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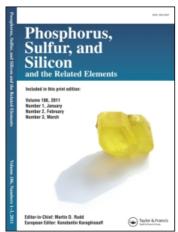
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Wolf-W. Du Mont^a; Ralph Hensel^a; Silvia Kubiniok^a; Lutz Lange^a; Tevfik Severengiz^a Fachbereich Chemie der Universität Oldenburg, Oldenburg, F.R. Germany

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

WOLF-W. DU MONT*, RALPH HENSEL, SILVIA KUBINIOK, LUTZ LANGE AND TEVFIK SEVERENGIZ Fachbereich Chemie der Universität Oldenburg Postfach 25 03, D-2900 Oldenburg, F.R. Germany

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 $\underline{1}^{[1]}$. Excess of Te never led to significant further oxidation of $\underline{1}$ nor to di-insertion. Differently, tetra-t-butyldi-phosphane reacts with equimolar amounts of grey selenium to give two products, selenobis(di-t-butylphosphane) $\underline{2}$ and the diseleno species $\underline{3}$. $\underline{3}$ 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.

$$t-Bu_2PPBu-t_2 + Te \longrightarrow t-Bu_2PTeBu-t_2$$

$$\frac{1}{2}$$
(1)

$$t-Bu_{2}PPBu-t_{2} + Se \longrightarrow t-Bu_{2}PSePBu-t_{2}$$

$$\downarrow 2 \qquad \qquad \downarrow (+ Se)$$

$$t-Bu \searrow PPBu-t_{2} \qquad \qquad \downarrow (2)$$

$$t-Bu \searrow PPBu-t_{3} \qquad \qquad \downarrow (2)$$

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

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

$$i-Pr_2PPPr-i_2 + Te \rightleftharpoons i-Pr_2PTePPr-i_2$$

$$\frac{4}{2}$$
(3)

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

$$\frac{4}{4} + C_7 H_8 Cr(CO)_4 \xrightarrow{\qquad \qquad } (CO)_4 Cr \xrightarrow{\qquad p \qquad } Te \qquad (4)$$

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

The reaction of $tri-\underline{t}$ -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 $(t-BuP)_3$ Te $(\underline{7})$, but subsequently, intermolecular rearrangements lead to mixtures, that contain, inter alia, up to 10 % of the telluradiphosphirane $(t-BuP)_2$ Te $(\underline{6})$ [31 P-n.m.r.] and increasing amounts of $(t-BuP)_4$. Detelluration of tellurocyclo-

phosphanes leads finally to $(t-BuP)_3$ (that re-inserts Te!) and $(t-BuP)_4$ (that may regarded as product of a tellurium catalysed ring to ring rearrangement reaction). In a similar way, pure $\underline{6}$ decomposes at room temperature in THF solution with precipitation of elemental tellurium (eqn. 6).

DISMUTATION REACTIONS WITH P-P BONDS

The reactivity of $(t-BuP)_3$ and $(t-BuP)_4$ towards elemental tellurium is very much related to their tendency to undergo 2+2 dismutation reactions with di-p-tolylditelluride. The cyclotetra-phosphane 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 comple-

tely consumed (color change of the reaction mixture) by reaction with an equimolar amount of the cyclotriphosphane, the reaction product is $1,2-di-t-butyl-1,2-di-p-tolyltellurodiphosphane <math>\underline{11}$.

$$ArTe = O + : \underline{11}$$

$$Ar = O + : no reaction$$

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-butyl-phenyl substituents at Te or Se disfavour 2+2 dismutation reactions. In these cases metal halide elimination reactions give better results.

REFERENCES

- W.-W. du Mont, R. Hensel and T. Severengiz Phosphorus Sulfur 18, 73 (1983)
- W.-W. du Mont and H.H. Karsch, unpublished results
- 3. W.-W. du Mont, S. Kubiniok and T. Severengiz Z.Anorg.Allg.Chem. 531, 21 (1985)