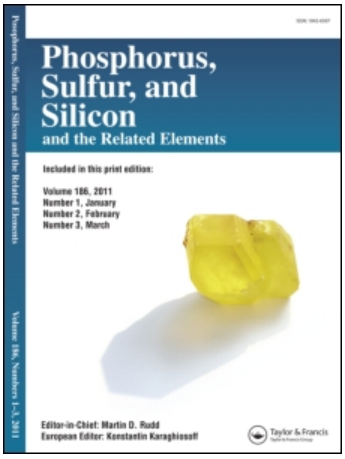

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Investigations of Compounds Containing the Four-Membered PN_2Te and Te_2N_2 Rings

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INVESTIGATIONS OF COMPOUNDS CONTAINING THE FOUR-MEMBERED PN_2Te AND Te_2N_2 RINGS: A DIMER OF A TELLURIUM DIIMIDE

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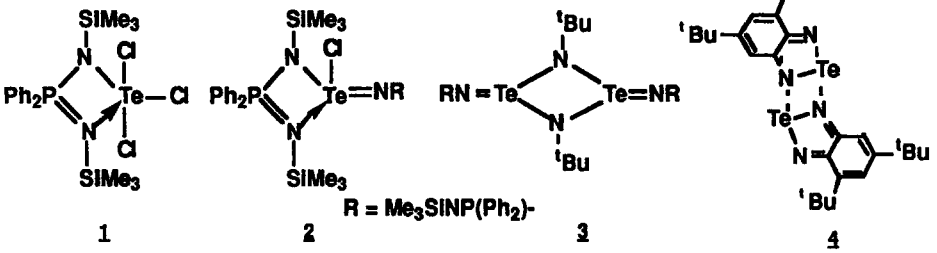
Abstract The preparation and structures of compounds containing four-membered PN_2Te rings, a dimer of tellurium diimide, and a telluradiazole are described.

INTRODUCTION

The cyclocondensation reaction of $Ph_2PN_2(SiMe_3)_3$ with (i) sulfur or selenium halides (ii) $RSeCl_3$ gives rise to eight-membered rings of the type $Ph_4P_2N_4E_2$ (E = S, Se) or $Ph_4P_2N_4Se_2R_2$ (R = Me, Et, Ph), respectively.[1] By contrast, the treatment of this reagent with $ArTeCl_3$ produces $Ph_2P(NSiMe_3)_2TeCl_2Ar$ identified as four-membered rings on the basis of NMR spectroscopic data.[2]

Tellurium diimides, like the sulfur and selenium analogues, are an important class of compounds. However, the only reported examples are the insoluble compounds formulated RN=Te=NR (R = CH_3CO, $C_6H_5SO_2$, p-$CH_3C_6H_5SO_2$) on the basis of elemental analysis.[3]

In this contribution the preparation and X-ray structures of the telluradiazaphosphetidines 1 and 2, the tellurium diimide dimer 3 and the telluradiazole 4 will be described.



R = $Me_3SiNP(Ph_2)$-

1 2 3 4

PREPARATION AND STRUCTURES OF 1 AND 2

The reaction of $TeCl_4$ with $[Ph_2P(NSiMe_3)_2]Li$ in CH_2Cl_2 resulted in the formation of 1 in quantitative yield. A similar reaction, but in a molar ratio of 1:2, produced 2 in 92% yield.

The geometry at Te in 1 is a distorted square pyramid, while in 2 it is a distorted trigonal pyramid. Both 1 and 2 have a four-membered PN_2Te ring. In both cases, one endocyclic Te-N bond is substantially longer than the other. In 2, the Te-exocyclic nitrogen bond is quite short (1.90Å) and is represented as Te=N double bond.[4] This bond is almost perpendicular to the plane defined by Te and the two cyclic nitrogen atoms.

PREPARATION AND STRUCTURES OF 3 AND 4

The reaction of 2 with ^{t}BuNHLi in toluene produced 3 in almost quantitative yield. The by-product was proved by ^{31}P NMR to be $Ph_2P(NSiMe_3)(NHSiMe_3)$, (5). The formation of 3 is proposed to occur via the replacement of Cl by ^{t}BuNH followed by the elimination of 5 to produce ^{t}BuN=Te=NR, which dimerizes to give 3.

The dimer 3 has a Te_2N_2 ring with two ^{t}BuN groups bridging the two Te atoms. The geometry at the bridging nitrogens is nearly planar. The two Te=N double bonds are almost perpendicular to the TeN_2 planes and are trans to each other.

The telluradiazole 4 is produced from the reaction of 2, 4, 6-^{t}Bu$_3$C$_6$H$_2$NHLi with 2. The dimeric structure of 4 was established by X-ray crystallograpy. There is a quite strong intermolecular interaction between Te and N (d(Te-N) = 2.628Å) as found previously for other telluradiazoles.[5]

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