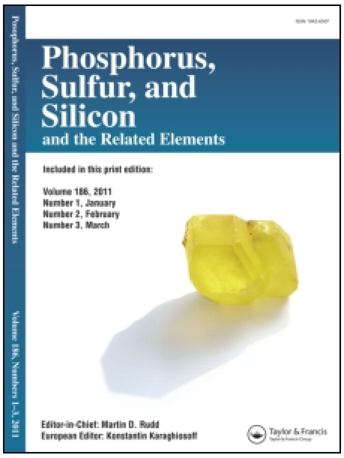

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Telluration and de-telluration: New ways for the cleavage and formation of P-P bonds

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TELLURATION AND DE-TELLURATION: NEW WAYS FOR THE CLEAVAGE AND FORMATION OF P-P BONDS

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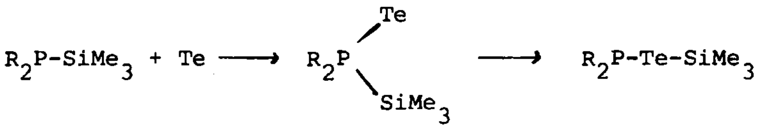
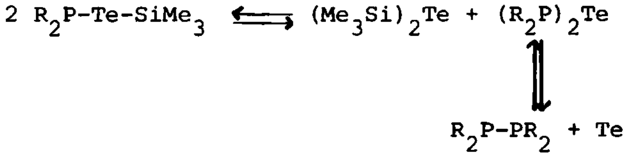
Phosphanes react with tellurium much more selectively than with oxygen, sulfur and selenium. Tertiary phosphanes give "phosphane tellurides" that can equivalently be described as coordination compounds of the phosphanes with Te(O); these are kinetically labile to (phosphane) ligand substitution reactions in the nmr time scale.[1]

$$R_3P + Te \longrightarrow R_3P\text{-}Te \xrightarrow[-\ R_3P]{R'_3P} R'_3P\text{-}Te \qquad \text{(A)}$$

Monosilylphosphanes $R_2P\text{-}SiMe_3$ do not give stable phosphane tellurides because trimethylsilyl groups migrate from P to Te, so that an overall tellurium insertion into the P-Si bond occurs. Subsequent scrambling reactions centered at Te lead to bis(trimethylsilyl)-telluride and diphosphinotellurium compounds; the latter can be de-tellurated thermally or photochemically:[2]



(B)



$$\begin{tikzcd} 2\,R_2P\text{-}Te\text{-}SiMe_3 \arrow[r, shift left] & (Me_3Si)_2Te + (R_2P)_2Te \arrow[l, shift left] \arrow[d, shift left] \\ & R_2P\text{-}PR_2 + Te \arrow[u, shift left] \end{tikzcd}$$

(C)

(D)

R = i-prop, t-bu, Ph

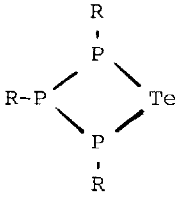
The reverse reaction of this de-telluration is the tellurium insertion in the P-P bond of certain bulky (R = t-bu, i-prop) diphosphanes. Spectroscopic techniques like ^{31}P- and ^{125}Te nmr[3] confirm P-Te-P moieties (not $\mathrm{P}\begin{smallmatrix}\diagup\!\!\!\diagup\,\mathrm{Te}\\ \diagdown\,\mathrm{P}\end{smallmatrix}$) in the novel tellurodiphosphanes. Excess of elemental tellurium does not lead tc λ^5-phosphorus functions in these compounds. Different from all other chalcogenes, Te ist not only a poor oxidation agent, but it is even a (novel) good leaving group.

A sequence of telluration and de-telluration steps (B-D) may explain the surprising reaction of t-butyl-bis-(trimethylsilyl)-phosphane with elemental tellurium under mild conditions (toluene, 20°C):

$\mathrm{RP(SiMe_3)_2 + 4/3\ Te \longrightarrow (Me_3Si)_2Te}$

R = t-bu

+ 1/3

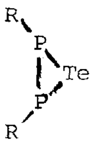


(E)

The telluratriphosphetane structure is consistent with ^{31}P nmr AM_2 and ^{125}Te nmr d,t patterns and with EI and FI mass spectra.[4]

Attempts to prepare the ditelluradiphosphetane $\mathrm{(t\text{-}BuP\text{-}Te)_2}$ lead again to precipitation of elemental tellurium and the first telluradiphosphirane was formed:

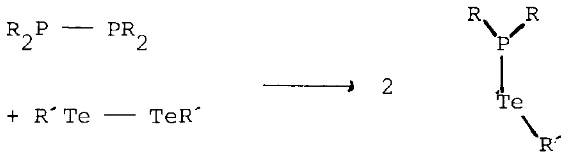
$\mathrm{2\ RPCl_2 + 2\ Na_2Te \longrightarrow Te + 2\ NaCl}$



(F)

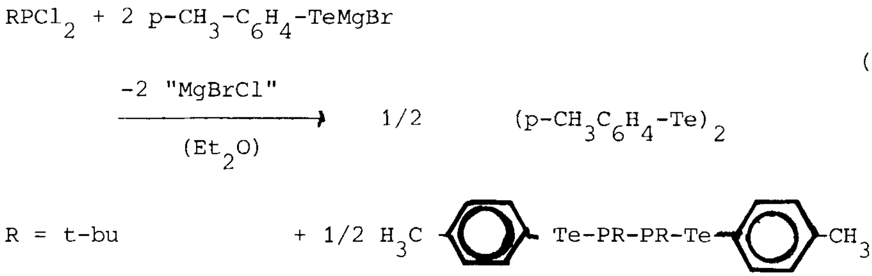
The telluratriphosphetane is a by-product of this reaction. Both compounds are also present in the reaction mixtures, when tri-t-butyltriphosphirane is heated with elemental tellurium, or when sodium telluride reacts with 1,2-di-t-butyl-1,2-dichlorodiphosphane.

The reactions of diphosphanes with elemental tellurium show certain similarities with the reactions of diphosphanes (diarsanes and distibanes) with dialkyl- or diarylditellurides, i.e. cleavage of P-P bonds and Te-Te bonds (of elemental Te or of R-Te-Te-R) and formation of P-Te bonds:



(G)

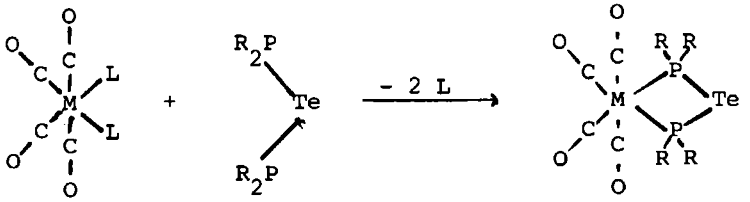
In the reverse reaction of this (2+2)dismutation the elimination of the ditelluride leads to P-P bond formation. This situation seems to be present when the preparation of the new phosphane $RP(TeR')_2$ is attempted:



(H)

The phosphane $RP(TeR')_2$ was detected by ^{31}P nmr, but only the diphosphane R'Te-PR-PR-TeR' was obtained in pure state after the work-up. This molecule with a Te-P-P-Te chain is also formed from ditolylditelluride with tri-t-butyltriphosphirane.

Tellurodiphosphanes are new interesting chelate ligands in coordination chemistry, both P and Te are typical soft donor atoms. First tellurodiphosphane chelate complexes have been obtained from telluro-bis(di-t-butylphosphane) with norbornadiene tetracarbonylchromium[5] or -molybdenum and di(acetonitrile)tetracarbonyltungsten:



(I)

M = Cr, Mo, W

R = t-bu

The phosphane acts as a bidentate chelate ligand, the structures of the complexes are consistent with the IR, ^{1}H-, ^{13}C, ^{31}P- and ^{125}Te nmr and MS data. But certain features of the complexes deserve special attention: the Cr complex is deep red, but the Mo and W complexes are pale yellow; upfield coordination shifts are observed in all cases in ^{31}P nmr, and downfield "coordination" shifts in ^{125}Te nmr; the ^{125}Te ^{3} shifts are significantly dependent on the nature of the transition metal, the order of ^{125}Te de-shielding is (M =) Cr > Mo > W. Attempts to include Te in the coordination sphere of the transition metal are in progress, as well as a study of the reactivity of the coordinated ligand towards oxidizing agents and lewis acids.

REFERENCES

1. W.-W. du Mont, H.-J. Kroth, J.Organometal.Chem. 113, C 35 (1976)
2. W.-W. du Mont, Angew.Chem.Int.Ed. 19, 554 (1980)
3. W.-W. du Mont, H.-J. Kroth, Z.Naturforsch. 36b, 332 (1980)
4. W.-W. du Mont, B. Meyer, T. Severengiz, Submitted to Angew. Chem. (1983)
5. W.-W. du Mont, E. Nordhoff, J.Organometal.Chem. 198, C 58 (1980)