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Tellurium Compounds

Formation of Mixed-Valent Aryltellurenyl Halides RX_2TeTeR**

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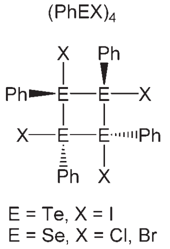
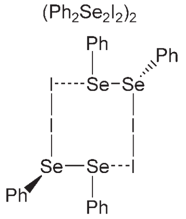
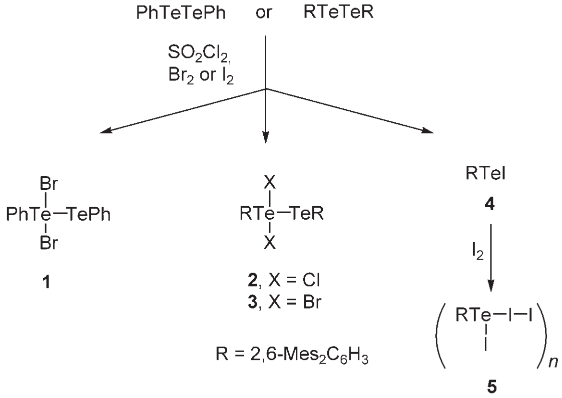
Extremely unstable sulfur difluoride, SF_2, dimerizes to give the slightly more stable mixed-valent dinuclear F_3SSF.[1] To date the only reported organic derivative of F_3SSF is $F_3CF_2SSCF_3$, which was identified during the disproportionation reaction of F_3CSF, affording F_3CSSCF_3 and F_3CSF_3.[2] While organoselenenyl(II) halides, such as PhSeX (X = Cl, Br), are more stable and often even commercially available, aryltellurenyl(II) halides, RTeX, are also intrinsically unstable and usually observed only as short-lived intermediates in halogenation reactions of diorganoditellurides, RTeTeR, or in synproportionation reactions of RTeTeR with $RTeX_3$.[3] A common decomposition pathway of aryltellurenyl(II) halides, RTeX, proceeds by migration of the organic substituents and produces diaryltellurium(IV) dihalides, R_2TeX_2, and elemental tellurium. From the decomposition of the sterically more encumbered MesTeI (Mes = 2,4,6-$Me_3C_6H_2$), the dinuclear complex $Mes_2TeTeMesI$, $MesTeI_3$, and elemental tellurium were isolated.[4] Very few kinetically stabilized aryltellurenyl(II) halides, such as 2,4,6-$t$$Bu_3C_6H_2TeX$ (X = Cl, Br, I), are known,[5] and they are monomers in the solid state. In 1974, Schulz and Klar described a number of metastable organotellurenyl halides, RTeX (e.g. R = Ph, 4-$MeOC_6H_4$, 4-PhC_6H_4; X = Br, I) containing smaller organic substituents, which on the basis of their rather poor solubility in most organic solvents and their rather dark color were presumed to have oligomeric and/or polymeric structures.[6] Recently, one of these compounds has been identified as the cyclic tetramer $(PhTeI)_4$.[7] The halogenation of PhSeSePh with Cl_2 and Br_2 produced analogous selenium tetramers $(PhSeX)_4$ (X = Cl, Br),[8] whereas the reaction with I_2 afforded a related charge transfer complex $Ph_2Se_2I_2$ having a dinuclear structure with secondary Se···I contacts.[9]





The prospect of finding novel oligomeric organotellurenyl(II) halides and related charge-transfer complexes prompted us to study the halogenation of two diarylditellurides in greater detail. The reaction of PhTeTePh with one equivalent of bromine provided the mixed-valent phenyltellurenyl bromide $PhBr_2TeTePh$ (**1**) in nearly quantitative yield, and the melting point and red-brown color are reminiscent of the compound described by Schulz and Klar (Scheme 1).[6]



Scheme 1. Synthesis of compounds **1**–**5**.

The halogenation of the sterically more encumbered compound RTeTeR (R = 2,6-$Mes_2C_6H_3$) with one equivalent of bromine or sulfuryl chloride produced the mixed-valent aryltellurenyl halides RX_2TeTeR (**2**, X = Cl; **3**, X = Br) in almost quantitative yield as blue and green crystalline materials, respectively (Scheme 1). Compounds **1**–**3** can be regarded as heavier congeners of $F_3CF_2SSCF_3$.[2] The molecular structures of **1**–**3** are shown in Figure 1 and Figure 2.[10] The Te–Te bond lengths of 2.7966(5) (**1**), 2.759(6) (**2**), and 2.7835(11) Å (**3**) are somewhat longer than those of the parent compounds PhTeTePh (2.712(2) Å)[11] and RTeTeR (2.711(1) Å, R = 2,6-$Mes_2C_6H_3$),[12] whereas the average Te–Cl and Te–Br bond lengths 2.517(5) and 2.695(2) Å compare well with those of Ph_2TeCl_2 (2.505(3) Å) and Ph_2TeBr_2 (2.6818(6) Å), respectively.[13] In the crystal lattice, individual molecules of $PhBr_2TeTePh$ (**1**) are associated by intermolecular Te···Br interactions of 3.328(4) Å that may explain the darker color and poorer solubility when compared to **2** and **3**, which lack similar contacts.

The reaction of RTeTeR (R = 2,6-$Mes_2C_6H_3$) with one and with three equivalents of iodine afforded 2,6-$Mes_2C_6H_3TeI$ (**4**)

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[**] X = Cl, Br; R = Ph, 2,6-$Mes_2C_6H_3$; Mes = 2,4,6-$Me_3C_6H_2$. We thank Mrs. Irene Brüdgam (Freie Universität Berlin) for the X-ray data collection. The Deutsche Forschungsgemeinschaft (DFG) is gratefully acknowledged for financial support.

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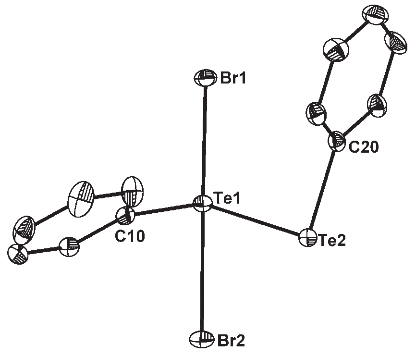

Figure 1. Molecular structure of PhBr$_2$TeTePh (**1**) with thermal ellipsoids set at 30% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Te1-C10 2.132(4), Te1-Br1 2.5995(6), Te1-Br2 2.7842(6), Te1-Te2 2.7966(5), Te2-C20 2.108(3); C10-Te1-Te2 98.52(10), C20-Te2-Te1 97.19(9), Br1-Te1-C10 90.73(9), Br1-Te1-Te2 96.98(2), Br2-Te1-C10 87.69(9), Br2-Te1-Te2 80.299(15), Br1-Te1-Br2 176.61(2), C10-Te1-Te2-C20 98.19(14).

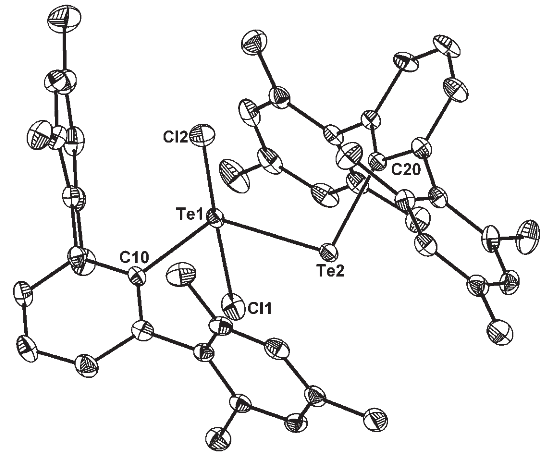

Figure 2. Molecular structure of RCl$_2$TeTeR (**2**, R = 2,6-Mes$_2$C$_6$H$_3$) with thermal ellipsoids set at 30% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Te1-C10 2.159(5), Te1-Cl1 2.498(5), Te1-Cl2 2.536(4), Te1-Te2 2.759(6), Te2-C20 2.149(5); C10-Te1-Te2 109.39(12), C20-Te2-Te1 96.35(12), Cl1-Te1-C10 86.68(11), Cl1-Te1-Te2 89.25(3), Cl2-Te1-C10 91.83(11), Cl2-Te1-Te2 86.08(3), Cl2-Te1-Cl1 174.33(4), C10-Te1-Te2-C20 154.71(16). The molecular structure of RBr$_2$TeTeR (**3**, R = 2,6-Mes$_2$C$_6$H$_3$) is almost identical. Selected bond lengths [Å] and angles [°]: Te1-C10 2.186(9), Te1-Br1 2.7011(15), Te1-Br2 2.6928(15), Te1-Te2 2.7835(11), Te2-C20 2.156(9); C10-Te1-Te2 109.2(2), C20-Te2-Te1 98.6(2), Br1-Te1-C10 87.8(2), Br1-Te1-Te2 87.53(3), Br2-Te1-C10 91.2(2), Br2-Te1-Te2 85.67(3), Br2-Te1-Br1 172.43(4), C10-Te1-Te2-C20 155.0(4).

and the charge transfer complex 2,6-Mes$_2$C$_6$H$_3$TeI···I$_2$ (**5**), respectively, as crystalline materials (Scheme 1). Complex **4** is a green solid similar to **3**, whereas the color of the charge-transfer complex **5** is red in the transmitted light of the microscope, but green with an intense metallic luster under reflective daylight (pleochroism). The molecular structures of **4** and **5** are shown in Figure 3 and Figure 4.[10] In the solid state, two molecules of **4** form a centrosymmetric dimer, which are associated by secondary Te···Te contacts of 4.057(2) Å. In contrast, one of the few known aryltellurenyl halides, 2,4,6-*t*Bu$_3$C$_6$H$_2$TeI, has both secondary Te···I and I···I interactions,[5b] and 2,4,6-*t*Bu$_3$C$_6$H$_2$TeX has only Te···X contacts (X = Cl, Br).[5c,d] However, similar intermolecular homoatomic (Cl···Cl) interactions were also observed in the crystal lattice of ClF.[14] The synthesis and full characterization of the tritelluride anions [(RTe)$_3$]$^-$ (R = Ph, CF$_3$)[15] and the related diiodotelluride anion [(I$_2$TeCF$_3$)]$^-$ and their similarity to the triiodide ion, I$_3^-$ have demonstrated that the RTe group has substantial pseudohalogen character, which is also evident in the charge-transfer complex **5**.

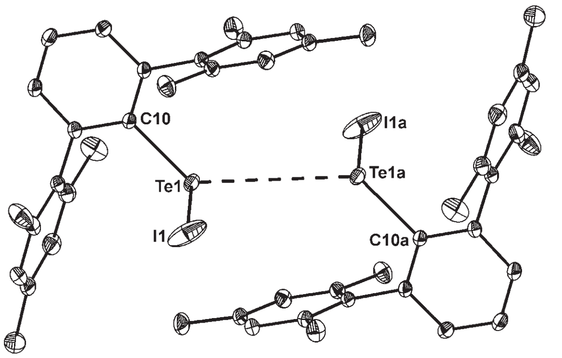

Figure 3. Molecular structure of 2,6-Mes$_2$C$_6$H$_3$TeI (**4**) with thermal ellipsoids set at 30% probability. Hydrogen atoms have been omitted for clarity. Symmetry code: *a* = −*x*, −*y*, −*z*. Selected bond lengths [Å] and angles [°]: C10-Te1 2.130(5), Te1-I1 2.676(1), Te1···Te1a 4.057(2), C10-Te1-I1 98.58(7).

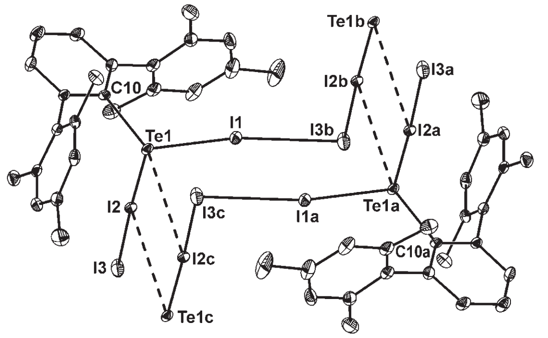

Figure 4. Molecular structure of 2,6-Mes$_2$C$_6$H$_3$TeI···I$_2$ (**5**) with thermal ellipsoids set at 30% probability. Hydrogen atoms have been omitted for clarity. Symmetry code: *b* = *x*−1, *y*, *z*; *c* = 1−*x*, −*y*, −*z*. Selected bond lengths [Å] and angles [°]: C10-Te1 2.148(5), Te1-I1 2.741(8), Te1-I2 2.839(9), I2-I3 3.003(10), I1-I3b 3.296(9); Te1···I2c 3.684(1), I1-Te1-I2 91.72(2), Te1-I2-I3 177.16(2), Te1-I1-I3b 170.97(2), I1-I3b-I2b 85.43(2).

The structure of **5** is that of a 1D coordination polymer consisting of an alternating sequences of −Te−I−I−I− chains. Adjacent 1D chains are associated by Te···I interactions (3.684(1) Å), whereas secondary I···I contacts are absent. The primary Te−I bond lengths of 2.741(8) and 2.839(9) Å are slightly longer than that of 2,6-Mes$_2$C$_6$H$_3$TeI (**4**) being 2.676(1) Å. The I−I bond lengths of 3.003(10) and 3.296(9) Å lie midway between intramolecular (2.715 Å) and intermolecular (3.496 Å) bond lengths of molecular iodine. The two Te-I-I angles are almost linear, whereas the I-I-I and the I-Te-I angles are close to right angles.

Compounds **1**–**5** are readily soluble in most common organic solvents. At −40 °C, the ^{125}Te NMR spectrum ([D$_8$]toluene) of $PhBr_2TeTePh$ (**1**) shows two equally intense, broad signals at $\delta = 1291.0$ and 823.7 ppm, which suggests that the molecular structure is retained in solution.[16] However, no spectrum of **1** was obtained at room temperature, which points to a dynamic exchange processes taking place under these conditions. The ^{125}Te NMR spectrum ($CDCl_3$) of RBr_2TeTeR (**3**, R = 2,6-Mes$_2C_6H_3$) exhibits only one sharp resonance at $\delta = 1683.8$ ppm, which is consistent with the idea that **3** undergoes a reversible, presumably entropically favored rearrangement reaction to 2,6-Mes$_2C_6H_3$TeBr (**3a**) upon dissolution.[16] The Te−Br and Te−Te bonds appear to be kinetically labile.

To estimate the relative stabilities of monomeric species REX, mixed-valent dinuclear species RX_2EER, and the disproportionation products REX_3 and REER (E = S, Se, Te; X = F, Cl, Br, I), ab initio calculations[17,18] of suitable model compounds with R = CH_3 were performed; the results are summarized in Table 1. Within the fluoride series, there is a strong thermodynamic driving force of the monomers H_3CEF (E = S, Se, Te) to undergo dimerization and disproportionation reactions to form either $H_3CF_2EECH_3$ or H_3CEF_3 and H_3CEECH_3, respectively. For both processes, the associated reaction energies per chalcogen atom (ΔE_1/ΔE_2) are almost identical and range between −11.93 and −19.44 kcal mol^{-1}, which is consistent with the observation that an equilibrium exists between F_3CSF and $F_3CF_2SSCF_3$ prior to disproportionation to F_3CSF_3 and F_3CSSCF_3.[2] Amongst all other halides, the tellurenyl species H_3CTeCl and H_3CTeBr reveal the highest propensity to undergo dimerization to form $H_3CCl_2TeTeCH_3$ ($\Delta E_1 = -12.58$ kcal mol^{-1}) and $H_3CBr_2TeTeCH_3$ ($\Delta E_1 = -11.11$ kcal mol^{-1}), respectively, while the alternative disproportion reactions are less favored ($\Delta E_2 = -8.72$ and -6.93 kcal mol^{-1}). In all remaining cases, the driving force to undergo rearrangement reactions is appears to be too small (ΔE_1, $\Delta E_2 > -10$ kcal mol^{-1}), which explains the stability of most monomeric tellurenyl iodides and selenenyl halides.[5,17]

Table 1: Zero-point-energy-corrected reaction energies per chalcogen atom of the dimerization ΔE_1 and disproportionation ΔE_2 of H_3CEX.[a]

	F	Cl	Br	I
S	−11.93 −13.40	−2.19 −0.87	−1.13 −0.06	0.05 0.27
Se	−14.42 −14.22	−6.12 −3.22	−4.50 −1.82	−8.01 −4.23
Te	−19.44 −18.74	−12.58 −8.72	−11.11 −6.93	−8.29 −4.44

[a] Upper value: ΔE_1 for dimerization, $2\,H_3CEX \rightarrow H_3CX_2EECH_3 + 2\,\Delta E_1$. Lower value: ΔE_2 for disproportionation, $3\,H_3CEX \rightarrow H_3CEX_3 + H_3CEECH_3 + 3\,\Delta E_2$. E = S, Se, Te; X = F, Cl, Br, I. Values in kcal mol^{-1}.

Experimental Section

1–**5**: A solution of the appropriate diarylditelluride (PhTeTePh: 0.410 g, 1.00 mmol for **1**, RTeTeR (R = 2,6-Mes$_2C_6H_3$):[12] 0.882 g, 1.00 mmol for **2**–**5**) in Et_2O or CH_2Cl_2 (30 mL) was cooled to 0 °C and slowly treated with the appropriate halogen or synthetic equivalent (Br_2: 160 mg, 1.00 mmol for **1**, SO_2Cl_2: 135 mg, 1.00 mmol for **2**, Br_2: 160 mg, 1.00 mmol for **3**, I_2: 253 mg, 1.00 mmol for **4**, I_2: 761 mg, 3.00 mmol for **5**). Analytically pure samples were obtained by crystallization from CH_2Cl_2/pentane (**1**), diethyl ether (**2**–**4**) and THF (**5**). Yields 550 mg, 0.96 mmol of **1** (96 %, m.p. 40 °C); 858 mg, 0.90 mmol of **2** (90 %); 990 mg, 0.95 mmol of **3** (95 %); 1.08 g, 1.90 mmol of **4** (95 %), 1.50 g, 1.82 mmol of **5** (91 %). Compounds **2**–**5** decompose without melting.

Analytical data: **1**: ^{125}Te NMR (126 MHz, [D$_8$]-toluene, −40 °C): $\delta = 1291.0$ (integral 50 %), 823.7 ppm (integral 50 %). UV (Et_2O, 0.1 mmol): $\lambda_{max} = 422$ nm. Elemental analysis (%) calcd for $C_{12}H_{10}Br_2Te_2$ (569.22 g mol^{-1}): C 25.32, H 1.77; found: C 25.19, H 1.71.

2: ^{125}Te NMR (126 MHz, $CDCl_3$): $\delta = 1374.9$ (integral 37 %), 1090.4 (integral 26 %), 1027.3 ppm (integral 37 %). UV (Et_2O, 0.1 mmol): $\lambda_{max} = 534$ nm. Elemental analysis (%) calcd for $C_{48}H_{50}Cl_2Te_2$ (953.09 g mol^{-1}): C 60.49, H 5.29; found: C 60.20, H 5.02.

3: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.37$ (t, $J = 7$ Hz, 1 H, Ar), 7.07 (d, $J = 7$ Hz, 2 H, Ph), 6.84 (s, 4 H, Mes), 2.27 (s, 6 H, CH_3), 1.99 ppm (s, 12 H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 148.2$, 139.0, 137.8, 136.4, 130.9, 128.4, 128.3, 128.0 (Ar), 21.2, 20.8 ppm (CH_3). ^{125}Te NMR (126 MHz, $CDCl_3$): $\delta = 1683.8$ ppm. UV (Et_2O, 0.1 mmol): $\lambda_{max} = 559$ nm. Elemental Analysis (%) calcd for $C_{48}H_{50}Br_2Te_2$ (1042.00 g mol^{-1}): C 55.33, H 4.84; found: C 54.95, H 4.82.

4: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.49$ (t, $J = 8$ Hz, 1 H, Ar), 7.14 (d, $J = 8$ Hz, 2 H, Ph), 6.96 (s, 4 H, Mes), 2.37 (s, 6 H, CH_3), 2.07 ppm (s, 12 H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 149.6$, 140.5, 137.6, 136.1, 130.9, 128.3, 128.0, 112.8 (Ar), 21.2, 21.0 ppm (CH_3). ^{125}Te NMR (126 MHz, $CDCl_3$): $\delta = 1018.0$ ppm. UV (Et_2O, 0.1 mmol): $\lambda_{max} = 622$ nm. Elemental analysis (%) calcd for $C_{24}H_{25}ITe$ (568.00 g mol^{-1}): C 50.75, H 4.44; found: C 50.35, H 4.41.

5: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.15$ (t, $J = 8$ Hz, 1 H, Ar), 6.98 (d, $J = 8$ Hz, 2 H, Ph), 6.95 (s, 4 H, Mes), 2.29 (s, 6 H, CH_3), 2.19 ppm (s, 12 H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 138.2$, 136.4, 135.7, 131.0, 129.0, 128.7, 127.8, 127.7, (Ar), 21.2, 21.0 ppm (CH_3). ^{125}Te NMR (126 MHz, $CDCl_3$): $\delta = 905.1$; (C_6D_6): $\delta = 945.6$ ppm. UV (toluene, 0.1 mmol): $\lambda_{max} = 496$ nm. Elemental analysis (%)calcd for $C_{24}H_{25}I_3Te$ (821.81 g mol^{-1}): C 35.08, H 3.07; found: C 35.24, H 3.32.

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[1] a) F. Seel, R. Budenz, W. Gombler, *Chem. Ber.* **1970**, *103*, 1701; b) M. V. Carlowitz, H. Oberhammer, H. Willner, J. E. Boggs, *J. Mol. Struct.* **1983**, *100*, 161.

[2] a) F. Seel, W. Gombler, *Angew. Chem.* **1969**, *81*, 789; *Angew. Chem. Int. Ed. Engl.* **1969**, *8*, 773; b) W. Gombler, *Z. Anorg. Allg. Chem.* **1978**, *439*, 193.

[3] a) W. L. Dorn, A. Knöchel, P. Schulz, G. Klar, *Z. Naturforsch. B* **1976**, *31*, 1043; b) N. W. Alcock, W. D. Harrison, *J. Chem. Soc. Dalton Trans.* **1984**, 869.

[4] G. N. Ledesma, E. S. Lang, E. M. Vázquez-López, U. Abram, *Inorg. Chem. Commun.* **2004**, *7*, 478.

[5] a) W.-W. du Mont, H. U. Meyer, S. Kubinoik, S. Pohl, W. Saak, *Chem. Ber.* **1992**, *125*, 761; b) T. M. Klapötke, B. Krumm, I.

Schwab, *Acta Crystallogr. Sect. E* **2005**, *61*, o4045; c) J. Beckmann, S. Heitz, M. Hesse, *Inorg. Chem.* **2007**, *46*, 3275; d) J. Beckmann, M. Hesse, *Acta Crystallogr. Sect. E* **2007**, *63*, o1674.

[6] a) P. Schulz, G. Klar, *Z. Naturforsch. B* **1975**, *30*, 40; b) P. Schulz, G. Klar, *Z. Naturforsch. B* **1975**, *30*, 43.

[7] a) E. S. Lang, R. M. Fernandes, Jr., E. T. Silverira, U. Abram, E. M. Vázquez-López, *Z. Anorg. Allg. Chem.* **1999**, *625*, 1401; b) P. D. Boyle, W. I. Cross, S. M. Godfrey, C. A. McAuliffe, R. G. Pritchard, S. Sarward, J. M. Sheffield, *Angew. Chem.* **2000**, *112*, 1866; *Angew. Chem. Int. Ed.* **2000**, *39*, 1796.

[8] P. D. Boyle, S. M. Godfrey, *Coord. Chem. Rev.* **2001**, *223*, 265.

[9] S. Kubiniok, W.-W. du Mont, S. Pohl, W. Saak, *Angew. Chem.* **1988**, *100*, 434; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 431.

[10] a) Crystal data for **1**: ($C_{12}H_{10}Br_2Te_2{\cdot}CH_2Cl_2$): $M_r = 651.70$, monoclinic space group $P2_1/c$, $a = 11.863(3)$, $b = 13.797(3)$, $c = 11.379(2)$ Å, $\beta = 103.615(4)°$, $V = 1810.0(6)$ Å^3, $Z = 4$, $\rho_{calcd} = 2.401$ mg m^{-3}, crystal dimensions $0.2 \times 0.1 \times 0.1$ mm^3. 19452 collected and 3386 unique reflections. After absorption correction, this and the following structures were solved by direct methods and refined anisotropically on F^2. Final residuals $R_1 = 0.0233$, $wR_2 = 0.0411$ ($I > 2\sigma(I)$); $R_1 = 0.0452$, $wR_2 = 0.0508$ (all data). GooF = 1.050, 229 parameters; b) Crystal data for **2** ($C_{48}H_{50}Cl_2Te_2$): $M_r = 953.00$, triclinic space group $P\bar{1}$, $a = 11.6979(16)$, $b = 14.1242(19)$, $c = 14.871(2)$ Å, $\alpha = 109.732(3)$, $\beta = 97.715(3)°$, $\gamma = 109.289(3)$, $V = 2097.7(5)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.509$ mg m^{-3}, crystal dimensions $0.25 \times 0.11 \times 0.08$ mm^3. 26336 collected and 8788 unique reflections. Final residuals $R_1 = 0.0402$, $wR_2 = 0.0798$ ($I > 2\sigma(I)$); $R_1 = 0.0925$, $wR_2 = 0.1068$ (all data). GooF = 1.017, 469 parameters; c) Crystal data for **3** ($C_{48}H_{50}Br_2Te_2$): $M_r = 1041.94$, monoclinic space group $P2_1/n$, $a = 12.036(5)$, $b = 27.064(11)$, $c = 13.914(5)$ Å, $\beta = 108.288(8)°$, $V = 4304(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.608$ mg m^{-3}, crystal dimensions $0.40 \times 0.16 \times 0.015$ mm^3. 34641 collected and 4882 unique reflections. Final residuals $R_1 = 0.0543$, $wR_2 = 0.1239$ ($I > 2\sigma(I)$); $R_1 = 0.1078$, $wR_2 = 0.1568$ (all data). GooF = 1.018, 469 parameters; d) Crystal data for **4** ($C_{24}H_{25}ITe$): $M_r = 567.94$, monoclinic space group $P2_1/n$, $a = 11.6436(19)$, $b = 12.6391(19)$, $c = 15.191(2)$ Å, $\beta = 92.911(4)°$, $V = 2232.7(6)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.690$ mg m^{-3}, crystal dimensions $0.55 \times 0.31 \times 0.08$ mm^3. 27262 collected and 5772 unique reflections. Final residuals $R_1 = 0.0350$, $wR_2 = 0.0925$ ($I > 2\sigma(I)$); $R_1 = 0.0437$, $wR_2 = 0.1013$ (all data). GooF = 1.050, 235 parameters; e) Crystal data for **5** ($C_{24}H_{25}I_3Te$): $M_r = 821.74$, monoclinic space group $P2_1/n$, $a = 8.263(2)$, $b = 14.659(4)$, $c = 21.186(5)$ Å, $\beta = 94.571(6)°$, $V = 2558.0(11)$ Å^3, $Z = 4$, $\rho_{calcd} = 2.134$ mg m^{-3}, crystal dimensions $0.23 \times 0.11 \times 0.04$ mm^3. 30687 collected and 5051 unique reflections. Final residuals $R_1 = 0.0460$, $wR_2 = 0.1066$ ($I > 2\sigma(I)$); $R_1 = 0.0862$, $wR_2 = 0.1251$ (all data). GooF = 1.012, 253 parameters. f) CCDC-651201 (**1**), CCDC-651202 (**2**), CCDC-651203 (**3**), CCDC-651204 (**4**), and CCDC-651205 (**5**) 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.

[11] G. Llabres, O. Dideberg, L. Dupont, *Acta Crystallogr. Sect. B* **1972**, *28*, 2438.

[12] The synthesis and molecular structure of RTeTeR (R = 2,6-$Mes_2C_6H_3$) is given in the Supporting Information.

[13] a) N. W. Alcock, W. D. Harrison, *J. Chem. Soc. Dalton Trans.* **1982**, 251; b) J. Beckmann, D. Dakternieks, A. Duthie, C. Mitchell, *Acta Crystallogr. Sect. E* **2004**, *60*, o2511.

[14] R. Boese, A. D. Boese, D. Bläser, M. Y. Antipin, A. Ellern, K. Seppelt, *Angew. Chem.* **1997**, *109*, 1538; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1489.

[15] a) A. C. Hillier, S.-Y. Liu, A. Sella, M. R. J. Elsegood, *Angew. Chem.* **1999**, *111*, 2918; *Angew. Chem. Int. Ed.* **1999**, *38*, 2745; b) D. Witthaut, K. Kirschbaum, O. Conrad, D. M. Giolando, *Organometallics* **2000**, *19*, 5238; c) H. T. M. Fischer, D. Naumann, W. Tyrra, *Chem. Eur. J.* **2006**, *12*, 2515.

[16] There is a correlation between the ^{125}Te NMR chemical shift of PhTeX (X = CN, H, Me) and the group electronegativity χ: $\delta(^{125}\mathrm{Te}) = 1689.7\chi - 3553.7$. Consequently, the expected ^{125}Te NMR chemical shift of monomeric PhTeBr is estimated to be $\delta(^{125}\mathrm{Te}) = 1431$ ppm. See Supporting Information for details.

[17] H. Poleschner, K. Seppelt, *Chem. Eur. J.* **2004**, *10*, 6565.

[18] The MP2 geometry-optimized energies including zero-point energy (ZPE) corrections were obtained using the basis sets 6-311 + G(3df,3pd) (C, H, F, Cl, Br, S, Se) and SDB-cc-pVTZ (I, Te) and partly with aug-cc-pVTZ (C, H) and aug-cc-pVTZ-pp (Se, I) with the appropriate relativistic electron core potentials (ECP). See Supporting Information for details.