2 and Cl_2 were used as supplied (Aldrich/BOC). I.r. spectra were measured as KBr discs on a Perkin Elmer 1720K spectrometer. ^{31}P-$\{^1H\}$ n.m.r. were obtained using a JEOL FX90Q spectrometer operating at 36.21 MHz and are referred to external 85% H_3PO_4. Mass spectra were obtained using the E.I. (electron impact) modes from a VG 2020 instrument. Microanalyses were provided by the Imperial College Microanalytical service.

CARE: Se_4N4 OBTAINED FROM THE FOLLOWING REACTIONS IS EXTREMELY EXPLOSIVE AND SHOULD BE HANDLED WITH CAUTION

Reaction of $Pt(Se_2N_2)$(dppe) (**1**) *with Halogens*

Iodine. To (**1**) (0.050 g, 0.064 mmol) in CH_2Cl_2 (10 ml) was added iodine (0.0164 g, 0.064 mmol), this caused an immediate darkening of the solution from orange to dark red. The reaction was stirred for three hours at room temperature by which time a small amount of orange/red precipitate (Se_4N_4, υ = 800vs, 781s, 570s, 426s and 310w cm^{-1}) had formed. The solution was evaporated to dryness, dissolved in $CH_2C\ell_2/CDC\ell_3$ and the ^{31}P n.m.r. obtained. This showed two species *ca* 80% $[Pt(Se_2N_2H)(dppe)]I$ (δ_A = 48.8, δ_X = =36.4, ^1J_A = 2683, ^1J_X = 3094); 20% PtI_2(dppe) (δ = 46.4, *J* = 3537). The n.m.r. solution was layered with n-hexane and allowed to stand at room temperature for three days to produce a red/orange solid at the bottom of the tube and a number of dark-red crystals of $3[PtI_2(dppe)]\cdot I_2\cdot 2[CH_2C\ell_2]$; M^+ = 847 (PtI_2(dppe)), M^+—I = 720. The red-orange solid was collected, washed with EtOH (5 ml), CH_2Cl_2 (5 ml) and air dried (i.r. υ = 800vs. 781s, 570s, 426s and 310w cm^{-1}, Se_4N_4,[5] 0.007 g, 0.018 mmol, 72%).

Chlorine and Bromine. The reaction conditions were repeated as above using the same stoichiometry of reagents. In both of these cases a dark orange-red precipitate was formed on addition of the halide. Isolation of the precipitate and washing with CH_2Cl_2 (20 ml), EtOH (10 ml), H_2O (10 ml) and EtOH (10 ml) gave Se_4N_4 (0.008 g, 0.020 mmol, 85%, υ = 800vs. 781s, 570s, 426s and 310w cm^{-1}). The filtrate from the initial reaction solution contained only PtX_2(dppe) by ^{31}P nmr (X = Cl, δ = 41.3 ppm, ^1J = 3623 Hz; X = Br, δ = 44.6 ppm, ^1J = 3565 Hz).

Crystal Data. $3[C_{26}H_{24}P_2PtI_2]\cdot I_2\cdot 2[CH_2C\ell_2]$, M = 988.5, monoclinic, a = 8.593(2), b = 28.199(10), c = 36.206(9) Å, β = 91.50(2)°, V = 8770 Å^3, space group $P2_1/n$, Z = 12 (3 crystallographically independent molecules), Dc = 2.25 gcm^{-3}. Crystal dimensions 0.07 × 0.10 × 0.23 mm, μ(Cu—K_α) = 338 cm^{-1}, λ = 1.54178 Å, $F(000)$ = 5464.

Data Collection and Processing. Nicolet R3m diffractometer, ω-scan method, ($\theta \leq 50°$), graphite monochromated Cu-K_α radiation; 8919 independent measured reflections, 6106 observed $[|F_0| > 3\sigma(|F_0|)]$, corrected for Lorentz and polarisation factors; numerical absorption correction (face indexed crystal), maximum and minimum transmission factors 0.207 and 0.032 respectively.

Structure Analysis and Refinement. The structure was solved by direct methods and the non-hydrogen atoms refined anisotropically. A ΔF map revealed the presence of four overlapping orientations of half-weight dichloromethane molecules. The carbon and hydrogen atoms of the solvent were not located. The positions of the remaining hydrogen atoms were idealised (C—H = 0.96 Å), assigned isotropic thermal parameters $U(H) = 1.2U\text{eq}(C)$ and allowed to ride on their parent carbons. Refinement was by block-cascade full-matrix least squares to $R = 0.086$, $R_w = 0.074$ ($w^{-1} = \sigma^2(F) + 0.00010F^2$). The maximum and minimum residual electron densities in the final ΔF map were 2.33 and -2.42 eÅ^{-3} and the mean and maximum shifts/error in the final refinement cycle were 0.071 and 0.232 respectively. Computations were carried out on an Eclipse S140 computer using the SHELXTL program system.[9]

ACKNOWLEDGEMENTS

We are grateful to Johnson Matthey for loans of precious metals and to the ULCRF for support.

REFERENCES

1. J. Adel, A. El-Kholi, W. Willing, U. Muller and K. Dehnicke, *Chimia*, 1988, **42**, 70.
2. J. Adel and K. Dehnicke, *Chimia*, 1988, **42**, 413.
3. P. F. Kelly, A. M. Z. Slawin, D. J. Williams and J. D. Woollins, *J. Chem. Soc., Chem. Commun.*, 1989, 408.
4. P. F. Kelly, I. P. Parkin, A. M. Z. Slawin, D. J. Williams and J. D. Woollins, *Angew. Chem., Int. Ed. Eng.*, 1989, **28**, 1047.
5. Gmelin, *Handbuch der Anorganishen Chemie*, Selenium supplement, B2, p. 365, Springer-Verlag, 1984.
6. J. Jander and V. Doetsch, *Chem. Ber.*, 1960, **93**, 561.
7. I. P. Parkin and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 1990, 925.
8. R. Jones, P. F. Kelly, D. J. Williams and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 1986, 2367.
9. G. M. Sheldrick, SHELXTL, An integrated system for solving, refining and displaying crystal structures from diffraction data, University of Gottingen, Federal Republic of Germany, 1978; Revision 5.1, 1989.