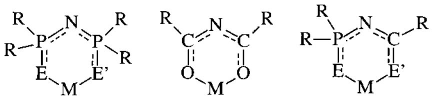
The First Six-Membered “True” Heterocycle – Hydrogen-Bond-Assisted Ladder Formation in a KOCNPS Ring System**

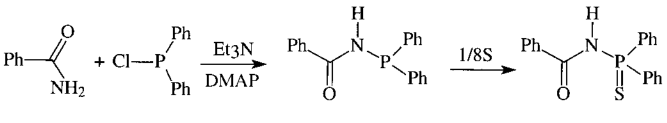
Tuan Q. Ly, Alexandra M. Z. Slawin, and
J. Derek Woollins*

Recently there has been a flurry of activity in the synthesis and structural characterization of $\mathrm{MEE'(PR)_2N}$ ring systems (**A**; (E, E′ = O, S, Se).[1] These metallacycles can be considered to be relatives of the more extensively studied acetylacetonato complexes but with the added ability to form nonplanar rings with more sterically demanding R groups at the phosphorus compared to the carbon substituents in β-diketonates (**B**)—this difference makes the phosphorus-containing systems useful in metal speciation and separation. The $\mathrm{ME_2(PR)_2N}$ systems have also been found to stabilize unusual geometries at some metal centers for example square-planar $\mathrm{Sn^{II}}$.[2] Intermediate systems (**C**) are also possible (Schmidpeter and Groeger have reported[3, 4] on the synthesis of thiourea derivatives in which E = E′ = S) and provide the opportunity to probe ring geometries in mixed carbon/phosphorus rings as well as to develop the syntheses of “true” heterocycles, that is heterocycles in which every ring atom is different.



A **B** **C**

We synthesized $\mathrm{Ph_2P(S)NHCOPh}$ **1** by a simple P–N bond-forming reaction between benzamide and $\mathrm{Ph_2PCl}$ in the presence of $\mathrm{Et_3N}$ and catalytic amounts of dimethylaminopyridine (DMAP), followed by oxidation of the $\mathrm{P^{III}}$ center using sulfur in a one-pot synthesis (Scheme 1). The use of DMAP as a catalyst results in better yields for reactions involving relatively nonacidic N–H protons, the yield of the reaction was also improved by using an excess of $\mathrm{Ph_2PCl}$, which causes no problems during the work-up as it remains in solution.



1

Scheme 1. One-pot synthesis of **1**.

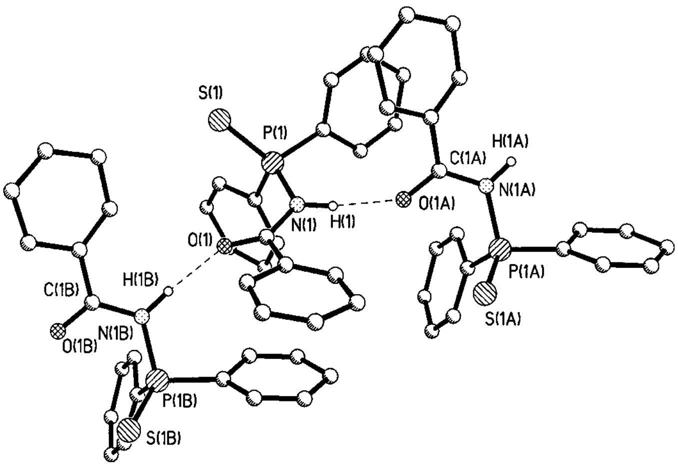


Figure 1. Structure of **1** in the crystal showing part of the hydrogen-bonded chain. Selected distances [pm] and angles [°]: P(1)–S(1) 194.1(6), P(1)–N(1) 172(1), C(1)–N(1) 136(2), C(1)–O(1) 122(2); S(1)-P(1)-N(1) 115.1(4), P(1)-N(1)-C(1) 120.0(1), N(1)-C(1)-O(1) 120(2).

The X-ray crystal structure analysis of **1**[5] (Figure 1) reveals a *gauche* conformation of the P=S and C=O groups (S-P ⋯ C–O “torsion” angle of 56°) with the molecules packing into chains through C=O ⋯ H–N hydrogen bonds (N ⋯ O 285 pm, H ⋯ O 190 pm, N–H ⋯ O 172.5°). The conformation of the system bears a striking resemblance to that of $i\mathrm{Pr_2P(S)NHP(S)}i\mathrm{Pr_2}$[6] but is different to that observed in $\mathrm{Ph_2P(S)NHP(S)Ph_2}$[7] which crystallizes as dimers. The O and S atoms in **1** are well arranged for coordination with an O ⋯ S distance of 340 pm.

Treatment of **1** with KOtBu in THF gave $\mathrm{K[Ph_2P(S)NCOPh]}$ (**2**) as a white solid after workup. Recrystallization of **2** from methanol gave **2** · MeOH, the first example of a six-membered “true” heterocycle. The X-ray structure analysis[8] of **2** · MeOH (Figure 2) reveals that the potassium atom is

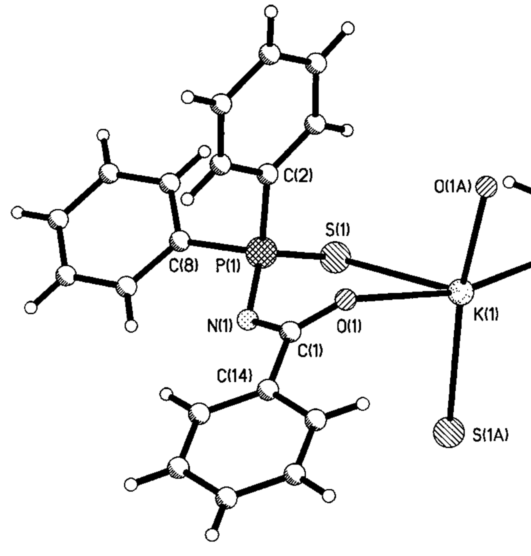


Figure 2. Structure of **2** · MeOH in the crystal showing the coordination shell. Selected distances [pm] and angles [°]: K(1)–O(1) 266.9(3), K(1)–S(1) 324.4(2), K(1)–O(1A) 268.7(3), K(1)–S(1A) 328.6(2), P(1)–S(1) 195.0(2), P(1)–N(1) 161.8(4), C(1)–N(1) 133.2(6), C(1)–O(1) 124.1(5); O(1)-K(1)-O(1A) 79.1(1), O(1)-K(1)-O(20) 159.6(1), O(1)-K(1)-S(1) 75.1(1), O(1A)-K(1)-S(1) 112.6(8), O(20)-K(1)-S(1) 85.4(1), O(1)-K(1)-S(1A) 102.1(1), O(20)-K(1)-S(1A) 79.2(1), S(1)-K(1)-S(1A) 77.8(4), K(1)-S(1)-P(1) 97.1(1), S(1)-P(1)-N(1) 118.4(1), P(1)-N(1)-C(1) 119.6(3), N(1)-C(1)-O(1) 125.7(4), C(1)-O(1)-K(1) 128.7(3).

---

[*] Prof. J. D. Woollins, Dr. T. Q. Ly, Dr. A. M. Z. Slawin
Department of Chemistry
Loughborough University
Loughborough, LE11 3TU (UK)
Fax: (+44) 1509-223925
E-mail: j.d.woollins@lboro.ac.uk

[**] We are grateful to the JREI for an equipment grant.

coordinated by the oxygen atom of methanol, one oxygen atom and one sulfur atom of the chelate ligand as well as an oxygen atom of the ligand above and a sulfur atom of the ligand below to give a ladder structure. The six-membered KSPNCO ring adopts a pseudo-boat conformation with P(1) at the prow and O(1) at the stern of the boat (maximum deviation from the O(1)-C(1)-N(1)-P(1) mean plane is 3 pm for C(1) and maximum deviation from the P(1)-S(1)-K(1)-O(1) mean plane is 9 pm for P(1); the planes are inclined by 129°). Within **2**·MeOH the P–S and C–O bond lengths are longer than in **1**, whilst the P–N and C–N bond lengths are somewhat shorter which is entirely compatible with increased delocalization into the π system as a consequence of deprotonation. The IR spectra support this view as both $\tilde{\nu}$(CO) and $\tilde{\nu}$(PS) are observed at lower frequency in **2**. The P-N-C angles in **1** and **2**·MeOH display values that are almost perfect for a trigonal structure, whereas the P-N-P angles in $[R_2P(E)NP(E)R_2]^-$[1] systems are generally larger than 120°. As mentioned above the S and O atoms of the anionic ligand are shared between neighboring potassium atoms to give a ladder structure made up of alternating K_2S_2 and K_2O_2 rings. The planar rings reflect the difference in the chalcogenide atom that they contain. Thus in the K_2S_2 ring the S···S distance is 410 pm and the K···K distance is 508 pm,[9] whereas in the K_2O_2 rings the O···O and K···K distances are 340 and 413 pm, respectively. The K_2S_2 and K_2O_2 rings are twisted by 70° with respect to each other. An intrachain hydrogen-bonding system consisting of methanol···ring-N O–H···N interactions (O(20)···N(1′) 295 pm, H(20)···N(1′) 199 pm, O–H···N 168°) runs along the edges of the chains to aid the ladder formation (Figure 3), indeed one could speculate that this hydrogen bonding is necessary for the organization of the molecules into a chain structure. A further weak K···C interaction between one of the aryl rings and the potassium atoms is also present (K···C(3A) 347 K···C(4A) 348 pm) to increase the effective coordination number of the metal ion—a similar effect was noted in $K[Ph_2P(S)NP(S)Ph_2]$.[9]

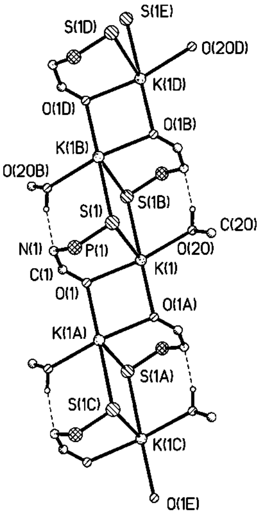


Figure 3. Structure of **2**·MeOH in the crystal showing the ladder formation in the infinite chains of alternating K_2S_2 and K_2O_2 rings. The intraring angles are: K-S-K 102.1(1), S-K-S 77.9(1), K-O-K 100.9(1), O-K-O 79.1(1)°.

Experimental Section

$PhC(O)NHP(S)Ph_2$: To a solution of $PhC(O)NH_2$ (3.2 g, 7.7 mmol) in THF (150 mL) was added Et_3N (3.9 mL, 30 mmol), DMAP (dimethylaminopyridine; 200 mg, 20 mmol), and neat Ph_2PCl (5 mL, 27.9 mmol)—the solution was heated at reflux overnight. After the mixture had been cooled, S_8 (1.78 g, 55.7 mmol) was added and the mixture was stirred overnight at room temperature. The solution was filtered and the filtrate was reduced to dryness to give a white powder. It was then triturated with Et_2O (200 mL) to give a yield of 6.43 g (34 %). M.p. 186–190 °C; ^{31}P NMR ($CDCl_3$): $\delta = 56$; IR (KBr): $\tilde{\nu}$(NH) 3159 m, 3060 w (CO) 1651 vs, (CN) 1454 vs, (PN) 880 w, 832 m, (PS) 636 vs cm^{-1}; FAB (*m/z*): 361 [*M*H+Na]$^+$, 337 [*M*H+H]$^+$: elemental analysis (%) calcd for $C_{19}H_{16}NOPS$: C 67.64, H 4.78, N 4.15; found: C 67.25, H 4.54, N 4.02.

$K[PhC(O)NP(S)Ph_2]$ **2**: A solution of $[PhC(O)NHP(S)Ph_2]$ (1 g, 2.96 mmol) and KO*t*Bu (0.57 g, 5.12 mmol) in THF (60 mL) was stirred for 30 min. The solution was filtered through celite, and then reduced to dryness to give 1.1 g (100 %) of white powder. Elemental analysis (%) calcd for $C_{19}H_{15}NOPSK$: C 60.78, H 4.03, N 3.73; found: C 60.34, H 4.12, N 3.45. Recrystallization of this compound from methanol gave **2**·MeOH. M.p. 286–290 °C. ^{31}P NMR ([D$_6$]DMSO): $\delta = 44$; IR (KBr): $\tilde{\nu}$(CN) = 1588 m, (CO) 1519 vs, (PN) 895 m, 838 s, (PS) 627 s, 612 s cm^{-1}; FAB (*m/z*): 399 [*M*H+Na]$^+$, 377 [*M*H+H]$^+$.

Received: April 7, 1998 [Z11698IE]
German version: *Angew. Chem.* **1998**, *110*, 2605–2607

Keywords: coordination modes · heterocycles · ladder structures · potassium · structure elucidation

---

[1] J. D. Woollins, *J. Chem. Soc. Dalton Trans.* **1996**, 2893–2901.

[2] R. Cea-Olivares, J. Novosad, A. M. Z. Slawin, J. D. Woollins, V. Garcia-Montalvo, G. Espinosa-Perez, P. G. Y. Garcia, *Chem. Commun.* **1996**, 519–520.

[3] A. Schmidpeter, H. Groeger, *Chem. Ber.* **1967**, *100*, 3052–3062.

[4] H. Groeger, A. Scmidpeter, *Chem. Ber.* **1967**, *100*, 3216–3224.

[5] Crystal structure analysis of **1** 0.11 × 0.11 × 0.03 mm, monoclinic, $P2_1/c$, $Z = 4$, $a = 894.2(8)$, $b = 1994(2)$, $c = 974(2)$ pm, $\beta = 100.3(1)°$, $V = 1708(4) \times 10^6$ pm^3, $\rho_{calcd} = 1.32$ g cm^{-3}, Cu$_{K\alpha}$ radiation $\lambda = 154.178$ pm, ω-scan, $T = 291$ K, 2815 measured, 2634 independent, and 962 observed reflections [$I > 1.5\sigma(I)$], absorption correction (T_{min}/T_{max}) 0.49/1.00, structure solved by direct methods and refined against F using teXsan, 209 refined parameters $R = 0.116$, R_w 0.085, residual electron density (max/min) 0.54/ – 0.48 e A^{-3}.[8b]

[6] D. Cupertino, R. W. Keyte, A. M. Z. Slawin, D. J. Williams, J. D. Woollins, *Inorg. Chem.* **1996**, *35*, 2695–2697.

[7] H. Noth, *Z. Naturforsch. B* **1982**, *37*, 1491–1498.

[8] a) Crystal structure analysis of **2**·MeOH: Crystal dimensions: 0.15 × 0.15 × 0.15 mm, monoclinic, $P2_1/c$, $Z = 4$, $a = 813.49(3)$, $b = 1202.05(4)$, $c = 2099.54(7)$ pm, $\beta = 91.705(1)°$, $V = 2052(1) \times 10^6$ pm^3, $\rho_{calcd} = 1.32$ g cm^{-3}, Mo$_{K\alpha}$ radiation $\lambda = 71.069$ pm, SMART system, hemisphere data collection using 0.3° slices, $T = 291$ K, 8793 measured, 3033 independent, and 2984 observed reflections [$I > 2\sigma(I)$], semiempirical absorption correction (T_{min}/T_{max}) 0.62/1.00, structure solved by direct methods and refined against F^2 using SHELXTL, 239 refined parameters $R = 0.0516$, R_w 0.1198, residual electron density (max./min.) 0.63/ – 0.76 e A^{-3}. b) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-101341. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[9] In $K[Ph_2P(S)NP(S)Ph_2]$ the potassium ion is formally four-coordinate and increases its coordination number to six by interaction with two phenyl rings, the K···K and S···S distances are 469 and 447 pm, respectively. A. M. Z. Slawin, J. Ward, D. J. Williams, J. D. Woollins, *J. Chem. Soc. Chem. Commun.* **1994**, 421–422.