

# Phosphino-urea chemistry: preparation and structure of chelate and P–N bond cleavage complexes

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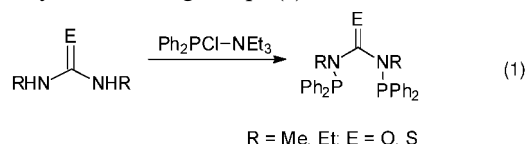
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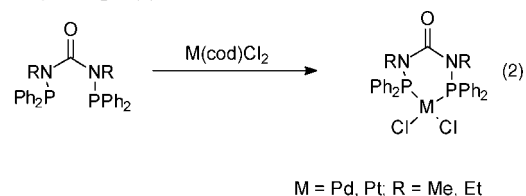
Reactions of  $\text{Ph}_2\text{PNRC(E)NRPPH}_2$  proceed to give simple *P,P* chelate complexes when  $\text{E} = \text{O}$  but give the unexpected five-membered true heterocycle  $\text{Pt}[\text{Ph}_2\text{PN(Me)C(NMeH)S}]\text{Cl}_2$  and an unusual six-membered  $\text{Pd}_2\text{P}_2\text{O}_2$  ring when  $\text{E} = \text{S}$ . The X-ray structures of three examples are reported.

Urea derivatives of the type  $[\text{Ph}_2\text{PNHC(E)NHPPH}_2]$  ( $\text{E} = \text{O}, \text{S}$ )<sup>1,2</sup> have recently been developed and shown to chelate to a range of late transition metals through both phosphorus and chalcogen donor atoms. However, the strong H-bonding that is a common feature of urea chemistry may limit the potential of these systems. Here we report on the preparation of some NR ( $\text{R} = \text{Me}, \text{Et}$ ) derivatives and their coordination chemistry, which proceeds as expected to give simple chelates as well as giving products from P–N bond cleavage for some reactions. These products include a five-membered ‘true heterocycle’ and a binuclear complex containing a  $\text{Pd}_2\text{P}_2\text{O}_2$  ring. The X-ray structures of demonstrative examples are reported.

Schmutzler *et al.*<sup>3–7</sup> have reported on the synthesis and properties of phosphine substituted urea/thiourea species. Along with other routes they noted that reaction of  $\text{Me}_3\text{SiN(Me)CO(Me)NSiMe}_3$  with  $\text{Ph}_2\text{PCL}$  gives  $\text{N,N}-(\text{Ph}_2\text{P})\text{N(Me)CO(Me)NPPH}_2$ . Thus, treatment of *N,N*-dialkylurea or *N,N*-dialkylthiourea with  $\text{Ph}_2\text{PCL}$  and triethylamine in dichloromethane gives the diphosphines in 70–80% yield according to eqn. (1).



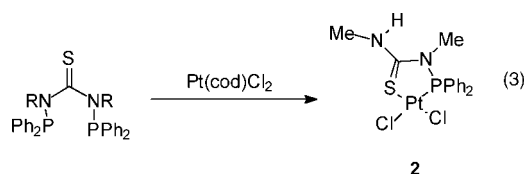
Surprisingly, almost no coordination chemistry has been described for these phosphines. Attempts to coordinate the urea derivatives proved satisfactory in some cases; for example, reaction of the urea derivatives with  $\text{M}(\text{cod})\text{Cl}_2$  ( $\text{M} = \text{Pd}, \text{Pt}$ ) gives the expected complexes quantitatively according to eqn. (2).



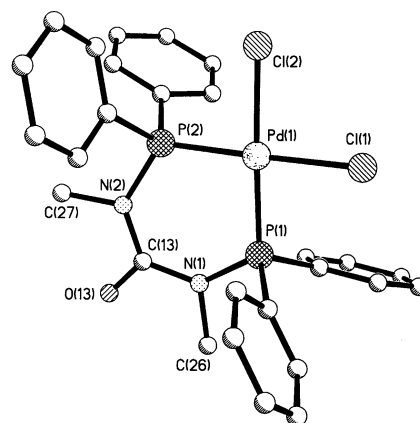
The X-ray structure of a typical example (**1**:  $\text{M} = \text{Pd}$ ,  $\text{R} = \text{Me}$ ) is shown in Fig. 1. The molecule adopts the expected square planar coordination at palladium with the six-membered  $\text{PdP}_2\text{N}_2\text{C}$  ring being in the coordination plane [maximum deviation from the  $\text{PdP}_2\text{N}_2\text{CCl}_2$  mean plane is  $-0.12 \text{ \AA}$  for  $\text{N}(2)$  with  $\text{O}(13)$  being  $0.06 \text{ \AA}$  from this mean

plane,  $\text{C}(26)$  and  $\text{C}(27)$  are  $+0.20$  and  $-0.21 \text{ \AA}$  from the plane]. The  $\text{P}(1)\text{--Pd--P}(2)$  bite angle is  $94.76(3)^\circ$  and the internal angle at phosphorus and carbon is close to trigonal whilst the  $\text{Pd--P--C}$  angles are somewhat enlarged from trigonal.

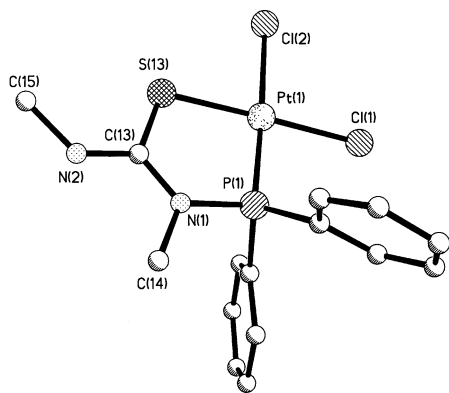
Reaction of the *N,N*-dimethylthiourea-phosphine with  $\text{Pt}(\text{cod})\text{Cl}_2$  in THF proceeds with P–N bond cleavage in 90% yield to give the novel five-membered ‘true heterocycle’ **2** (*i.e.*, a heterocycle in which every ring atom is different) according to eqn. (3).



According to a recent review there are very few fully characterised examples of 5-membered true heterocycles,<sup>8</sup> though there is a report of a related  $\text{PtSCNP}$  heterocycle.<sup>9</sup> The X-ray structure of **2** reveals (Fig. 2) square planar coordination of the platinum with the five-membered  $\text{PtPNCS}$  ring being almost perfectly planar [maximum deviation from the  $\text{PtPNCSCl}_2$  plane is  $0.11 \text{ \AA}$  for  $\text{S}(13)$  with  $\text{N}(2)$ ,  $\text{C}(14)$  and  $\text{C}(15)$  lying  $0.05$ ,  $0.18$  and  $-0.06 \text{ \AA}$  from this plane]. The bond lengths and angles within **2** are in the expected range. The  $\text{Pt--Cl}$  distances vary as a function of the *trans* element; within the five-membered  $\text{PtPNCS}$  heterocycle the P–N and C–N



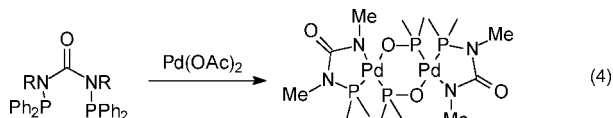
**Fig. 1** The X-ray structure of **1**. Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ):  $\text{Pd}(1)\text{--Cl}(1)$  2.3476(8),  $\text{Pd}(1)\text{--Cl}(2)$  2.342(1),  $\text{Pd}(1)\text{--P}(1)$  2.2003(8),  $\text{Pd}(1)\text{--P}(2)$  2.2072(8),  $\text{P}(1)\text{--N}(1)$  1.697(2),  $\text{P}(2)\text{--N}(2)$  1.704(2),  $\text{N}(1)\text{--C}(13)$  1.380(4),  $\text{N}(2)\text{--C}(13)$  1.377(4);  $\text{Cl}(1)\text{--Pd}(1)\text{--Cl}(2)$  91.47(3),  $\text{P}(1)\text{--Pd}(1)\text{--P}(2)$  94.76(3),  $\text{Pd}(1)\text{--P}(1)\text{--N}(1)$  118.19(9),  $\text{Pd}(1)\text{--P}(2)\text{--N}(2)$  118.41(9),  $\text{P}(1)\text{--N}(1)\text{--C}(13)$  132.6(2),  $\text{P}(2)\text{--N}(2)\text{--C}(13)$  131.5(2),  $\text{N}(1)\text{--C}(13)\text{--N}(2)$  122.9(3),  $\text{N}(1)\text{--C}(13)\text{--O}(13)$  118.6(3),  $\text{N}(2)\text{--C}(13)\text{--O}(13)$  118.5(3).



**Fig. 2** The X-ray structure of **2**. Selected bond lengths (Å) and angles (°): Pt(1)–Cl(1) 2.342(4), Pt–Cl(2) 2.387(3), Pt(1)–P(1) 2.188(3), Pt(1)–S(13) 2.256(4), P(1)–N(1) 1.739(10), N(1)–C(13) 1.34(2), C(13)–S(13) 1.737(13); Cl(1)–Pt(1)–Cl(2) 91.10(14), P(1)–Pt(1)–S(13) 88.02(13), Pt(1)–P(1)–N(1) 106.8(4), P(1)–N(1)–C(13) 118.7(8), N(1)–C(13)–S(13) 121.7(10).

bonds are effectively single bonds whilst C(13)–S(13) is slightly longer [1.737(13) Å] than a formal C=S double bond.

We also found that reaction of the urea-phosphines with Pd(OAc)<sub>2</sub> results in a P–N cleavage reaction together with formation of a [Ph<sub>2</sub>PO]<sup>−</sup> ligand incorporated into a Pd<sub>2</sub>P<sub>2</sub>O<sub>2</sub> heterocycle in 60–65% yield according to eqn. (4).

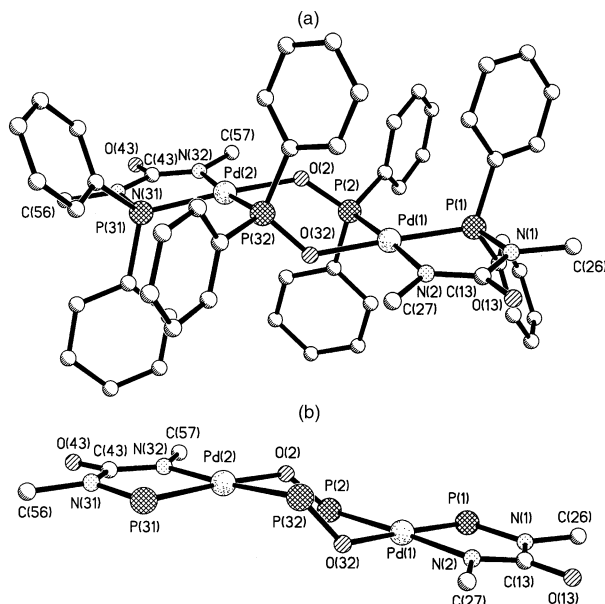


3

The X-ray structure of **3** reveals (Fig. 3) that the square planar palladium centres are spiro centres in the tricyclic system. The PdPN<sub>2</sub>C rings are close to planar [maximum deviations for the two rings are 0.01 Å for N(2) and −0.05 Å for N(31)] with the C=O and NMe groups being effectively coplanar with the PdPN<sub>2</sub>C rings. The internal nitrogen angles in the PdPN<sub>2</sub>C ring are close to trigonal whilst the angle at phosphorus is slightly reduced from a perfect tetrahedral angle and the internal angles at C(13)/C(43) are intermediate between trigonal and tetrahedral. It is noticeable that the C–N bond lengths are quite localised with C(13)–N(2) being substantially shorter than C(13)–N(1). There are very few examples of crystallographically characterised M<sub>2</sub>P<sub>2</sub>O<sub>2</sub> rings [M = any metal, less than 8 examples; M = Pd, Pt, one example for each metal]. In **3** the central Pd<sub>2</sub>P<sub>2</sub>O<sub>2</sub> ring adopts a cyclohexane chair-type geometry with the central P<sub>2</sub>O<sub>2</sub> core having two PdOP planes inclined by *ca.* 138°. Within this ring the P–O bond lengths [P(2)–O(2) 1.536(4) and 1.539(3) Å] are appropriate for a coordinated [Ph<sub>2</sub>PO]<sup>−</sup> anion and similar to those reported for a Pd<sub>2</sub>P<sub>2</sub>O<sub>2</sub> ring,<sup>10</sup> but slightly shorter than those reported for (Ph<sub>3</sub>P)Pt(Ph<sub>2</sub>PO)<sub>2</sub>Pt(PPh<sub>3</sub>).<sup>11</sup> The Pd···Pd distance in **3** is 4.442 Å, which is considerably longer than that found previously [3.32 Å] and may suggest that the complex reported<sup>10</sup> by Matt *et al.* is a Pd<sup>I</sup> system.

## Experimental

All new complexes gave satisfactory microanalyses and the expected parent ions in their mass spectra. Formation of **1–3** was under essentially identical conditions, *i.e.*, reaction at room temperature in CH<sub>2</sub>Cl<sub>2</sub>. Selected spectroscopic data: [Ph<sub>2</sub>PN(Me)]<sub>2</sub>CO δ<sub>p</sub> 54.6, [Ph<sub>2</sub>PN(Et)]<sub>2</sub>CO δ<sub>p</sub> 56.1, [Ph<sub>2</sub>PN(Me)]<sub>2</sub>CS δ<sub>p</sub> 63.3, [Ph<sub>2</sub>PN(Et)]<sub>2</sub>CS δ<sub>p</sub> 67.8. **1**: δ<sub>p</sub> 76.2, **2**: δ<sub>p</sub> 78.31, <sup>1</sup>J{<sup>31</sup>P–<sup>195</sup>Pt} 3968 Hz, **3**: δ<sub>p</sub> (CDCl<sub>3</sub>) 84.4 and 71.2.



**Fig. 3** The X-ray structure of **3**: (a) the full molecule and (b) view showing the core geometry. Selected bond lengths (Å) and angles (°) (NB: the molecule has approximate molecular two-fold symmetry, the numbers in square brackets allow comparison of the symmetry related parameters): Pd(1)–N(2) 2.083(4) [2.059(4)], Pd(1)–P(1) 2.2043(14) [2.1985(14)], Pd(1)–O(32) 2.092(3) [2.075(3)], Pd(1)–P(2) 2.2764(14) [2.2600(14)], P(1)–N(1) 1.674(5) [1.676(5)], N(1)–C(13) 1.424(7) [1.414(7)], C(13)–N(2) 1.323(7) [1.328(7)], C(13)–O(13) 1.235(6) [1.240(6)], P(2)–O(2) 1.536(4) [1.539(3)]; P(1)–Pd(1)–N(2) 81.81(13) [81.90(13)], Pd(1)–P(1)–N(1) 102.6(2) [102.3(2)], P(1)–N(1)–C(13) 119.4(3) [119.2(3)], N(1)–C(13)–N(2) 114.6(5) [114.2(5)], C(13)–N(2)–Pd(1) 121.6(4) [121.9(4)], Pd(1)–P(2)–O(2) 113.9(2) [112.8(2)], Pd(1)–O(32)–P(32) 128.4(7) [134.8(2)].

## Crystal data

Common to all determinations: Bruker SMART diffractometer, Mo<sub>K</sub> radiation, minimum full hemisphere of data, *T* = 296 K, refinements employed SHELXTL. **1**: C<sub>27</sub>H<sub>26</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>2</sub>Pd, *M* = 633.7, monoclinic, *P*<sub>2</sub>/*c* (no. 14), *a* = 9.9076(1), *b* = 14.700(1), *c* = 19.051(1) Å, β = 101.70(1)°, *U* = 2717(1) Å<sup>3</sup>, ρ<sub>calcd</sub> 1.549 g cm<sup>−3</sup>, *Z* = 4, μ(Mo–K<sub>α</sub>) 1.02 mm<sup>−1</sup>, 11 787 reflections measured, 3866 independent with *I* > 2σ(*I*) to yield *R* = 0.0263 and *wR*<sub>2</sub> = 0.0576 for 317 parameters. **2**·DMSO·CHCl<sub>3</sub>: C<sub>18</sub>H<sub>23</sub>Cl<sub>5</sub>N<sub>2</sub>O<sub>2</sub>Pd<sub>2</sub>S<sub>2</sub>, *M* = 750.81, triclinic, *P*<sub>1</sub>, *a* = 11.404(1), *b* = 11.563(1), *c* = 11.927(1) Å, α = 69.23(1), β = 71.929(1), γ = 74.871(1)°, *U* = 1378(1) Å<sup>3</sup>, ρ<sub>calcd</sub> 1.810 g cm<sup>−3</sup>, *Z* = 2, μ(Mo–K<sub>α</sub>) 5.80 mm<sup>−1</sup>, 5986 reflections measured, 3829 independent with *I* > 2σ(*I*) to yield *R* = 0.0503 and *wR*<sub>2</sub> = 0.1149 for 272 parameters. **3**·H<sub>2</sub>O·2CH<sub>2</sub>Cl<sub>2</sub>: C<sub>56</sub>H<sub>58</sub>Cl<sub>4</sub>N<sub>4</sub>O<sub>5</sub>P<sub>4</sub>Pd<sub>2</sub>, *M* = 1345.5, triclinic, *P*<sub>1</sub>, *a* = 11.695(1), *b* = 15.487(1), *c* = 18.541(1) Å, α = 76.184(1), β = 71.834(1), γ = 72.806(1)°, *U* = 3008(1) Å<sup>3</sup>, ρ<sub>calcd</sub> 1.486 g cm<sup>−3</sup>, *Z* = 2, μ(Mo–K<sub>α</sub>) 0.93 mm<sup>−1</sup>, 14 316 reflections measured, 8512 with *I* > 2σ(*I*) to yield *R* = 0.0430 and *wR*<sub>2</sub> = 0.113 for 668 parameters. In all structures all of the non-H atoms were refined anisotropically and the solvents were included in the refinements. H-atoms were usually located from difference maps (or at least the leading proton on methyl groups) and refined in idealised geometries.

CCDC reference number 440/158. See <http://www.rsc.org/suppdata/nj/a9/a908153d/> for crystallographic files in .cif format.

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