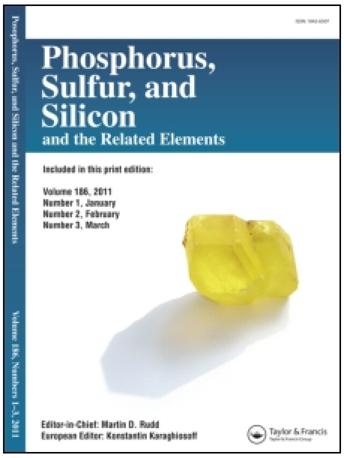

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Oxidative Addition Reactions of Cyclodiphosph(III)Azanes

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The *ansa* compound $\{[t\text{-BuN})P]_2[O\text{-}6\text{-}t\text{-Bu-}4\text{-Me-}C_6H_2]_2CH_2\}$ (2) reacts with two mole equivalents of selenium to afford the bis(seleno) compound $\{[t\text{-BuN})P(Se)]_2[O\text{-}6\text{-}t\text{-Bu-}4\text{-Me-}C_6H_2]_2CH_2\}$ (3); under analogous conditions sulfur gives the P(III)-N-P(V) derivative $\{[(t\text{-BuN})PN(t\text{-Bu})P(S)][O\text{-}6\text{-}t\text{-Bu-}4\text{-Me-}C_6H_2]_2CH_2\}$ (4). These reactions are compared with those using $[(ArO)PN(t\text{-Bu})]_2$ (5) and the macrocycle $\{[t\text{-BuN-P}]_2(OCH_2CMe_2CH_2O)\}_2$(6).

Keywords: cyclodiphosph(III)azanes; oxidative addition; X-ray structure

INTRODUCTION

Cyclodiphosph(III)azanes $[ClPNR]_2$ (**1**: R = *t*-Bu; **2**: R = Ph) and their derivatives with alcohols/ phenols $[(R'O)PNR]_2$ have two or more phosphorus centers that can be used for further oxidative addition reactions with, say, chalcogens or quinones leading to either P(V)-N-P(V) or P(III)-N-P(V) systems. In this paper we describe an interesting difference in the reactivity of

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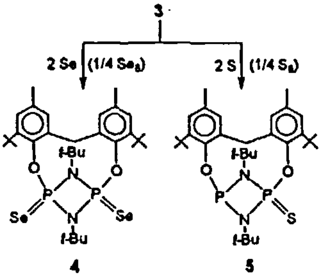
the *ansa* compound $\{[(t\text{-BuN})P]_2[O\text{-}6\text{-}t\text{-Bu-4-Me-}C_6H_2]_2CH_2\}$ (3; δ(P): 143.9)[1] with sulfur and selenium. These reactions are further compared with the ones using $[(ArO)PN(t\text{-Bu})]_2$ (6)[2] and the macrocycle $\{[t\text{-BuN-P}]_2(OCH_2CMe_2CH_2O)\}_2$ (9).[3]

RESULTS AND DISCUSSION

The *ansa* compound $\{[(t\text{-BuN})P]_2[O\text{-}6\text{-}t\text{-Bu-4-Me-}C_6H_2]_2CH_2\}$ (3) has been obtained by reacting 1 with the corresponding diol in the presence of triethylamine.[1] Reaction of 3 with two mole eq of selenium afforded the novel bis(seleno) compound $\{[(t\text{-BuN})P(Se)]_2[O\text{-}6\text{-}t\text{-Bu-4-Me-}C_6H_2]_2CH_2\}$ (4, mp 260°C, δ(P): 21.7); under the same conditions sulfur gave the P(III)-N-P(V) derivative $\{[(t\text{-BuN})PN(t\text{-Bu})P(S)][O\text{-}6\text{-}t\text{-Bu-4-Me-}C_6H_2]_2CH_2\}$ (5, mp 206-208°C, δ(P): 104.7, 48.4, ^2J = 16.0 Hz). Treatment of 3 with three mole eq of sulfur also did not yield the fully sulfurized derivative.

Scheme 3



We also reacted the bis-aryloxy derivatives $[(ArO)PN(t\text{-Bu})]_2$ (**6a**: Ar = 4-MeO-C_6H_4; **6b**: Ar = 4-t-Bu-C_6H_4)[2] with sulfur under similar conditions. Whereas **6a** gave the bis derivative $[(4\text{-MeO-}C_6H_4O)(S)PN(t\text{-Bu})]_2$ [7: δ(P) 46.2], 6b gave a mixture of mono $\{[(4\text{-}t\text{-Bu-}C_6H_4O)_2(S)(PN(t\text{-Bu}))_2]$ (8): δ(P) 109.7, 55.3. J = 17 Hz} and bis $\{[(4\text{-}t\text{-Bu-}C_6H_4O)(S)PN(t\text{-Bu})]_2$ (9): δ(P) 45.0} derivatives (ratio 2:1). These results suggest that electronic effects on the cyclophosphazane ring may also affect the relative ease of sulfurization.

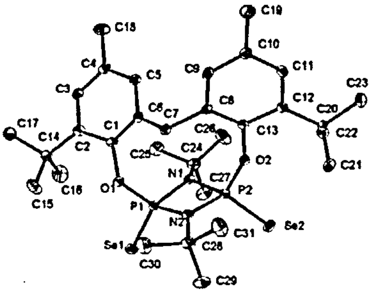


FIGURE 1. An ORTEP drawing of 4. Selected bond parameters (Å and °): P(1)-Se(1) 2.066(2), P(2)-Se(2) 2.073(2), P(1)-O(1) 1.589(4), P(2)-O(2) 1.565(3), P(1)-N(1) 1.682(4), P(2)-N(1) 1.679(4), P(1)-N(2) 1.674(4), P(2)-N(2) 1.675(4); N(2)-P(1)-N(1) 83.6(2), N(2)-P(2)-N(1) 83.6(2), P(1)-N(1)-P(2) 95.4(2), P(1)-N(2)-P(2) 95.8(2).

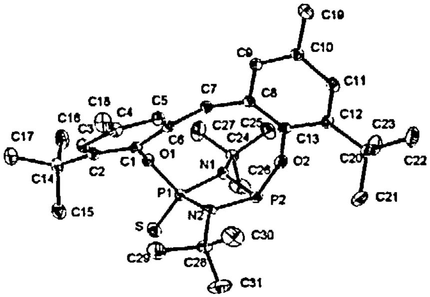
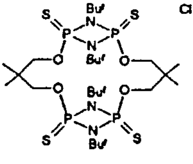


FIGURE 2. An ORTEP drawing of 5. Selected bond parameters (Å and °): P(1)-S 1.921(2), P(2)-O(2) 1.608(3), P(1)-O(1) 1.611(3), P(2)-N(1) 1.730(3), P(1)-N(1) 1.667(3), P(2)-N(2) 1.737(4), P(1)-N(2) 1.665(3); N(1)-P(1)-N(2) 85.34(17), N(1)-P(2)-N(2) 81.29(2), P(1)-N(1)-P(2) 95.62(18), P(1)-N(2)-P(2) 95.40(17).

Reaction of 1 with 2,2-dimethyl-1,3-propanediol in the presence of Et$_3$N led to a microcrystalline solid for which we now assign a structure with the composition {(OCH$_2$CMe$_2$CH$_2$O)(P-N-*t*-Bu)$_2$}$_2$.[1, 3] This solid upon reacting with the required mole equivalents of sulfur in toluene afforded the fully sulfurized macrocycle **10** [δ(P): 49.1]; reaction of $\{(OCH_2CMe_2CH_2O)(P\text{-}N\text{-}t\text{-}Bu)_2\}_2$ with two mole equivalents of *o*-chloranil afforded the symmetrical diphosphorane **11** [δ(P) 82.8 and -39.0; J = 26 Hz]. The structures of these two macrocycles have been confirmed by X-ray crystallography.



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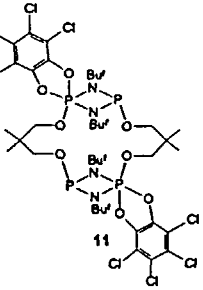

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To summarize, we have observed that elemental selenium is more effective than elemental sulfur in doubly chalcogenating cyclodiphosph(III)azane derivatives. The results are also useful for analyzing complex products formed in the reactions of **1** with difunctional reagents. It is also of interest to further investigate the chemistry of these macrocycles with respect to oxidative addition and complexation reactions.

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