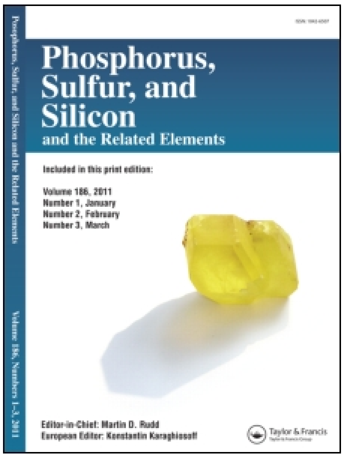

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INSERTION AND 2+2 DISMUTATION REACTIONS INCLUDING P-P, Te-Te AND Se-Se BONDS

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Abstract Reactions of diphosphanes and cyclophosphanes with selenium, tellurium and organic ditellurides have been studied

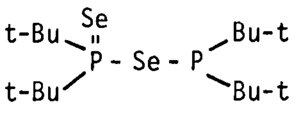
TELLURIUM AND SELENIUM INSERTION REACTIONS

The first case of an insertion of tellurium into a phosphorus-phosphorus bond was established when tetra-t-butyldiphosphane reacted with elemental tellurium in boiling toluene, leading to pure and thermally remarkably stable tellurobis(di-t-butylphosphane 1 [1]. Excess of Te never led to significant further oxidation of 1 nor to di-insertion. Differently, tetra-t-butyldiphosphane reacts with equimolar amounts of grey selenium to give two products, selenobis(di-t-butylphosphane) 2 and the diseleno species 3. 3 was isolated as pure colorless crystals, its n.m.r., i.r. and mass spectra are consistent with a non-fluxional P^{III}/P^{V} structure.

$$\text{t-Bu}_2\text{PPBu-t}_2 + \text{Te} \longrightarrow \underset{1}{\text{t-Bu}_2\text{PTeBu-t}_2} \qquad (1)$$

$$\text{t-Bu}_2\text{PPBu-t}_2 + \text{Se} \longrightarrow \underset{2}{\text{t-Bu}_2\text{PSePBu-t}_2} \qquad (2)$$

$$\downarrow \text{(+ Se)}$$



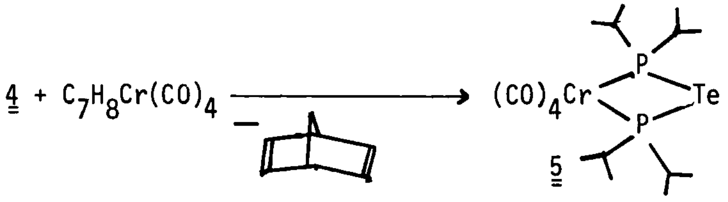
3

Pure $\underline{\underline{2}}$ was obtained from sodium selenide with di-t-butyl(chloro)-phosphane by sodium chloride elimination.

With less bulky tetraalkyldiphosphanes like tetra-i-propyl-diphosphane and tetramethyldiphosphane [2], tellurium insertion proceeds at comparatively mild conditions, but the insertion reactions remain uncomplete, leading to diphosphane/tellurobisphosphane

$$\text{i-Pr}_2\text{PPPr-i}_2 + \text{Te} \rightleftharpoons \underset{\underline{\underline{4}}}{\text{i-Pr}_2\text{PTePPr-i}_2} \qquad (3)$$

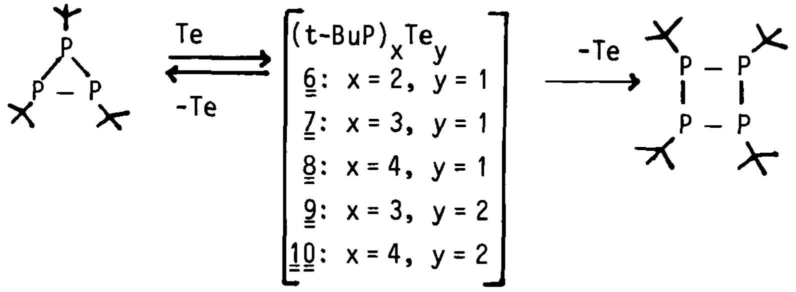
mixtures. Similarly, sodium telluride and chloro-di-i-propylphosphane react with formation of tellurobis(di-i-propylphosphane) $\underline{\underline{4}}$, but some tellurium precipitation with formation of tetra-i-propyldiphosphane appears to be inevitable. Crystallisation from pentane afforded pure yellow $\underline{\underline{4}}$ in low yield. Alternatively, $\underline{\underline{4}}$ may be trapped from its mixture with the parent diphosphane and elemental tellurium by a selective coordination reaction with tetracarbonyl(norbornadiene)chromium(0):



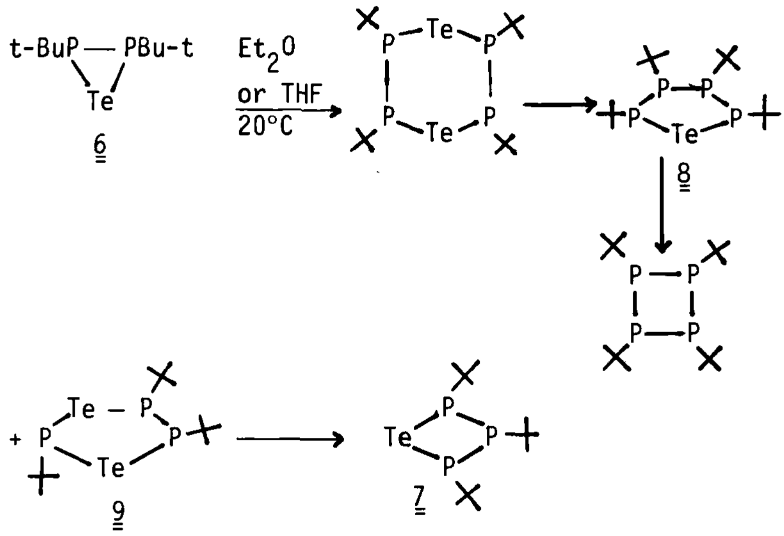
(4)

The chelate complex $\underline{\underline{5}}$ does not suffer from thermal loss of tellurium and can be purified by repeated recrystallisations.

The reaction of tri-t-butyl-cyclotriphosphane with elemental tellurium is the first case of a tellurium insertion into the P-P bond of a cyclophosphane (tetra-t-butylcyclotetraphosphane is inert towards tellurium). Primarily, ring expansion by tellurium insertion leads to $(\text{t-BuP})_3\text{Te}$ ($\underline{\underline{7}}$), but subsequently, intermolecular rearrangements lead to mixtures, that contain, inter alia, up to 10 % of the telluradiphosphirane $(\text{t-BuP})_2\text{Te}$ ($\underline{\underline{6}}$) [^{31}P-n.m.r.] and increasing amounts of $(\text{t-BuP})_4$. Detelluration of tellurocyclophosphanes leads finally to $(t\text{-BuP})_3$ (that re-inserts Te!) and $(t\text{-BuP})_4$ (that may regarded as product of a tellurium catalysed ring to ring rearrangement reaction). In a similar way, pure 6 decomposes at room temperature in THF solution with precipitation of elemental tellurium (eqn. 6).



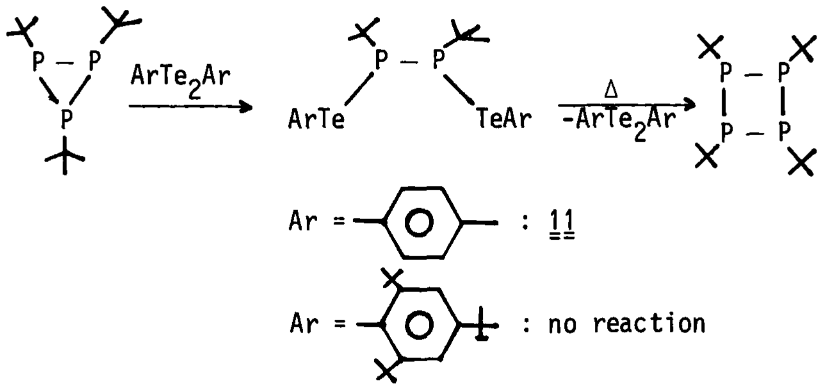
(5)



(6)

DISMUTATION REACTIONS WITH P-P BONDS

The reactivity of $(t\text{-BuP})_3$ and $(t\text{-BuP})_4$ towards elemental tellurium is very much related to their tendency to undergo 2+2 dismutation reactions with di-p-tolylditelluride. The cyclotetraphosphane does not react even under vigorous (thermal) conditions, but the cyclotriphosphane reacts smoothly at room temperature in an inert solvent. Interestingly, when the ditelluride is completely consumed (color change of the reaction mixture) by reaction with an equimolar amount of the cyclotriphosphane, the reaction product is 1,2-di-t-butyl-1,2-di-p-tolyltellurodiphosphane 11.



(7)

Highly branched alkyl substituents at phosphorus appear to favour P-Te bond formation in [>P-P< + -Te-Te- = 2 >P-Te] dismutation equilibria [3], but extremely bulky 2-,4-,6-tri-*t*-butylphenyl substituents at Te or Se disfavour 2+2 dismutation reactions. In these cases metal halide elimination reactions give better results.

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