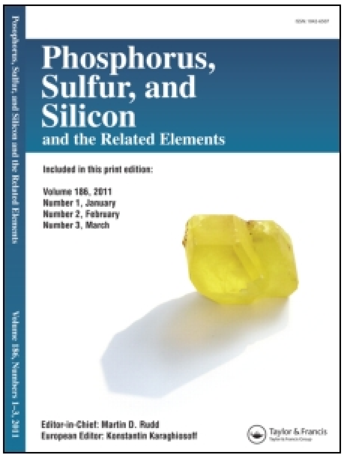


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Coordination Chemistry of Dithioimidophosphinates.

Dominico Cupertino; Robin W. Keyte; Alexandra M. Z. Slawin; David. J. Williams; J. Derek Woollins

To cite this Article Cupertino, Dominico , Keyte, Robin W. , Slawin, Alexandra M. Z. , Williams, David. J. and Woollins, J. Derek(1996) 'Coordination Chemistry of Dithioimidophosphinates.', Phosphorus, Sulfur, and Silicon and the Related Elements, 109: 1, 193 — 196

To link to this Article: DOI: 10.1080/10426509608545123

URL: http://dx.doi.org/10.1080/10426509608545123

Phosphorus, Sulfur, and Silicon, 1996, Vols. 109–110, pp. 193–196
Reprints available directly from the publisher
Photocopying permitted by license only

COORDINATION CHEMISTRY OF DITHIOIMIDOPHOSPHINATES.

DOMINICO CUPERTINO, ROBIN W. KEYTE, ALEXANDRA M.Z.SLAWIN, DAVID. J. WILLIAMS AND J. DEREK WOOLLINS
Zeneca Research Specialities Division, Blackley, Manchester M9 8ZS
Dept. of Chemistry, Loughborough University, LE11 3TU, UK
Dept. of Chemistry, Imperial College, SW7 2AY, UK

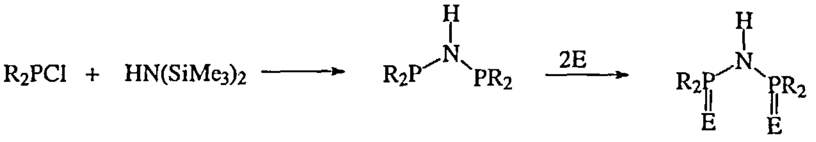
Abstract The preparation of $^{i}Pr_2P(S)NHP(S)^{i}Pr_2$ and its reaction to form simple chelate complexes $M(^{i}Pr_2P(S)NP(S)^{i}Pr_2)_2$ (M = Pd, Pt) is described. The neutral starting material forms H-bonded chains in the solid state whilst there are dramatic differences in ring geometry on changing M from Pd to Pt.

INTRODUCTION

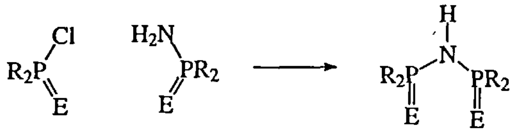
The coordination chemistry of $R_2P(E)NHP(E)R_2$ and $[R_2P(E)NP(E)R_2]^-$ (E= O, S, Se) is of interest for a number of reasons. These ligands represent inorganic analogues of the more extensively studied β-diketonates, they are readily deprotonated to form stable six-membered inorganic rings which have potentially interesting bonding properties (π-bonding involving d-orbitals may have a role) and they have the potential to behave as metal selective ligands as a result of the extensive range of chalcogenides and R groups which may be introduced. There have been several studies on systems with R = Ph and E = S [1,2] and some work on R = Me, E = S.[3,4] Here we report on our investigations into the sulfur compounds were R = ^{i}Pr.

RESULTS AND DISCUSSION

$R_2P(E)NHP(E)R_2$ may be prepared by a variety of routes. Simple condensation of the phosphine halide with $HN(SiMe_3)_2$ followed by oxidation with the appropriate chalcogen is appropriate for the synthesis of symmetric systems (eqn 1) whilst asymmetric compounds can be obtained by condensation of amine and chloro species (eqn 2). For the preparation of $^{i}Pr_2P(S)NHP(S)^{i}Pr_2$ **1** we chose the former method and obtained a 60 % yield of the pure compound ($\delta\ ^{31}P\text{-}\{^{1}H\}$ = 91.2 ppm).



eqn. 1



eqn. 2

The X-ray structure of **1** reveals that the P=S groups are disposed approximately *gauche* with respect to the P....P vector. The P-N distances are 1.678(3) and 1.681(3) Å whilst the P-S distances are 1.943(1) and 1.951(1) Å and the P-N-P angle is 132.0(2)°. The molecules pack (Figure 1) to form chains *via* P-S...H-N hydrogen bonds (S...N 3.58, H...S 2.97 Å. Reaction of **1** with simple metal halides yields ML_2 complexes with deprotonation at the central nitrogen. Here, we highlight two examples which illustrate the ring geometries which we have observed to date. Thus, the palladium complex $Pd(^{i}Pr_2P(S)NP(S)^{i}Pr_2)_2$ **2** is essentially square planar about the metal with P-S bondlengths of 2.023(2) and 2.030(2) Å and P-N bondlengths of

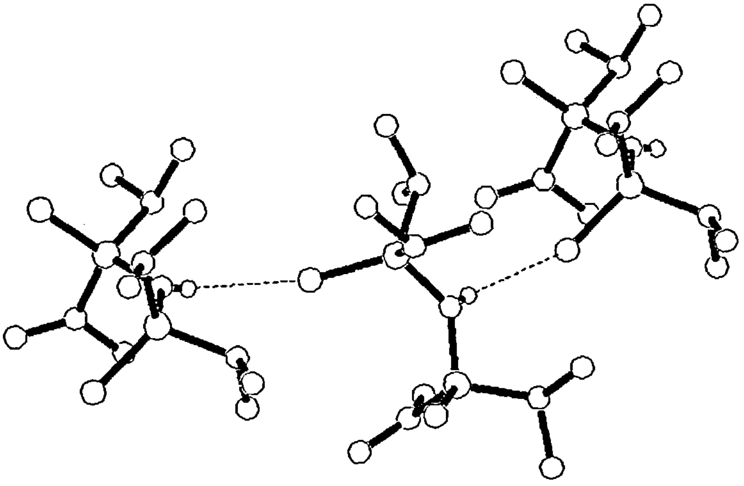


FIGURE 1 P-S...H-N Hydrogen bonding in $^{i}Pr_2P(S)NHP(S)^{i}Pr_2$

1.598(4) and 1.588(4) Å ie., the P-S bonds lengthen and the P-N bonds shorten upon deprotonation/complexation which is compatable with a more delocalised structure in the complex. As can be seen from Figure 2 the PdS_2P_2N rings in **2** are distinctly puckered in what might be described as a distorted boat conformation. Remarkably, the platinum complex $Pt(^iPr_2P(S)NP(S)^iPr_2)_2$ **3** has a substantially different ring geometry. The platinum centre is a approximately square planar whilst the P-S bondlengths (2.034(2) and 2.038(1) Å) and P-N bondlengths (1.586(4) and 1.575(4) Å) are not significantly different from those in **2** but the ring conformation changes to give a close to planar S_2P_2N fragment. The P-N-P angle does not differ markedly in **2** and **3** (130.2(2) and 135.0(2)° respectively) but the M-S-P angles are significantly reduced in **3** (104.07(5) and 99.62(7) in **3** cf. 114.04(6) and 108.62(6) in **2**) and this must imply the use of different orbitals for the coordination to the metal centres.

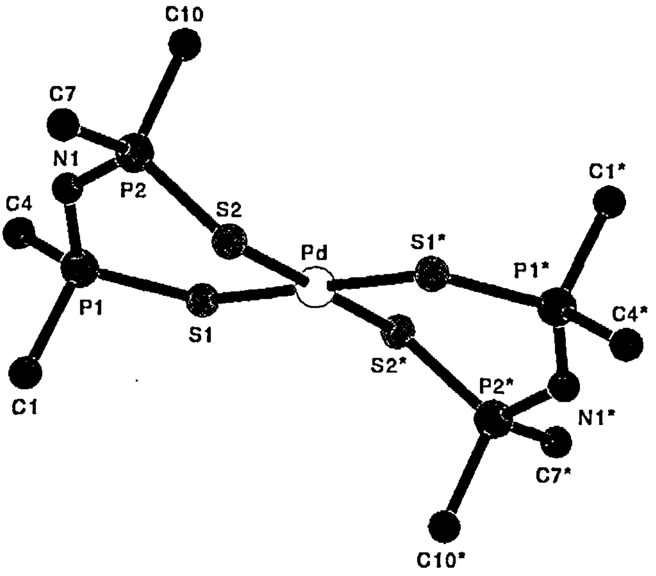


FIGURE 2 The X-Ray structure of $Pd(^iPr_2P(S)NP(S)^iPr_2)_2$ **2**

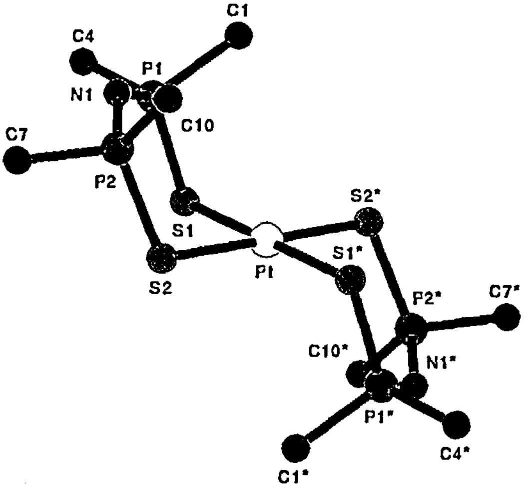


FIGURE 3 The X-Ray structure of Pt(^{i}Pr$_2$P(S)NP(S)^{i}Pr$_2$)$_2$ 3

We have observed the puckered, boat, conformation in the tetrahedral zinc, cadmium and nickel complexes and it would appear that the more symmetric structure is the unusual case. Further studies are in progress.

REFERENCES

1. I.HAIDUC, C.SILVESTRU, H.ROESKY, H-G.SCHMIDT and M.NOLTEMEYER, Polyhedron, 12,69 (1993).
2. P.BHATTACHACHARYYA, J.NOVOSAD, J.PHILLIPS, A.M.Z.SLAWIN, D.J.WILLIAMS AND J.D.WOOLLINS,J.Chem.Soc.,Dalton Trans.,1607 (1995).
3. A.SCHMIDPETER and J.EBELING, Chem.Ber., 101,815 (1969)
4 D.WILLIAMS, J.TRAVIS and K.BERGBAUER, J.Coord.Chem.,16,315 (1987)