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An Unusual Ditelluride: Synthesis, Molecular and Electronic Structures of The Dimer of The Tellurium-Centered Radical [TePiPr₂NiPr₂PTe][•]**

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The coordination chemistry of diselenoimidodiphosphinate ligands $[\text{SePR}_2\text{NR}_2\text{PSe}]^-$ (**1a** and **1b**)^[1] has been extensively investigated.^[2] In a series of recent articles, O'Brien and co-workers have demonstrated that metal complexes of the *iso*-propyl derivative **1b** are suitable single-source precursors for the generation of thin semi-conducting films, e.g., MSe ($\text{M} = \text{Zn}, \text{Cd}$),^[3] HgSe ,^[4] M_2Se_3 ($\text{M} = \text{Ga}, \text{In}$),^[5] PbSe ,^[6] Bi_2Se_3 ,^[7] and CuInSe_2 ,^[8] as well as CdSe quantum dots.^[9] The analogous tellurium-containing ligands were not available until recently when we described a new synthetic methodology that facilitated the generation of the phenyl derivative **1c**.^[10] Since a reasonably high volatility is needed for metal complexes in CVD applications, we turned our attention to the synthesis of the *iso*-propyl analogue **1d** and its protonated precursor (**2**). We report here that the attempted synthesis of **2** unexpectedly produced the dimer **3**, which can be viewed to result from the association of two tellurium-centered radicals $[\text{TePiPr}_2\text{NiPr}_2\text{PTe}]^\bullet$. The monotelluride **4** is obtained as the P-H tautomer $\text{HPiPr}_2\text{NiPr}_2\text{PTe}$ (**4a**) rather than the N-H tautomer **4b**.

The reaction of $\text{PiPr}_2\text{NH}i\text{Pr}_2\text{P}$ with one equivalent of tellurium in *n*-hexane at 23 °C produced the monotelluride **4** in 81% yield. Complex **4** was characterized in solution by NMR spectroscopy and in the solid state by IR spectroscopy and an X-ray structural determination.^[11] The NMR spectra indicated the preferential formation of the P-H tautomer **4a**; there was no indication of the presence of the N-H tautomer **4b**. The resonance for the P-H proton in the ^1H NMR spectrum appears as a doublet of doublets of multiplets located at $\delta = 6.34$, with a $^1J_{\text{P-H}}$ coupling of 443 Hz consistent with values reported for related systems.^[13-16] In the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, two mutually coupled phosphorus resonances were observed, one of which exhibits ^{125}Te satellites ($^1J_{\text{Te-P}} = 1654$ Hz). In the proton-coupled ^{31}P NMR spectrum the other resonance appears as a doublet ($^1J_{\text{P-H}}$ *ca.* 445 Hz) of multiplets. The solid-state IR spectrum of **4a** exhibits a sharp band at 2329 cm^{-1} which is in the middle of the range of values ($2200\text{-}2460\text{ cm}^{-1}$) reported for analogous compounds with a $\text{P}^{\text{V}}\text{-H}$ functionality.^[13-16]

The X-ray structure (Figure 1) confirms the assignment of **4a** as the P-H tautomer. The P-H proton was located in the electron difference map and refined. The two P-N bond distances are significantly different [P1-N1 1.622(2) vs P2-N1 1.589(2) Å]. The phosphorus-tellurium bond length of 2.3798(8) Å is similar to that observed in related compounds containing a terminal P=Te bond.^[17] The preferential formation of the P-H tautomer **4a** may be contrasted with the series of monochalcogenides PPh₂NHPh₂P(E) (E = O, S, Se), which all exist exclusively as the N-H tautomer, both in solution and in the solid state.^[18, 19] Consequently, we prepared the monoselenide by stoichiometric oxidation of PiPr₂NHiPr₂P with selenium in *n*-hexane at 23 °C. This product also exhibits the characteristic spectroscopic signatures of a P^V-H functionality, viz. a resonance centered at δ 6.49 with ¹J_{P-H} = 441 Hz in the ¹H NMR spectrum and a strong band at 2342 cm⁻¹ in the IR spectrum. Substituents which increase the basicity of the lone pair on phosphorus are known to favor the formation of the P-H tautomer in related systems, *e.g.*, HP(NMe₂)₂NPh₂S.^[16] The present results show that a change in the substituent on phosphorus from phenyl to *iso*-propyl is sufficient to tip the balance in favor of the P-H tautomer.

Attempts to oxidize both phosphorus(III) centers in PiPr₂NHiPr₂P **2** by direct reaction of tellurium to give **2** were unsuccessful under a variety of reaction conditions. During the course of these investigations it was observed that direct exposure of pale yellow solutions of **4a** to air resulted in the rapid formation of deep red solutions from which dark red, X-ray quality crystals of **3** could be grown. An X-ray structure determination revealed that **3** is the centrosymmetric dimer [TePiPr₂NPiPr₂Te-]₂ (Figure 2).^[20]

The Te-Te distance of 2.946(1) Å in **3** indicates a significantly weaker bond than that in organic ditellurides (2.72-2.76 Å)^[21] or the dianion [Te-Te]²⁻ (2.79 Å).^[22] The two phosphorus-tellurium bonds in **3** differ in length by *ca.* 0.1 Å, with the shorter distance indistinguishable from that observed for the terminal P=Te bond in **4a**. The metrical parameters of the PNP backbone in **3** and **4a** are also similar.

In the light of the structural determination, an alternative high-yield (87%) synthesis of **3** was devised involving the stoichiometric oxidation of the sodium salt of **1d** with iodine.

Complex **3** can be viewed to involve the association of two $[\text{TePiPr}_2\text{NH}i\text{Pr}_2\text{PTe}]^\bullet$ radicals via a $\text{Te}\cdots\text{Te}$ contact. In order to gain some insight into the nature of the bonding in the dimer **3**, we have carried out DFT calculations for the model system $[\text{TePMe}_2\text{NPM}_2\text{Te-}]_2$ and the corresponding radical $[\text{TePMe}_2\text{NPM}_2\text{Te}]^\bullet$.^[23] The PBE0/TZVP optimized structure for the C_i symmetric dimer is in reasonable agreement with the X-ray structure of the *i*Pr derivative **3** (Figure 2). Of particular note, the calculated Te-Te bond length is 2.954 Å, *cf.* 2.946(1) Å in **3**. The structure of $[\text{TePMe}_2\text{NPM}_2\text{Te}]^\bullet$ is C_2 symmetric and the radical has a ^2B doublet ground state. The calculated Te-P and P-N bond lengths are 2.431 Å and 1.626 Å, respectively. The \angle PNP and \angle TePN bond angles are 123.2° and 115.7°, respectively, and the dihedral angle τ TePNP is 23.8°. A comparison with the metrical parameters of the ditelluride shows the bond angles to be virtually identical, and the bond lengths and the dihedral angle to be exactly averages of the bond parameters found for the monomeric unit in the dimer.

The bonding interaction between the SOMOs of two radicals is depicted in Figure 3. The SOMO is an almost pure linear combination of tellurium p_x and p_y orbitals. Mulliken population analysis shows that the spin density distribution mirrors the composition of the SOMO and is equally distributed among both tellurium centers. The spin densities on both nitrogen and phosphorus atoms are very small, 0.004 and 0.009 respectively. In consequence, the EPR spectrum of $[\text{TePR}_2\text{NPR}_2\text{Te}]^\bullet$ is expected to show large hyperfine couplings to two tellurium atoms and only very small couplings to nitrogen and two phosphorus centers. The calculated hyperfine coupling constants validate this hypothesis; hyperfine couplings of -68.1, 4.8 and -0.8 G were obtained for ^{125}Te , ^{31}P and ^{14}N , respectively. Dissociation of the dimer **3** into the corresponding radical was not detectable by EPR spectroscopy in hexane, toluene or THF solutions within the temperature range 20-90 °C.

In view of the modest steric protection around radical centers in $[\text{TePMe}_2\text{NPM}_2\text{Te}]^\bullet$ and the composition of the spin density in the SOMO, both the ease and the direction of the dimerization are apparent (see Figure 3). However, the spatial orientation of monomers in the dimer and the multicentered nature of the radical SOMO effectively weakens the Te-Te bonding interaction in $(\text{TePR}_2\text{NR}_2\text{Te})_2$ compared to that in organic ditellurides, RTe-TeR . The calculated dimerization energy for the reaction $2[\text{TePMe}_2\text{NPM}_2\text{Te}]^\bullet \rightarrow (\text{TePMe}_2\text{NMe}_2\text{Te})_2$ is -80 kJ mol^{-1} , *cf.*, $D(\text{Te-Te} = 138 \text{ kJ mol}^{-1})$.^[27] An electron localization function (ELF)-based^[28] bonding analysis is in agreement with this result as it revealed that no pure disynaptic, bonding, valence basin can be found between Te1 and Te1A. This indicates a Te-Te covalent bond order of less than one for $(\text{TePMe}_2\text{NMe}_2\text{Te})_2$. Calculations done for the $\text{R} = \text{H}$ derivative $(\text{TePH}_2\text{NH}_2\text{Te})_2$ show that the absence of organic R-groups allows the dimeric structure to deform, and a twisted C_1 symmetric structure with a Te-Te bond length of 2.802 \AA now becomes the global minima. On the other hand the predicted Te-Te distance for the *tert*-butyl derivative $(\text{TePtBu}_2\text{NtBu}_2\text{Te})_2$ is 3.010 \AA implying that the use of very bulky substituents on phosphorus may foster dissociation into the radical monomer $[\text{TePR}_2\text{NPR}_2\text{Te}]^\bullet$.

The NMR spectra for **3** exhibit broad resonances at room temperature. The broad resonance observed in the $^{31}\text{P} \{^1\text{H}\}$ NMR spectrum at $23 \text{ }^\circ\text{C}$ $\text{D}_8\text{-THF}$ resolves into two resonances at $0 \text{ }^\circ\text{C}$, that sharpen into mutually coupled doublets (δ 45.8 and 42.2) at $-60 \text{ }^\circ\text{C}$. Each resonance exhibits ^{125}Te satellites. The magnitude of the $^1J_{\text{Te-P}}$ coupling constants differs substantially (1500 vs 1026 Hz) reflecting the difference in the P-Te bond lengths. At $+80 \text{ }^\circ\text{C}$ in $\text{D}_8\text{-toluene}$, a relatively narrow resonance at δ 43 ($\Delta\omega_{1/2} \sim 80 \text{ Hz}$) with ^{125}Te tellurium satellites is observed. The value of the $^1J_{\text{Te-P}}$ (1290 Hz) is approximately the average of the two distinct coupling constants observed at $-60 \text{ }^\circ\text{C}$. Thus, the ^{31}P NMR data indicate that a rapid exchange process leading to equivalent phosphorus environments on the NMR time scale occurs above $0 \text{ }^\circ\text{C}$. Attempts to distinguish between an

intermolecular or an intermolecular exchange process by variable concentration ^{31}P NMR experiments were inconclusive as a result of the very low solubility of **3**.

In summary, the characterization of the novel ditelluride **3** represents a new aspect of the well-studied chemistry of dichalgenodiphosphate ligands. The facile formation of **3** suggests that the synthesis of potential single-source precursors of binary metal tellurides via reactions of the anionic ligand **1d** with metal halides may be accompanied by a redox transformation for certain p- or d-block metals. The dimer **3** also exemplifies a new type of reagent for the direct synthesis of ditelluroimidodiphosphate complexes by oxidative addition to electropositive metal centers, *e.g.*, upon photochemical activation.

Experimental Section

All reactions and the manipulations of products were performed under an argon atmosphere by using standard Schlenk techniques or an inert atmosphere glove box. Solvents were freshly distilled, dried and degassed prior to use. NMR spectra were obtained using a Bruker AMX 300 spectrometer. ^{125}Te NMR spectra were referenced to the external standard Te_2Ph_2 . The reagent $(\text{tmeda})\text{NaN}(\text{PiPr}_2\text{Te})_2$ was prepared by modification of the procedure reported for the corresponding phenyl derivative.^[10]

3: A solution of $(\text{tmeda})\text{NaN}(\text{PiPr}_2\text{Te})_2$ (0.204 g, 0.32 mmol) in THF (25 mL) was cooled to $-78\text{ }^\circ\text{C}$ and a cold ($-78\text{ }^\circ\text{C}$) solution of I_2 (0.040 g, 0.16 mmol) in THF (25 mL) was added dropwise via a cannula over 15 min. The resulting cherry red solution was stirred at $-78\text{ }^\circ\text{C}$ for 30 min and then warmed slowly to $23\text{ }^\circ\text{C}$, producing a deep red solution which was stirred for an additional 30 min. The solvent was removed in vacuo and the residue was dissolved in toluene and then filtered to remove NaI. Toluene was then removed in vacuo affording **3** as a dark red powder (0.138 mg, 87%). Elemental Analysis Calcd (%) for $\text{C}_{24}\text{H}_{56}\text{N}_2\text{P}_4\text{Te}_4$: C 28.62, H 5.61, N 2.78; found: C 29.07, H 5.66, N 2.64. ^1H NMR ($\text{D}_8\text{-THF}$, $23\text{ }^\circ\text{C}$): $\delta = 2.23$ [br, 4H; $\text{CH}(\text{CH}_3)_2$], 1.31 [d, $^3J(\text{H,H}) = 6\text{ Hz}$, 6H; $\text{CH}(\text{CH}_3)_2$], 1.25 [d, $^3J(\text{H,H}) = 6\text{ Hz}$, 12H; $\text{CH}(\text{CH}_3)_2$], 1.19 ppm [d, $^3J(\text{H,H}) = 6\text{ Hz}$, 6H; $\text{CH}(\text{CH}_3)_2$];

$^{31}\text{P}\{^1\text{H}\}$ NMR: $\delta = 42.4$ ppm (br). ^1H NMR (-60 °C): $\delta = 2.36$ [m, 2H; $\text{CH}(\text{CH}_3)_2$], 1.95 [m, 2H; $\text{CH}(\text{CH}_3)_2$], 1.44, 1.39, 1.30, 1.24, 1.17, 1.15, 1.11, 1.08 ppm [eight doublets, $^3J(\text{H,H}) = 6$ Hz, 3H each; $\text{CH}(\text{CH}_3)_2$]; $^{31}\text{P}\{^1\text{H}\}$ NMR: $\delta = 45.8$ (d, $^2J(\text{P,P}) = 26$ Hz, $^1J(^{125}\text{Te,P}) = 1026$ Hz), 42.2 ppm (d, $^2J(\text{P,P}) = 26$ Hz, $^1J(^{125}\text{Te,P}) = 1500$ Hz). X-ray quality crystals of **3** were grown from a THF:*n*-hexane solution.

4: To a mixture of elemental tellurium (1.20 g, 9.40 mmol) and $\text{PiPr}_2\text{NHiPr}_2\text{P}$ (2.00 g, 8.02 mmol) was added *n*-hexane (120 mL) and the solution was stirred at 23 °C for 16 h. The resulting pale yellow solution was filtered and concentrated to ca. 10 mL, causing **4** to precipitate as a pale yellow crystalline solid (2.45 g, 81%). Elemental Analysis Calcd (%) for $\text{C}_{12}\text{H}_{29}\text{NP}_2\text{Te}$: C 38.24, H 7.76, N 3.72; found: C 38.59, H 7.73, N 3.76. ^1H NMR (D_8 -toluene, 23 °C): $\delta = 6.34$ [ddm, $^1J(\text{P,H}) = 443$ Hz, $^3J(\text{P,H}) = 10$ Hz, 1H; PH], 1.86 [m, 4H; $\text{CH}(\text{CH}_3)_2$], 1.14, 1.10, 1.08, 1.04, 0.93, 0.90, 0.87, 0.84 ppm [eight doublets, $^3J(\text{H,H}) = 6$ Hz, 3H each; $\text{CH}(\text{CH}_3)_2$]; $^{31}\text{P}\{^1\text{H}\}$ NMR: $\delta = 48.2$ [d, $^2J(\text{P,P}) = 18$ Hz, $^1J(^{125}\text{Te,P}) = 1654$ Hz; $\text{P}(\text{Te})$], 44.0 ppm [d, $^2J(\text{P,P}) = 18$ Hz; PH]. $^{125}\text{Te}\{^1\text{H}\}$ NMR: $\delta = -846$ ppm [dd, $^1J(^{125}\text{Te,P}) = 1642$ Hz, $^3J(^{125}\text{Te,P}) = 13$ Hz].

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- [11] Crystal data for **3** : $C_{24}H_{56}N_2P_4Te_4$, $M_r = 1006.99$, triclinic, space group $P-1$, $a = 7.603(2)$, $b = 7.955(2)$, $c = 15.303(3)$ Å, $\alpha = 95.31(3)$, $\beta = 96.89(3)$, $\gamma = 92.90(3)^\circ$, $V = 913.1(3)$ Å³, $Z = 1$, $\rho_{\text{calcd}} = 1.831$ g cm⁻³, $\mu = 3.354$ mm⁻¹, $T = 173(2)$ K. A dark red, block-like crystal (0.10 x 0.10 x 0.06 mm³) was coated with Paratone 8277 oil and mounted on a glass fiber. Data were collected on a Nonius Kappa CCD diffractometer using MoK α radiation ($\lambda = 0.71073$ Å) using ω and ϕ scans and the data were scaled based on equivalent reflections using SCALEPACK (Nonius, B.V. 1998). The structure was solved by direct methods using the SHELX-TL V6.1 software package, and the model refined using the SHELXL-97 program.^[12] Of the 11150 reflections collected ($2\theta_{\text{max}} = 50.06^\circ$), 3201 were unique ($R_{\text{int}} = 0.062$) and used to refine 154 parameters. The molecule was well ordered and no special considerations for the refinement were necessary. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were calculated geometrically and were riding on their respective carbon atoms. Refinement was carried out on F^2 against all independent reflections by the full-matrix least-squares method and converged at $R_1 = 0.0389$ [for 2475 reflections with $I > 2\sigma(I)$] and $wR_2 = 0.0851$ (for all data).

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- [20] Crystal data for **4** : C₁₂H₂₉NP₂Te, *M*_r = 376.90, triclinic, space group *P*-1, *a* = 8.639(2), *b* = 9.001(2), *c* = 11.685(2) Å, α = 101.89(3), β = 101.12(3), γ = 91.43(3)°, *V* = 870.4(3) Å³, *Z* = 2, ρ_{calcd} = 1.438 g cm⁻³, μ = 1.874 mm⁻¹, *T* = 173(2) K. A pale yellow prismatic crystal (0.10 x 0.06 x 0.03 mm³) was coated with Paratone 8277 oil and mounted on a glass fiber. Data collection, structure solution and refinement followed the procedures outlined above for **3**. Of the 16995 reflections collected ($2\theta_{\text{max}}$ = 54.88°), 3942 were unique (*R*_{int} = 0.035) and used to refine 149 parameters. The molecule was well ordered and no special considerations for the refinement were necessary. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atom on P2 was located and refined. All other hydrogen atoms were calculated geometrically and were riding on their respective atoms. Refinement converged at *R*₁ = 0.0245 [for 3411 reflections with *I* > 2σ(*I*)] and *wR*₂ = 0.0552 (for all data). CCDC-266932 and CCDC-266933 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing

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[23] Computational details: The structures of the diamagnetic dimer (TePMe₂NMe₂Te⁻)₂ and paramagnetic monomers [TePMe₂NPMe₂Te][•] were optimized in their ground states using density functional theory and the hybrid PBE0 exchange-correlation functional.^[24] The calculations utilized the Ahlrichs' triple-zeta valence basis set augmented by one set of polarization functions (TZVP); for tellurium, the corresponding ECP basis set was used. Hyperfine coupling constants were calculated for the [TePMe₂NPMe₂Te][•] radical by a single point calculation employing the optimized geometry, PBEPBE GGA functional,^[24] QZ4P STO basis set and a fully relativistic ZORA spin-orbit formalism. All geometry optimizations were done with the Turbomole 5.71 program package,^[25] whereas ADF 2004.01 was used in the calculation of hyperfine couplings.^[26]

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CAPTIONS TO FIGURES

Figure 1. Molecular structure of **4** with hydrogen atoms on all carbon atoms omitted for clarity. Selected bond distances (Å) and angles (°): P1-Te1 2.3798(8), P1-N1 1.622(2), P2-N1 1.589(2), P1-N1-P2 127.3(1), τ P2-N1-P1-Te1 3.2(1), τ H2D-P2-P1-Te1 30.1(1).

Figure 2. Molecular structure of **3** with hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (°) [Calculated values are given in brackets]: Te1-Te1A 2.946(1) [2.954], P1-Te1 2.489(2) [2.475], P2-Te2 2.394(2) 2.388], P1-N1 1.571(5) [1.610], P2-N1, 1.623(5) [1.642], P1-N1-P2 135.2(3) [124.5], τ P1-Te1-Te1A-P2 180.0 [180.0], τ Te1A-Te1-P1-N1 147.7 [135.1], τ Te1-P1-N1-P2 30.1 [37.7], τ P1-N1-P2-Te2 2.4 [10.0].

Figure 3. The bonding interaction between two [TePMe₂NPMe₂Te][•] SOMOs (± 0.065 isosurface level). Hydrogen atoms are omitted for clarity.

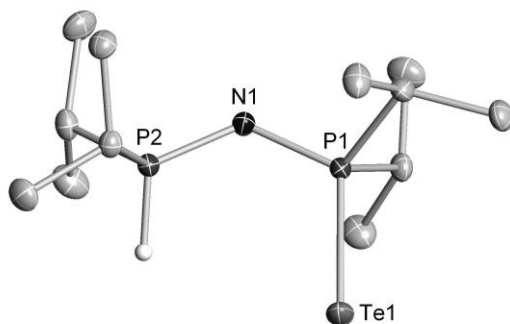


Figure 1.

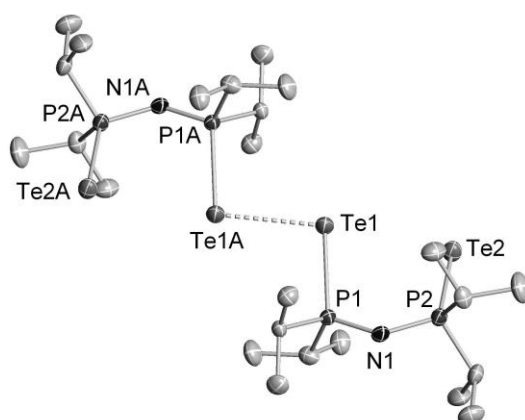


Figure 2.

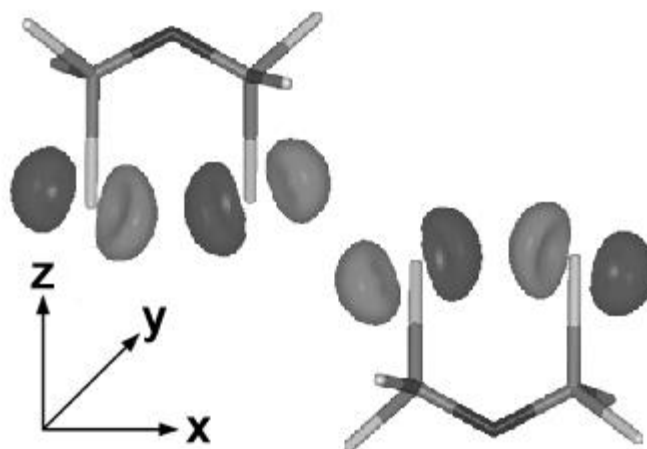
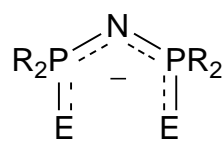


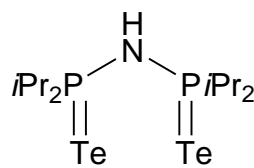
Figure 3.



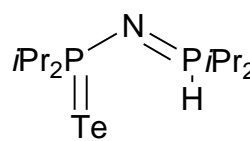
1a (E = Se, R = Ph)

1b (E = Se, R = *i*Pr)

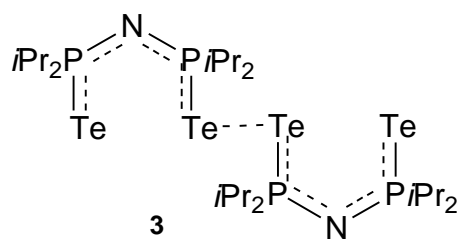
1c (E = Te, R = Ph)

1d (E = Te, R = *i*Pr)

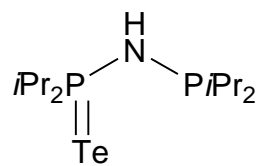
2



4a



3



4b