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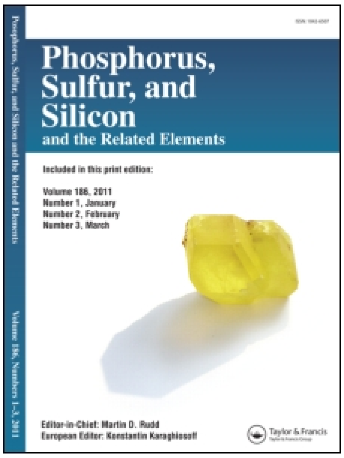

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Ring Systems Incorporating the Ambidentate Dianions $[^t\mathrm{BuN(E)P}(\mu\text{-}\mathrm{N}^t\mathrm{Bu})_2\mathrm{P(E)N}^t\mathrm{Bu}]^{2-}$ (E = S, Se)

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Ring Systems Incorporating the Ambidentate Dianions $[{}^tBuN(E)P(\mu\text{-}N^tBu)_2P(E)N^tBu]^{2-}$ (E = S, Se)

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Alkali metal derivatives of the ambidentate dianions $[{}^tBuN(E)P(\mu\text{-}N^tBu)_2P(E)N^tBu]^{2-}$(E = S, Se) are readily prepared by metallation of the diprotonated precursors with Li^tBu or $MN(SiMe_3)_2$ (M = Na, K). In the dilithiated derivative the dianion adopts a bis-chelated (N,S) bonding mode involving four-membered $\overline{\text{LiNPS}}$ rings. By contrast, the structures of disodium and dipotassium derivatives reveal a preference for the formation of six-membered $\overline{\text{MNPNPN}}$ and $\overline{\text{MEPNPE}}$ rings.

Keywords: Ambidentate ligands; P_2N_2 rings; sulfur; selenium; alkali metals

INTRODUCTION

The coordination chemistry of monoanions of the type $[R_2P(E)NP(E)R_2]^-$ (**1**) continues to be an active area of investigation.[1] The interest in metal complexes of these ligands includes their use in catalysis.[2] The dianionic bis(amide) P(III) ligand (**2**) has also been

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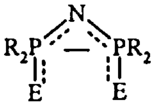
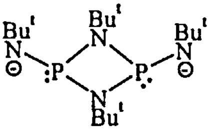
studied for possible applications in catalysis[3] and as a ligand for main group metals.[4] We describe here the synthesis and X-ray structures of the first alkali metal derivatives of the P(V) dianions **3a** and **3b**. Such ligands are of interest in view of their ability to engage in bis-chelation via either $(N,E)_2$ or N,N′/E,E′ bonding modes, both of which may generate metal-containing polymers.



1 (E = O, S, Se)



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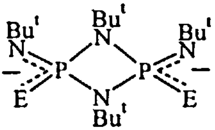
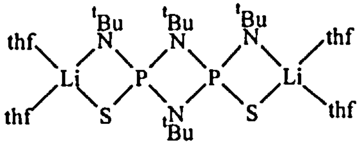


3a, E = S
3b, E = Se

The Dianions [^{t}BuN(E)P(μ-N^{t}Bu)$_2$P(E)N^{t}Bu]$^{2-}$ (E = S, Se)

The dianions **3a** and **3b** are obtained as their disodium or dipotassium salts by reaction of *cis*-[(^{t}BuNH)(E)P(μ-N^{t}Bu)$_2$P(E)(NH^{t}Bu)] (**4**) with two equiv. of $MN(SiMe_3)_2$ (M = Na, K) in THF at 23°C.[5] The corresponding dilithium derivative is prepared by heating **4** (E = S) with two equiv. of Li^{t}Bu in THF at reflux for 2 days.

The X-ray structures of five complexes of the type $[(THF)_xM]_2$[(^{t}BuN)(E)P(μ-N^{t}Bu)$_2$P(E)(N^{t}Bu)] (**5**, M = Li, E = S, x = 2; **6a**/**6b**, M = Na, E = S/Se, x = 2; **7a**, M = K, E = S, x = 1; **7b**, M = K, E = Se, x = 1.5) have been determined. In the dilithiated derivative **5** the dianion **3a** adopts a bis-chelated (N, S) bonding mode involving four-membered $\overline{\text{LiNPS}}$ rings. By contrast, the structures of **6a,b** and **7a,b** reveal a preference for the formation of six-membered $\overline{\text{MNPNPN}}$ and $\overline{\text{MEPNPE}}$ rings, i.e. bis-chelation involves N,N′ and E,E′ coordination modes for the larger alkali metal cations.



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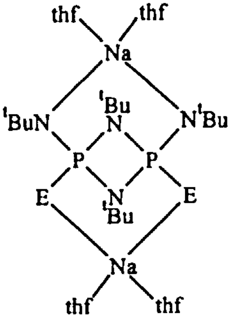

6a, E = S
6b, E = Se

The bis-solvated disodium complexes **6a** and **6b** are monomeric, but the analogous dipotassium complexes **7a** and **7b** form dimers with a central K_2E_2 ring via K• • •E interactions. The dimeric units in **7a** and **7b** associate further through weak K• • •E contacts involving the other K^+ ions and the two-coordinate Se centre of a neighbouring dimer to give an infinite network of twenty-membered $K_6E_6P_4N_4$ rings.[5]

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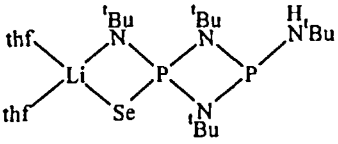
Interestingly, the reaction of **4** (E = Se) with Li^{t}Bu results in partial deselenation and the formation of the monolithiated P(III)/P(V) complex **8**.



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References

[1] For reviews, see: J.D. Woollins, *J. Chem. Soc., Dalton Trans.*, 2893 (1996); I. Haiduc, R. Cea-Olivares, S. Hernandez-Ortega and C. Silvestru, *Polyhedron*, 14, 2041 (1995).

[2] W-H. Leung, H. Zheng, J.L.C. Chim, J. Chan, W-T. Wong and I.D. Williams, *J. Chem. Soc., Dalton Trans.*, 423 (2000).

[3] L. Grocholl, L. Strahl and R.J. Staples, *Chem. Commun.*, 1465 (1997).

[4] I. Schranz, D.F. Moser, L. Stahl and R.J. Staples, *Inorg. Chem.*, **38**, 5814 (1999); L. Grocholl, I. Schranz, L. Stahl and R.J. Staples, *Inorg. Chem.*, **37**, 2496 (1998); I. Schranz, L. Stahl and R.J. Staples, *Inorg. Chem.*, **37**, 1493 (1998).

[5] T. Chivers, M. Krahn and M. Parvez, *Chem. Commun.*, 463 (2000).

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