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INVESTIGATIONS OF COMPOUNDS CONTAINING THE FOUR-MEMBERED PN₂Te AND Te₂N₂ RINGS: A DIMER OF A TELLURIUM DIIMIDE

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Abstract The preparation and structures of compounds containing fourmembered PN₂Te rings, a dimer of tellurium diimide, and a telluradiazole are described.

INTRODUCTION

The cyclocondensation reaction of Ph₂PN₂(SiMe₃)₃ with (i) sulfur or selenium halides (ii) RSeCl₃ gives rise to eight-membered rings of the type Ph₄P₂N₄E₂ (E = S, Se) or Ph₄P₂N₄Se₂R₂ (R = Me, Et, Ph), respectively.¹ By contrast, the treatment of this reagent with ArTeCl₃ produces Ph₂P(NSiMe₃)₂TeCl₂Ar 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 = CH₃CO, C₆H₅SO₂, p-CH₃C₆H₅SO₂) 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.

SiMe₃ SiMe₃
$$^{t}Bu$$
 ^{t}Bu t

PREPARATION AND STRUCTURES OF 1 AND 2

The reaction of TeCl₄ with [Ph₂P(NSiMe₃)₂]Li in CH₂Cl₂ 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 PN₂Te 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 ^tBuNHLi in toluene produced 3 in almost quantitative yield. The by-product was proved by ³¹P NMR to be Ph₂P(NSiMe₃)(NHSiMe₃), (5). The formation of 3 is proposed to occur via the replacement of Cl by ^tBuNH followed by the elimination of 5 to produce ^tBuN=Te=NR, which dimerizes to give 3.

The dimer 2 has a Te₂N₂ ring with two ^tBuN 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 TeN₂ planes and are trans to each other.

The telluradiazole 4 is produced from the reaction of 2, 4, 6- tBu_3C_6H_2NHLi with $\underline{2}$. 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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