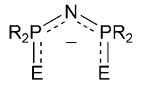
Main Group Chemistry

DOI: 10.1002/ange.200501138

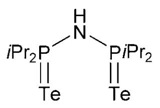
An Unusual Ditelluride: Synthesis and Molecular and Electronic Structures of the Dimer of the Tellurium-Centered Radical $[\mathrm{TeP}i\mathrm{Pr_2N}i\mathrm{Pr_2PTe}]^{\bullet}$**

Tristram Chivers, Dana J. Eisler, Jamie S. Ritch, and Heikki M. Tuononen*

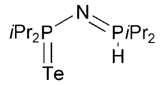
The coordination chemistry of diselenoimidodiphosphinate ligands $[\mathrm{SePR_2NR_2PSe}]^-$ (**1a** and **1b**)[1] has been extensively investigated.[2] In a series of recent articles, O'Brien and coworkers demonstrated that metal complexes of the isopropyl derivative **1b** are suitable single-source precursors for the generation of thin semiconducting films such as MSe (M = Zn, Cd),[3] HgSe,[4] M_2Se_3 (M = Ga, 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 isopropyl analogue **1d**, and its protonated precursor, **2**. We report herein 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 $[\mathrm{TeP}i\mathrm{Pr_2N}i\mathrm{Pr_2PTe}]^{\bullet}$. The monotelluride **4** is obtained as the P–H tautomer $\mathrm{HP}i\mathrm{Pr_2N}i\mathrm{Pr_2PTe}$ (**4a**) rather than the N–H tautomer **4b**.



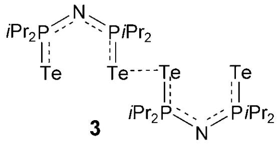
1a (E = Se, R = Ph)
1b (E = Se, R = *i*Pr)
1c (E = Te, R = Ph)
1d (E = Te, R = *i*Pr)



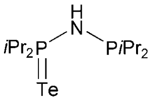
2



4a



3



4b

The reaction of $\mathrm{P}i\mathrm{Pr_2NH}i\mathrm{Pr_2P}$ with one equivalent of tellurium in *n*-hexane at 23 °C produced **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 ^{1}H NMR spectrum appears as a doublet of doublets of multiplets located at δ = 6.34 ppm, with a $^1J_{\mathrm{P,H}}$ coupling of 443 Hz, which is consistent with values reported for related systems.[13–16] In the $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum, two mutually coupled signals for phosphorus are observed, one of which exhibits ^{125}Te satellites ($^1J_{\mathrm{Te,P}}$ = 1654 Hz). In the proton-coupled ^{31}P NMR spectrum the other signal appears as a doublet ($^1J_{\mathrm{P,H}} \approx 445$ 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 (2200–2460 cm^{-1}) reported for analogous compounds with a $\mathrm{P^V}$–H functionality.[13–16]

The X-ray crystal 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 lengths are significantly different (P1–N1 1.622(2) versus P2–N1 1.589(2) Å). The phosphorus–tellurium bond length of 2.3798(8) Å is similar to that observed in related compounds that contain a terminal P=Te bond.[17] The preferential formation of the P–H tautomer, **4a**, may be contrasted with the series of monochalcogenides

---

[*] Prof. T. Chivers, Dr. D. J. Eisler, J. S. Ritch, H. M. Tuononen
Department of Chemistry
University of Calgary
Calgary, AB T2N1N4 (Canada)
Fax: (+1) 403-289-9488
E-mail: chivers@ucalgary.ca

[**] The authors gratefully acknowledge financial support from the Natural Sciences and Engineering Research Council (Canada), the Alberta Ingenuity Fund (D.J.E.), Helsingin Sanomain 100-vuotissäätiö (H.M.T.), and the University of Calgary for financial support.

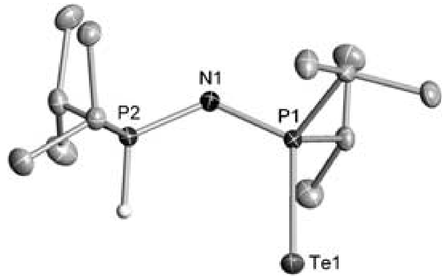


Figure 1. Molecular structure of **4** with hydrogen atoms on all carbon atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: P1-Te1 2.3798(8), P1-N1 1.622(2), P2-N1 1.589(2), P1-N1-P2 127.3(1); τ P2-N1-P1-Te1 3.2(1), τ H2D-P2-P1-Te1 30.1(1).

$PPh_2NHPh_2P(E)$ (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 P*i*Pr$_2$NH*i*Pr$_2$P with selenium in *n*-hexane at 23 °C. This product also exhibits the characteristic spectroscopic signatures of a P^V–H functionality, namely, a signal centered at $\delta = 6.49$ ppm with $^1J_{P,H} = 441$ Hz in the ^{1}H NMR spectrum and a strong band at 2342 cm^{-1} in the IR spectrum. Substituents that increase the basicity of the lone pair on the phosphorus atom are known to favor the formation of the P–H tautomer in related systems, for example, $HP(NMe_2)_2NPPh_2S$.[16] The present results show that a change in the substituent on the phosphorus atom from phenyl to isopropyl is sufficient to tip the balance in favor of the P–H tautomer.

Attempts to oxidize both phosphorus(III) centers in P*i*Pr$_2$NH*i*Pr$_2$P by the direct reaction with 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 crystal-structure determination revealed that **3** is the centrosymmetric dimer [(TeP*i*Pr$_2$NP*i*Pr$_2$Te-)$_2$] (Figure 2).[20]

The Te–Te interatomic distance of 2.946(1) Å in **3** indicates a significantly weaker bond than those in organic ditellurides (2.72–2.76 Å)[21] or that in the dianion $[Te–Te]^{2-}$ (2.79 Å).[22] The two P–Te bonds in **3** differ in length by about 0.1 Å, with the shorter separation indistinguishable from that observed for the terminal P=Te bond in **4a**. The metrical parameters of the P-N-P backbone in **3** and **4a** are also similar. In light of the structural determination, an alternative high-yield (87 %) synthesis of **3** was devised that involved the stoichiometric oxidation of the sodium salt of **1d** with iodine.

Complex **3** can be viewed as involving the association of two [TeP*i*Pr$_2$NH*i*Pr$_2$PTe]$^\bullet$ radicals through a Te···Te contact. To gain some insight into the nature of the bonding in **3**, we have carried out density functional theory (DFT) calculations for the model system $[(TePMe_2NPMe_2Te\text{-})_2]$ and the corresponding radical $[TePMe_2NPMe_2Te]^\bullet$.[23] The structure optimized with the PBE0/TZVP functions for the C_i symmetric dimer is in reasonable agreement with the X-ray crystal structure of **3** (Figure 2). Of particular note, the calculated

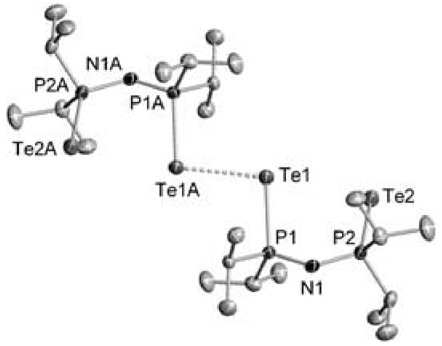


Figure 2. Molecular structure of **3** with hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°] [calculated values are given in brackets]: Te1–Te1A 2.946(1) [2.954], P1-Te1 2.489(2) [2.475], P2-Te2 2.394(2) [2.388], P1-N1 1.571(5) [1.610], P2-N1, 1.623(5) [1.642], P1-N1-P2 135.2(3) [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].

Te–Te bond length is 2.954 Å, compared with 2.946(1) Å in **3**. The structure of $[TePMe_2NPMe_2Te]^\bullet$ is C_2 symmetric and the radical has a ^{2}B doublet ground state. The calculated Te–P and P–N bond lengths are 2.431 Å and 1.626 Å, respectively. The P-N-P and Te-P-N bond angles are 123.2° and 115.7°, respectively, and the dihedral angle τ Te-P-N-P 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 singly occupied molecular orbitals (SOMOs) of two radicals is depicted in Figure 3. The SOMO is an almost pure linear combination of

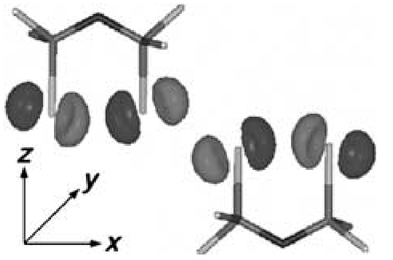


Figure 3. The bonding interaction between two $[TePMe_2NPMe_2Te]^\bullet$ SOMOs (± 0.065 isosurface level). Hydrogen atoms are omitted for clarity.

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. Consequently, the EPR spectrum of $[TePR_2NPR_2Te]^\bullet$ 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 the radical centers in $[\mathrm{TePMe_2NPMe_2Te}]^{\bullet}$ 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 $[(\mathrm{TePR_2NR_2Te}\text{-})_2]$ compared with that in organic ditellurides, RTe−TeR. The calculated dimerization energy for the reaction $2\,[\mathrm{TePMe_2NPMe_2Te}]^{\bullet} \rightarrow [(\mathrm{TePMe_2NMe_2Te}\text{-})_2]$ is $-80\ \mathrm{kJ\,mol^{-1}}$, (Te−Te, $D = 138\ \mathrm{kJ\,mol^{-1}}$).[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 finding indicates a Te−Te covalent bond order of less than one for $[(\mathrm{TePMe_2NMe_2Te}\text{-})_2]$. Calculations done for the R = H derivative $[(\mathrm{TePH_2NH_2Te}\text{-})_2]$ 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 Å now becomes the global minima. However, the predicted Te−Te bond length for the *tert*-butyl derivative $[(\mathrm{TeP}t\mathrm{Bu_2N}t\mathrm{Bu_2Te}\text{-})_2]$ is 3.010 Å, which implies that the use of very bulky substituents on the phosphorus atom may foster dissociation into the radical monomer $[\mathrm{TePR_2NPR_2Te}]^{\bullet}$.

The NMR spectra of **3** exhibit broad signals at room temperature. The broad signal observed in the ^{31}P{^{1}H} NMR spectrum at 23 °C [D$_8$]THF resolves into two signals at 0 °C, which sharpen into mutually coupled doublets ($\delta = 45.8$ and 42.2 ppm) at −60 °C. Each signal exhibits ^{125}Te satellites. The magnitude of the $^{1}J_{\mathrm{Te,P}}$ coupling constants differs substantially (1500 versus 1026 Hz), which reflects the difference in the P−Te bond lengths. At +80 °C in [D$_8$]toluene, a relatively narrow signal at $\delta = 43$ ppm ($\Delta\omega_{1/2} \approx 80$ Hz) with ^{125}Te tellurium satellites is observed. The value of the $^{1}J_{\mathrm{Te,P}}$ (1290 Hz) is approximately the average of the two distinct coupling constants observed at −60 °C. Thus, the ^{31}P NMR spectroscopic data indicate that a rapid exchange process that leads to equivalent phosphorus environments on the NMR time scale occurs above 0 °C. Attempts to distinguish between an intermolecular and an intramolecular exchange process by variable-concentration ^{31}P NMR spectroscopy 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 dichalgenoimidodiphosphinate ligands. The facile formation of **3** suggests that the synthesis of potential single-source precursors of binary metal tellurides from reactions of the anionic ligand **1d** with metal halides may be accompanied by a redox transformation for certain p- or d-block metals. Compound **3** also exemplifies a new type of reagent for the direct synthesis of ditelluroimidodiphosphinate complexes by oxidative addition to electropositive metal centers, for example, 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 by using a Bruker AMX 300 spectrometer. ^{125}Te NMR spectra were referenced to the external standard $\mathrm{Te_2Ph_2}$. The reagent $[(\mathrm{tmeda})\mathrm{NaN}(\mathrm{P}i\mathrm{Pr_2Te})_2]$ (tmeda = *N*,*N*,*N*′,*N*′-tetramethyl-1,2-ethanediamine)was prepared by modification of the procedure reported for the corresponding phenyl derivative.[10]

3: A solution of $[(\mathrm{tmeda})\mathrm{NaN}(\mathrm{P}i\mathrm{Pr_2Te})_2]$ (0.204 g, 0.32 mmol) in THF (25 mL) was cooled to −78 °C and a cold (−78 °C) solution of $\mathrm{I_2}$ (0.040 g, 0.16 mmol) in THF (25 mL) was added dropwise by cannula over 15 min. The resulting cherry red solution was stirred at −78 °C for 30 min and then warmed slowly to 23 °C to give 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 then filtered to remove NaI. Toluene was then removed in vacuo to afford **3** as a dark red powder (0.138 mg, 87 %). Elemental analysis calcd (%) for $\mathrm{C_{24}H_{56}N_2P_4Te_4}$: C 28.62, H 5.61, N 2.78; found: C 29.07, H 5.66, N 2.64; ^{1}H NMR ([D$_8$]THF, 23 °C): $\delta = 2.23$ (br, 4H; C*H*(CH$_3$)$_2$), 1.31 (d, ^{3}J(H,H) = 6 Hz, 6H; CH(C*H*$_3$)$_2$), 1.25 (d, ^{3}J(H,H) = 6 Hz, 12H; CH(C*H*$_3$)$_2$), 1.19 ppm (d, ^{3}J(H,H) = 6 Hz, 6H; CH(C*H*$_3$)$_2$); ^{31}P{^{1}H} NMR: $\delta = 42.4$ ppm (br); ^{1}H NMR (−60 °C): $\delta = 2.36$ (m, 2H; C*H*(CH$_3$)$_2$), 1.95 (m, 2H; C*H*(CH$_3$)$_2$), 1.44, 1.39, 1.30, 1.24, 1.17, 1.15, 1.11, 1.08 ppm (eight doublets, ^{3}J(H,H) = 6 Hz, 3H each; CH(C*H*$_3$)$_2$); ^{31}P{^{1}H} NMR: $\delta = 45.8$ (d, ^{2}J(P,P) = 26 Hz, ^{1}J(^{125}Te,P) = 1026 Hz), 42.2 ppm (d, ^{2}J(P,P) = 26 Hz, ^{1}J(^{125}Te,P) = 1500 Hz). X-ray quality crystals of **3** were grown from a THF/*n*-hexane solution.

4: *n*-Hexane (120 mL) was added to a mixture of elemental tellurium (1.20 g, 9.40 mmol) and $\mathrm{P}i\mathrm{Pr_2NH}i\mathrm{Pr_2P}$ (2.00 g, 8.02 mmol) and the mixture was stirred at 23 °C for 16 h. The resulting pale yellow solution was filtered and concentrated to about 10 mL, which caused **4** to precipitate as a pale yellow crystalline solid (2.45 g, 81 %). Elemental analysis calcd (%) for $\mathrm{C_{12}H_{29}NP_2Te}$: C 38.24, H 7.76, N 3.72; found: C 38.59, H 7.73, N 3.76; ^{1}H NMR ([D$_8$]toluene, 23 °C): $\delta = 6.34$ (ddm, ^{1}J(P,H) = 443 Hz, ^{3}J(P,H) = 10 Hz, 1H; PH), 1.86 (m, 4H; C*H*(CH$_3$)$_2$), 1.14, 1.10, 1.08, 1.04, 0.93, 0.90, 0.87, 0.84 ppm (eight doublets, ^{3}J(H,H) = 6 Hz, 3H each; CH(C*H*$_3$)$_2$); ^{31}P{^{1}H} NMR: $\delta = 48.2$ (d, ^{2}J(P,P) = 18 Hz, ^{1}J(^{125}Te,P) = 1654 Hz; P(Te)), 44.0 ppm (d, ^{2}J(P,P) = 18 Hz; PH); ^{125}Te{^{1}H} NMR: $\delta = -846$ ppm (dd, ^{1}J(^{125}Te,P) = 1642 Hz, ^{3}J(^{125}Te,P) = 13 Hz).

Received: March 31, 2005

Keywords: dimerization · electronic structure · phosphorus · tautomerism · tellurium

---

[1] a) D. Cupertino, D. J. Birdsall, A. M. Z. Slawin, J. D. Woollins, *Inorg. Chim. Acta* **1999**, *290*, 1; b) P. Bhattacharyya, J. Novasad, J. Phillips, A. M. Z. Slawin, D. J. Williams, J. D. Woollins, *J. Chem. Soc. Dalton Trans.* **1995**, 1607.

[2] For a review, see: C. Silvestru, J. E. Drake, *Coord. Chem. Rev.* **2001**, *223*, 117.

[3] a) M. Afzall, D. Crouch, M. A. Malik, M. Motevalli, P. O'Brien, J.-H. Park, J. D. Woollins, *Eur. J. Inorg. Chem.* **2004**, 171; b) M. Afzall, D. Crouch, M. A. Malik, M. Motevalli, P. O'Brien, J.-H. Park, *J. Mater. Chem.* **2003**, *13*, 639.

[4] D. J. Crouch, P. M. Hatton, M. Helliwell, P. O' Brien, J. Raftery, *Dalton Trans.* **2003**, 2761.

[5] J.-H. Park, M. Afzall, M. Helliwell, M. A. Malik, P. O'Brien, J. Raftery, *Chem. Mater.* **2003**, *15*, 4205.

[6] M. Afzall, K. Ellwood, N. l. Pickett, P. O'Brien, J. Raftrey, J. Waters, *J. Mater. Chem.* **2004**, *14*, 1310.

[7] a) J. Waters, D. Crouch, J. Raftery, P. O'Brien, *Chem. Mater.* **2004**, *16*, 3289; b) D. J. Crouch, M. Helliwell, P. O'Brien, J.-J. Park, J. Waters, D. J. Williams, *Dalton Trans.* **2003**, 1500.

[8] M. Afzaal, D. J. Crouch, P. O'Brien, J. Raftery, P. J. Skabara, A. J. P. White, D. J. Williams, *J. Mater. Chem.* **2004**, *14*, 233.

[9] D. J. Crouch, P. O'Brien, M. A. Malik, P. J. Skabara, S. P. Wright, *Chem. Commun.* **2003**, 1454.

[10] G. G. Briand, T. Chivers, M. Parvez, *Angew. Chem.* **2002**, *114*, 3618–3620; *Angew. Chem. Int. Ed.* **2002**, *41*, 3468.

[11] Crystal data for **3**: $C_{24}H_{56}N_2P_4Te_4$, $M_r = 1006.99$, triclinic, space group $P\bar{1}$, $a = 7.603(2)$, $b = 7.955(2)$, $c = 15.303(3)$ Å, $\alpha = 95.31(3)$, $\beta = 96.89(3)$, $\gamma = 92.90(3)°$, $V = 913.1(3)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.831\,g\,cm^{-3}$, $\mu = 3.354\,mm^{-1}$, $T = 173(2)$ K. A dark red, blocklike crystal ($0.10 \times 0.10 \times 0.06\,mm^3$) was coated with Paratone 8277 oil and mounted on a glass fiber. Data were collected on a Nonius Kappa CCD diffractometer with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) and with ω and ϕ scans and the data were scaled based on equivalent reflections by using SCALEPACK (Nonius, B.V. 1998). The structure was solved by direct methods by using the SHELX-TL V6.1 program and the model refined by using the SHELXL-97 program.[12] Of the 11150 reflections collected ($2\theta_{max} = 50.06°$), 3201 were unique ($R_{int} = 0.062$) 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).

[12] G. M. Sheldrick, SHELXL-97, Program for refinement of crystal structures, University of Göttingen, Göttingen (Germany), **1997**.

[13] L. T. Burke, E. Hevia-Freire, R. Holland, J. C. Jeffery, A. P. Leedham, C. A. Russell, A. Steiner, A. Zagorski, *Chem. Commun.* **2000**, 1769.

[14] N. Burford, J. A. C. Clyburne, S. Mason, J. F. Richardson, *Inorg. Chem.* **1993**, *32*, 4988.

[15] H. R. O'Neal, R. H. Neilson, *Inorg. Chem.* **1984**, *23*, 1372.

[16] A. Schmidpeter, H. Rossknecht, *Angew. Chem.* **1969**, *81*, 572; *Angew. Chem. Int. Ed. Engl.* **1969**, *8*, 614.

[17] G. G. Briand, T. Chivers, M. Parvez, G. Schatte, *Inorg. Chem.* **2003**, *42*, 525.

[18] P. Bhattacharyya, A. M. Z. Slawin, D. J. Williams, J. D. Woollins, *J. Chem. Soc. Dalton Trans.* **1995**, 3189.

[19] P. Bhattacharyya, A. M. Z. Slawin, M. B. Smith, J. D. Woollins, *Inorg. Chem.* **1996**, *35*, 3675.

[20] Crystal data for **4**: $C_{12}H_{29}NP_2Te$, $M_r = 376.90$, triclinic, space group $P\bar{1}$, $a = 8.639(2)$, $b = 9.001(2)$, $c = 11.685(2)$ Å, $\alpha = 101.89(3)$, $\beta = 101.12(3)$, $\gamma = 91.43(3)°$, $V = 870.4(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.438\,g\,cm^{-3}$, $\mu = 1.874\,mm^{-1}$, $T = 173(2)$ K. A pale yellow prismatic crystal ($0.10 \times 0.06 \times 0.03\,mm^3$) 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 ($2\theta_{max} = 54.88°$), 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 $I > 2\sigma(I)$) 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 from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[21] S-P. Huang, M. G. Kantzidis, *J. Am. Chem. Soc.* **1992**, *114*, 5477.

[22] P. Böttcher, J. Getszchmann, R. Keller, *Z. Anorg. Allg. Chem.* **1993**, *619*, 476.

[23] Computational details: The structures of the diamagnetic dimer $[(TePMe_2NMe_2Te\text{-})_2]$ and paramagnetic monomers $[TePMe_2NPMe_2Te]^{\bullet}$ were optimized in their ground states by using density functional theory and the hybrid PBE0 exchange-correlation functional.[24] The calculations used the Ahlrichs' triple-zeta valence basis set augmented by one set of polarization functions (TZVP); for tellurium, the corresponding effective core potential (ECP) basis set was used. Hyperfine coupling constants were calculated for the $[TePMe_2NPMe_2Te]^{\bullet}$ 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,[25] whereas ADF 2004.01 was used in the calculation of hyperfine couplings.[26]

[24] a) J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865; b) J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1997**, *78*, 1396; c) J. P. Perdew, M. Ernzerhof, K. Burke, *J. Chem. Phys.* **1996**, *105*, 9982.

[25] R. Ahlrichs, et al., TURBOMOLE, Program Package for ab initio Electronic Structure Calculations, Version 5.71, University of Karlsruhe, Karlsruhe (Germany), **2004**.

[26] ADF2004.01, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam (The Netherlands), http://www.scm.com.

[27] L. Pauling, *The Nature of the Chemical Bond*, 3rd ed. Cornell University Press, Ithaca, NY, **1960**, p. 85.

[28] For a description of ELF see A. Savin, R. Nesper, S. Wengert, T. F. Fassler, *Angew. Chem.* **1997**, *109*, 1892; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1808.