Inorg. Chem. **2005**, *44*, 5254–5265

Inorganic Chemistry
Article

Kinetic and Donor Stabilization of Organotellurenyl Iodides and Azides[†]

Thomas M. Klapötke,* Burkhard Krumm, Heinrich Nöth, Juan Carlos Gálvez-Ruiz, Kurt Polborn, Ingo Schwab, and Max Suter

Chair of Inorganic Chemistry, Ludwig-Maximilian University of Munich,
Butenandtstrasse 5-13(D), D-81377 Munich, Germany

Received December 17, 2004

The first tellurium compounds containing the extremely bulky tris(phenyldimethylsilyl)methyl (Tpsi) and 2,6-bis-(2,4,6-triisopropylphenyl)phenyl (2,6-$Trip_2C_6H_3$) moieties have been synthesized and isolated. Careful oxidation of the tellurolate TpsiTeLi (**1**) resulted in the formation of the crowded ditellane $(TpsiTe)_2$ (**2**), and iodination of **2** gave the alkanetellurenyl iodide TpsiTeI (**3**). In a similar fashion, the terphenyl-substituted ditellane (2,6-$Trip_2C_6H_3Te)_2$ (**9**) and the arenetellurenyl iodide 2,6-$Trip_2C_6H_3TeI$ (**10**) were prepared. Reaction of the iodides TpsiTeI (**3**) and 2,6-$Trip_2C_6H_3TeI$ (**10**), as well as TripTeI, Mes*TeI (Trip = 2,4,6-triisopropylphenyl, Mes* = 2,4,6-tri-*tert*-butylphenyl), and the donor-stabilized 2-$Me_2NCH_2C_6H_4TeI$, with AgN_3 resulted in the formation and isolation of the corresponding tellurenyl azides $TpsiTeN_3$ (**4**), $TripTeN_3$ (**7**), Mes*TeN_3 (**8**), 2,6-$Trip_2C_6H_3TeN_3$ (**11**), and 2-$Me_2NCH_2C_6H_4TeN_3$ (**12**). Furthermore, the corresponding tris(ethyldimethylsilyl)methyl-containing (Tesi) tellurium compounds $(TesiTe)_2$, TesiTeI (**5**), and $TesiTeN_3$ (**6**) have been prepared but could not be isolated in pure form. The crystal structures of TpsiTeLi (**1**), $(TpsiTe)_2$ (**2**), $TpsiTeN_3$ (**4**), 2,6-$Trip_2C_6H_3TeI$ (**10**), 2,6-$Trip_2C_6H_3TeN_3$ (**11**), and 2-$Me_2NCH_2C_6H_4TeN_3$ (**12**) have been determined by X-ray diffraction. Additionally, computational studies of the molecules for which experimental structural data were available were performed.

Introduction

During the last years, the chemistry of covalent organotellurium azides rapidly developed covering predominantly Te(IV) azides[1-4] and most recently also Te(VI) azides.[5] Nevertheless, the first organotellurium azide, $TsiTeN_3$ (Tsi = $(Me_3Si)_3C$)), was synthesized in 1991,[6] owing its stability to the bulky alkyl substituent. Unfortunately, no structural information about TsiTeX (X = (pseudo)halide) compounds was available, leaving the existence of a monomeric $RTeN_3$ moiety uncertain. The major obstacle is the strong propensity of Tsi compounds to disorder, as shown for the unusual tritellane TsiTeTeTeTsi,[7] one of the starting materials for $TsiTeN_3$. Since tellurenyl halides RTeHal (Hal = Cl, Br, I) usually undergo rapid dismutation or disproportionation reactions, the stabilization of tellurenyl species in general can be attained by the use of either kinetical stabilization with bulky substituents or coordinating functional groups. In this fashion, some 2,4,6-$R_3C_6H_2TeHal$ (R = *i*-Pr (Trip), *t*-Bu (Mes*); Hal = Br, I)[8] and TsiTeHal (Hal = Cl, Br, I),[9] as well as several donor-stabilized tellurenyl halides, could be isolated.[10,11] To the best of our knowledge, the only

---

* To whom correspondence should be addressed. E-mail: tmk@cup.uni-muenchen.de. Fax: (+49) 89-2180-77492.

[†] This work has been presented, in part, at the International Conference on Coordination Chemistry, Merida, Mexico, July 18–23, 2004; Abstr. O-4.20.

(1) Wiberg, N.; Schwenk, G.; Schmid, K. H. *Chem. Ber.* **1972**, *105*, 1209–1215; Johnson, J. P.; MacLean, G. K.; Passmore, J.; White, P. S. *Can. J. Chem.* **1989**, *67*, 1687–1692. Magnus, P.; Roe, M. B.; Lynch, V.; Hulme, C. *J. Chem. Soc., Chem. Commun.* **1995**, 1609–1610. Klapötke, T. M.; Krumm, B.; Mayer, P.; Ruscitti, O. P. *Inorg. Chem.* **2000**, *39*, 5426–5427. Haiges, R.; Boatz, J. A.; Gerken, M.; Schneider, S.; Schroer, T.; Christe, K. O. *Angew. Chem., Int. Ed.* **2003**, *42*, 5847–5851.

(2) Klapötke, T. M.; Krumm, B.; Mayer, P.; Piotrowski, H.; Ruscitti, O. P.; Schiller, A. *Inorg. Chem.* **2002**, *41*, 1184–1193.

(3) Klapötke, T. M.; Krumm, B.; Mayer, P.; Schwab, I. *Angew. Chem., Int. Ed.* **2003**, *42*, 5843–5846.

(4) Klapötke, T. M.; Krumm, B.; Mayer, P.; Naumann, D.; Schwab, I. *J. Fluorine Chem.* **2004**, *125*, 997–1005.

(5) Klapötke, T. M.; Krumm, B.; Polborn, K.; Schwab, I. *J. Am. Chem. Soc.* **2004**, *126*, 14166–14175.

(6) Fimml, W.; Sladky, F. *Chem. Ber.* **1991**, *124*, 1131–1133.

(7) Sladky, F.; Bildstein, B.; Rieker, C.; Gieren, A.; Betz, H.; Hübner, T. *J. Chem. Soc., Chem. Commun.* **1985**, 1800–1801.

(8) Du Mont, W.-W.; Meyer, H. U.; Kubiniok, S.; Pohl, S.; Saak, W. *Chem. Ber.* **1992**, *125*, 761–766.

(9) Giselbrecht, K.; Bildstein, B.; Sladky, F. *Chem. Ber.* **1989**, *122*, 1255–1256.

(10) Sudha, N.; Singh, H. B. *Coord. Chem. Rev.* **1994**, *135/136*, 469–515.

(11) Kaur, R.; Singh, H. B.; Butcher, R. J. *Organometallics* **1995**, *14*, 4755–4763.

10.1021/ic048219s CCC: $30.25

structurally characterized organotellurenyl (pseudo)halide species without additional functional groups is the tetrameric $(PhTeI)_4$,[12] while the bulky arenetellurenyl iodide 2,4,6-$Ph_3C_6H_2TeI$ was not studied in detail.[13] The application of bulky substituents not only confers kinetical stability upon the RTeHal compounds but causes unusual structural features of the parent ditellanes as well. For both $(TsiTe)_2$[7,14] and the hypersilyl ditellane $[(Me_3Si)_3SiTe]_2$[15] an unusual green color was observed, which in both cases was attributed to a possible antiperiplanar conformation of the RTeTeR moiety, caused by the sterically demanding substituents. To gain structural insight, our interest was to introduce the promising Tpsi ($(PhMe_2Si)_3C$) and terphenyl (2,6-$Trip_2C_6H_3$) ligands[16−18] into tellurium chemistry and as well to compare to a donor-stabilized substituent, the 2-((dimethylamino)methyl)phenyl moiety 2-$Me_2NCH_2C_6H_4$.[10,19]

Results and Discussion

Ditellanes and Tellurenyl Iodides. The first step in the synthesis of ditellanes usually is the generation of RTeLi, the tellurolate (tellanide), by reaction of tellurium metal with organolithiums. This is usually accomplished in high yields, perfluorinated aryllithiums being an exception.[4] Despite the bulkiness of TpsiLi[17,20] and 2,6-$Trip_2C_6H_3Li$,[18] the insertion of activated tellurium takes place within a few hours at room temperature. Unlike the reaction of TsiLi with tellurium, for which the reported formation of the ditellurolate RTeTeLi in THF solution[7] could be confirmed (^{125}Te NMR: δ −32 and −190 ppm), TpsiLi was proven by ^{125}Te NMR not to form ditellurolates with more than 1 equiv of tellurium. The monotellurolate/tellanide TpsiTeLi (**1**; ^{125}Te NMR: δ −141 ppm), however, can be prepared in THF solution and crystallizes, in sharp contrast to TsiTeLi, after addition of saturated hydrocarbons and subsequent cooling to −25 °C as orange prisms, space group $P2_1/n$ with $Z = 4$. The lithium cations in **1** are tetrahedrally coordinated by four THF molecules; the distance to the nearest tellurium atom exceeds 6 Å (see Figure 1). Unlike the other lithium silyl and aryl tellurolates which were investigated in the solid phase until now, i.e., $(Me_3Si)_3SiTeLi{\cdot}THF$,[15] Mes*TeLi$(THF)_3$, and 2-$Me_2NCH_2C_6H_4TeLi(DME)$,[21] **1** does neither exhibit Te···Li contacts nor stabilization by coordination to Lewis bases. Similar to $[(12\text{-crown-}4)_2Li][TeSi(SiMe_3)_3]$,[22] **1** consists of discrete ion pairs with well-separated $Li(THF)_4^+$ cations and “free” tellurolate anions. Together with [*n*-BuTeLi·TMEDA]$_2$,[23] **1** is the only alkyl tellurolate structurally characterized so far, but the two compounds show completely different structures. Whereas the [*n*-BuTeLi·TMEDA]$_2$ dimer features short Te···Li coordination (2.802(6)−2.824(6) Å) similar to the above-mentioned aryl and silyl compounds, **1** is a monomer with an exposed tellurium atom, the only neighbor within 3.6 Å being the singly bonded C1(sp^3) of its Tpsi substituent. The Te1−C1 bond length of 2.270(4) Å is even larger than the Te−C distance in [*n*-BuTeLi·TMEDA]$_2$ (2.191(4) and 2.26(1) Å); all Te−C(sp^2) bond lengths in 2-$Me_2NCH_2C_6H_4TeLi(DME)$, Mes*TeLi$(THF)_3$, and $[CpFe\{C_5H_3(CH_2NMe_2)TeLi(DME)\}]$[24] (2.122(2)−2.184(4) Å) are shorter as well. All phenyl groups of the $PhMe_2Si$ subunits are oriented away from the center, obviously to minimize steric strain. Although the negatively polarized tellurium center is not completely surrounded by the Tpsi substituent and can be regarded as very soft and strongly nucleophilic, in addition to the lack of Te···Li coordination typical for other tellurolate anions, there is no indication for any kind of interaction between the phenyl or methyl groups and the tellurium atom. Of all X-ray structures containing the Tpsi substituent in this report (**1**, **2**, and **4**) in **1**, the geometrical deviations from equivalence for the $PhMe_2Si$ groups are the smallest: the C1−Si distances are very similar, the silicon atoms lie almost exactly in the planes

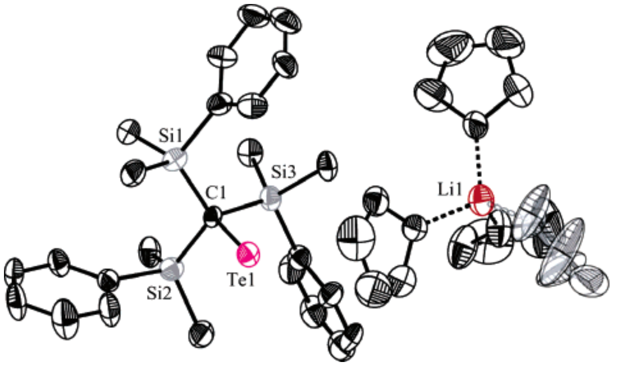


Figure 1. Molecular structure of one ion pair in $[TpsiTe][Li(THF)_4]$ (**1**), with hydrogen atoms omitted. The $TpsiTe^-$ moiety is monomeric, and the closest Te···Li approach is 6.128(5) Å. Selected bond lengths (Å) and angles (deg): Te1−C1 2.270(4), C1−Si1 1.874(5), C1−Si2 1.866(5), C1−Si3 1.884(5); Te1−C1−Si1 104.4(2), Te1−C1−Si2 105.0(2), Te1−C1−Si3 105.0(2), Si1−C1−Si2 114.4(2), Si1−C1−Si3 114.2(2), Si2−C1−Si3 112.5(2).

---

(12) Schulz Lang, E.; Fernandes, R. M., Jr.; Silveira, E. T.; Abram, U.; Vazquez-Lopez, E. M. *Z. Anorg. Allg. Chem.* **1999**, *625*, 1401−1404. Boyle, P. D.; Cross, W. I.; Godfrey, S. M.; McAuliffe, C. A.; Pritchard, R. G.; Sarwar, S.; Sheffield, J. M. *Angew. Chem., Int. Ed.* **2000**, *39*, 1796−1798.

(13) Schulz Lang, E.; Abram, U.; Strähle, J. *Z. Anorg. Allg. Chem.* **1997**, *623*, 1968−1972.

(14) Bildstein, B. Ph.D. Thesis, Leopold-Franzens-Universität, Innsbruck, Austria, 1985.

(15) Becker, G.; Klinkhammer, K. W.; Lartiges, S.; Böttcher, P.; Poll, W. *Z. Anorg. Allg. Chem.* **1992**, *613*, 7−18.

(16) Eaborn, C.; Hitchcock, P. B.; Lickiss, P. D. *J. Organomet. Chem.* **1984**, *269*, 235−238. Al-Juaid, S. S.; Dhaher, S. M.; Eaborn, C.; Hitchcock, P. B.; McGeary, C. A.; Smith, J. D. *J. Organomet. Chem.* **1989**, *366*, 39−51. Al-Juaid, S. S.; Al-Rawi, M.; Eaborn, C.; Hitchcock, P. B.; Smith, J. D. *J. Organomet. Chem.* **1998**, *564*, 215−226. Niemeyer, M.; Power, P. P. *Inorg. Chim. Acta* **1997**, *263*, 201−207. Hino, S.; Brynda, M.; Phillips, A. D.; Power, P. P. *Angew. Chem., Int. Ed.* **2004**, *43*, 2655−2658.

(17) Al-Juaid, S. S.; Eaborn, C.; Habtemariam, A.; Hitchcock, P. B.; Smith, J. D.; Tavakkoli, K.; Webb, A. D. *J. Organomet. Chem.* **1993**, *462*, 45−55.

(18) Schiemenz, B.; Power, P. P. *Organometallics* **1995**, *15*, 958−964.

(19) Manzer, L. E. *J. Am. Chem. Soc.* **1978**, *100*, 8068−8073.

(20) Eaborn, C.; Hitchcock, P. B.; Smith, J. D.; Sullivan, A. C. *J. Chem. Soc., Chem. Commun.* **1983**, 1390−1391; Eaborn, C.; Mansour, A. I. *J. Chem. Soc., Perkin Trans. 2* **1985**, 729−735. Uhl, W.; Jantschak, A.; Saak, W.; Kaupp, M.; Wartchow, R. *Organometallics* **1998**, *17*, 5009−5017.

(21) Bonasia, P. J.; Arnold, J. *J. Organomet. Chem.* **1993**, *449*, 147−157.

(22) Bonasia, P. J.; Gindelberger, D. E.; Dabbousi, B. O.; Arnold, J. *J. Am. Chem. Soc.* **1992**, *114*, 5209−5214.

(23) Clegg, W.; Davies, R. P.; Snaith, R.; Wheatley, A. E. H. *Eur. J. Inorg. Chem.* **2001**, 1411−1413.

(24) Gornitzka, H.; Besser, S.; Herbst-Irmer, R.; Kilimann, U.; Edelmann, F. T. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1260−1261.

of the phenyl rings, all three C1−Si−*ipso*-C angles are about 112°, and the Me−Si−C1−Te torsion angles are 46 and 166°, respectively.

The oxidation of **1** to the corresponding ditellane $(TpsiTe)_2$ (**2**) turned out to be difficult. Whereas most tellurolates can be obtained with several standard methods, e.g. for TsiTeLi/$(TsiTe)_2$ by pouring the tellurolate solution into ice−water followed by oxidation with air,[7,14] **1** immediately extrudes elemental tellurium upon contact with moist air. Reaction with molecular oxygen under exclusion of moisture did also not furnish the ditellane, and besides the tritellane $(TpsiTe)_2Te$, several tellurium-containing unidentified side products were detected. Alternative procedures such as reaction of **1** with $HgCl_2$ or CuCl[14,22] were not successful. After numerous attempts, the only feasible synthesis for **2** was the slow addition of iodine to freshly prepared and filtered solutions of the tellurolate **1** in THF/pentane (see eq 1), upon which a green precipitate of **2** could be obtained. In this reaction, the TpsiTeI formed by reaction of TpsiTeLi with iodine reacts with further present TpsiTeLi to form the ditellane **2**, which, compared to $(TsiTe)_2$ and the impurities present from its synthesis, is soluble in THF to a much lesser extent and can be further purified by extraction of the contaminants with pentane and MeOH.

$$\text{TpsiH} \xrightarrow[-\text{MeH}]{\text{MeLi/THF/4 h reflux}} \text{TpsiLi} \xrightarrow{+\text{Te/3 h}} \text{TpsiTeLi } (\mathbf{1}) \xrightarrow[-\text{LiI}]{+0.5\ \text{I}_2\text{/pentane/2 h}} (\text{TpsiTe})_2\ (\mathbf{2}) \quad (1)$$

Compared to $(TsiTe)_2$, which was prepared for confirmation of its reported properties,[7,14] **2** seems to be more stable than $(TsiTe)_2$ in the solid state but much more labile in solution and when exposed to daylight. Solid **2** can be stored for more than 1 year in the dark, whereas $(TsiTe)_2$ turns brown and malodorous at the same conditions due to decomposition. Solutions of **2** are only stable for a few hours at room temperature in the dark, and a single ^{125}Te NMR resonance at δ 442 ppm is found. According to ^{125}Te NMR spectroscopy, after 2 weeks in $CDCl_3$ **2** was completely decomposed into the tritellane $(TpsiTe)_2Te$ (^{125}Te NMR: δ 519, 496 ppm). Nonetheless, crystallization of **2** could be carried out by rapid evaporation of a solution in CH_2Cl_2, yielding green prisms without solvate molecules. Sublimation experiments at 30−100 °C/10^{-3}−10^{-5} mbar remained unsuccessful; above 100 °C slow decomposition occurred. The unusual green color of **2** (ditellanes usually are orange or red) already indicates a special steric arrangement.[15]

The dialkyl ditellane **2** crystallizes in green prisms in the monoclinic system, space group $P2_1/n$, with $Z = 2$ (see Figure 2). It is obvious that the molecular structure is governed by the required space of the two extremely bulky Tpsi substituents, which arrange in such a manner that the phenyl groups of the $PhMe_2Si$ moieties face the gap between two such groups of the opposite end of the molecule. Thus, it can be understood that **2** adopts a favorable antiperiplanar conformation (C_i symmetry), with the center of inversion lying between the two tellurium atoms. Since the species $(RE)_2$ (E = O, S, Se, Te) usually exhibit R−E−E−R dihedral angles around 100°, thus having nonplanar anticlinal (gauche, C_2) conformation, the antiperiplanar conformation caused by the extremely bulky Tpsi ligands in $(TpsiTe)_2$ is exceptional. The planarity of both $(2\text{-MeOC}_6H_4COTe)_2$[25] and $(3\text{-Cl-2-TeC}_5H_3N)_2$ (deep blue color)[26] most likely results from electronic influences of the substituents or functional groups, respectively; moreover $(3\text{-Cl-2-TeC}_5H_3N)_2$ features an acute C−Te−Te angle, indicating an intramolecular Te···N interaction. The only equivalent, i.e., antiperiplanar, dichalcogen derivative is the partly disordered $(TsiSe)_2$,[27] making $(TpsiTe)_2$ the only structurally characterized planar dialkyl ditellane. Furthermore, the Te−Te distance in $(TpsiTe)_2$ (2.7717(5) Å) is, to the best of our knowledge, the longest ever observed for ditellanes (Pauling's single bond length: 2.74 Å[28]), and the C1−Te−Te(*i*) angle (106.71(9)°) is somewhat widened compared to the usual angles of about 100° in other ditellanes. This reflects that the effect of the steric strain caused by the bulky substituents is superior to lone pair repulsion in **2**. Apart from a footnote in ref 9 about a slightly longer Te−Te bond (2.783 Å) in $(TsiTe)_2$, no further data regarding this structure could be found, not even in the original theses.[14,29] In contrast to **1**, the $PhMe_2Si$ groups of the ditellane **2** are far from equivalent but exhibit different

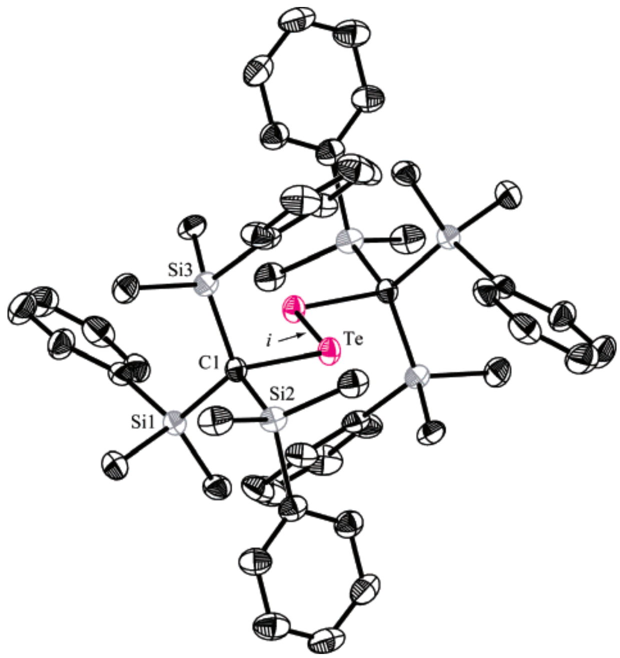


Figure 2. Molecular structure of $(TpsiTe)_2$ (**2**, C_i) with hydrogen atoms omitted, perfectly planar regarding the C−Te−Te−C moiety. Selected bond lengths (Å) and angles (deg): Te1−Te1(*i*) 2.7717(5), Te1−C1 2.221(3), C1−Si1 1.923(3), C1−Si2 1.938(1), C1−Si3 1.907(3); C1−Te1−Te1(*i*) 106.71(9), Te1−C1−Si1 112.5(2), Te1−C1−Si2 97.8(1), Te1−C1−Si3 104.9(1), Si1−C1−Si2 110.6(2), Si1−C1−Si3 116.5(2), Si2−C1−Si3 112.9(2).

---

(25) Niyomura, O.; Kato, S.; Inagaki, S. *J. Am. Chem. Soc.* **2000**, *122*, 2132−2133.

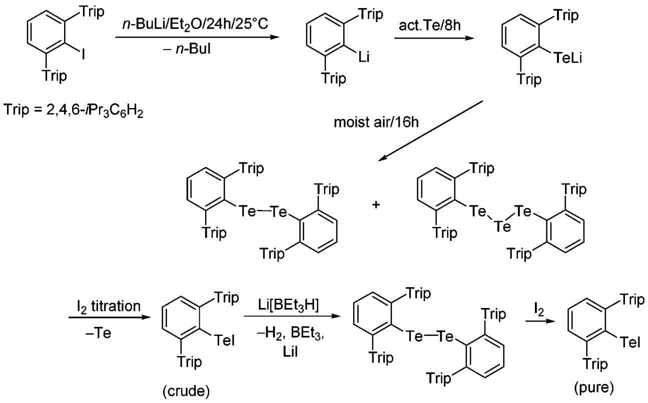
(26) Junk, T.; Irgolic, K. J.; Meyers, E. A. *Acta Crystallogr.* **1993**, *C49*, 975−976.

(27) Wagner, I.; Du Mont, W.-W.; Pohl, S.; Saak, W. *Chem. Ber.* **1990**, *123*, 2325−2327.

(28) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

(29) Giselbrecht, K. Diploma Thesis, Leopold-Franzens-Universität, Innsbruck, Austria, 1987.

Scheme 1. Reactions for the Synthesis of Pure (2,6-$Trip_2C_6H_3Te)_2$ (**9**) and 2,6-$Trip_2C_6H_3TeI$ (**10**)



structural deviations. The C1−Si distances vary between 1.938(1) and 1.907(3) Å, and the Te−C−Si angles lie between 97.8(1) and 112.5(2)°. The conformations around the C1−Si axis are also quite different, because the Te−C1−Si−Me torsion angles span 35.2(2)−58.6(2) and 156.9(2)−179.1(2)°, respectively.

Upon reaction of $(TpsiTe)_2$ (**2**) with iodine, the tellurenyl iodide TpsiTeI (**3**; ^{125}Te NMR: δ 1199 ppm) could be obtained as a dark green solid (blue in THF solution), similar to the reaction previously outlined for the analogous TsiTeI (^{125}Te NMR: δ 1182 ppm).[30] Similar to its parent ditellane **2**, also **3** decomposes in solution not by the usual dismutation pathway into **2** and iodine but into TpsiI under extrusion of elemental tellurium.

Since, due to this instability, **3** was not available in spectroscopically pure form, we concluded that the alkyl Tpsi substituent is bulky enough to prevent dismutation but may be inferior to an extremely bulky aryl substituent regarding the stability of the C−Te−I moiety. Therefore, we probed the usefulness not only of the already known TripTeI and Mes*TeI (Trip = 2,4,6-i-$Pr_3C_6H_2$; Mes* = 2,4,6-t-$Bu_3C_6H_2$)[8] but also of 2,6-$Trip_2C_6H_3TeI$ as possible candidates for the synthesis of stable tellurenyl azides. The lithium compound 2,6-$Trip_2C_6H_3Li$[18] reacts with activated tellurium powder to deep red solutions of 2,6-$Trip_2C_6H_3TeLi$ which in contrast to TpsiTeLi (**1**) can be oxidized in moist air to yield mixtures of the ditellane (2,6-$Trip_2C_6H_3Te)_2$ (**9**; ^{125}Te NMR: δ 332 ppm) and the tritellane (2,6-$Trip_2C_6H_3Te)_2Te$ (554 ppm, *Te*−Te−*Te*; 425 ppm, Te−*Te*−Te) (Scheme 1). Reaction of these mixtures with excess mercury in analogy to the successful conversion of $(TsiTe)_2Te$ to $(TsiTe)_2$ was not feasible but led to the ditellane **9** only in minor yields. Instead, besides an unidentified resonance at δ 402 ppm, the insertion product (2,6-$Trip_2C_6H_3Te)_2Hg$ was unambiguously identified (^{199}Hg NMR δ −1802 ppm, $^1J_{^{199}Hg-^{125}Te}$ = 7050 Hz; ^{125}Te NMR δ 199 ppm, coupling to ^{199}Hg confirmed). Since the tritellane (2,6-$Trip_2C_6H_3Te)_2Te$ and the ditellane **9** could not be separated on a preparative scale, they were converted to the exceptionally stable tellurenyl iodide 2,6-$Trip_2C_6H_3TeI$ (**10**; ^{125}Te NMR: δ 944 ppm). Unfortunately, the reaction solutions always contain variable amounts of 2,6-$Trip_2C_6H_3I$ from incomplete lithiation, partial hydrolysis, or the oxidative step. The separation of 2,6-$Trip_2C_6H_3I$ from the desired tellurenyl iodide **10** could only be achieved in reasonable yields (up to 30%) by reduction of **10** with Li[BEt_3H] and subsequent column chromatography of the resulting green (blue in CH_2Cl_2, hydrocarbons, and ethers) ditellane (2,6-$Trip_2C_6H_3Te)_2$ (**9**). Neither an excess of Li[BEt_3H] nor lithium powder resulted in further reduction of **9**. Although **9** and the tellurenyl iodide **10** are stable at room temperature in daylight in the solid state as well as in solution, the cleavage of **9** into **10** with iodine and the reduction of **10** into **9** with Li[BEt_3H], respectively, are surprisingly fast. However, compared to $(TpsiTe)_2$ (**2**), TpsiTeI (**3**), and Mes*TeI, which decompose either in solution or during light exposure, respectively, the stability of **9** and **10** toward air, moisture, irradiation, and dismutation at room temperature is extraordinary. By slow evaporation of solutions in CH_2Cl_2/pentane at ambient temperature, **10** was crystallized as dark blue platelets in the orthorhombic system, space group *Pnma*, with $Z = 4$ (see Figure 3). Although several tellurium−iodine compounds exist, to the best of our knowledge only two neutral organotellurium(II) iodides, $(PhTeI)_4$[12] and 2-$Me_2NCH_2C_6H_4TeI$,[11] have been investigated by crystal structure analysis before. The extremely bulky terphenyl-substituted tellurenyl iodide **10** is the first kinetically stabilized monomeric species among them. The Te−I moiety in crystalline **10** is best described as disordered over the mirror plane which bisects the molecule. The Te−I distance in **10** is significantly shorter than in $(PhTeI)_4$ and 2-$Me_2NCH_2C_6H_4TeI$ (2.617(1) vs 2.799−2.842(4) and 2.898(4) Å), and the C−Te−I angle is larger than found in the tetrameric species (106.2(2) vs 92.3−94.0°). The i-Pr groups of the adjacent Trip substituents are oriented away from the heavy atoms; as expected, their ring planes are tilted away from the iodine atom to minimize steric strain. Neither the tellurium nor the iodine atoms in **10** show intermolecular secondary interactions; therefore, the crystal structure of **10** has to be regarded as the first of a

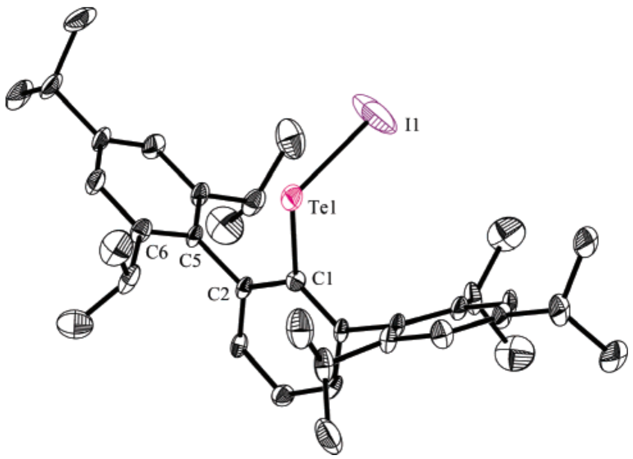


Figure 3. Molecular structure of 2,6-$Trip_2C_6H_3TeI$ (**10**) with hydrogen atoms and second, symmetry-generated Te−I moiety omitted. Selected bond lengths (Å) and angles (deg): I1−Te1 2.617(1), Te1−C1 2.136(6); C1−Te1−I1 106.2(2), I1−Te1−C1−C2 103.5(4), Te1−C1−C2−C3 170.4(3), C1−C2−C5−C6 83.8(6).

---

(30) Fimml, W. Diploma Thesis, Leopold-Franzens-Universität, Innsbruck, Austria, 1990.

Table 1. ^{125}Te NMR Shifts of the Tellurenyl Iodides, Tellurenyl Azides, and Their Parent Diorgano Polytellanes

substituent R =	solvent	RTeTeTeR	RTeTeR	RTeI	$RTeN_3$
Tpsi (=$(PhMe_2Si)_3C$)	$CDCl_3$	519, 496	442 (**2**)	1199 (**3**)	1952 (**4**)
Tsi (=$(Me_3Si)_3C$)	$CDCl_3$	504, 352	363[a]	1182[a]	2032
Tesi (=$(EtMe_2Si)_3C$)	C_6D_6	498, 397	376	1195 (**5**)	2031 (**6**)
Trip (=2,4,6-i-$Pr_3C_6H_2$)	C_6D_6		204[a]	842[a]	2235 (**7**)
Mes* (=2,4,6-t-$Bu_3C_6H_2$)	C_6D_6		568[a,b]	1162[a]	1981 (**8**)
2,6-$Trip_2C_6H_3$	C_6D_6	554, 425	332 (**9**)	944 (**10**)	1860 (**11**)
2-$Me_2NCH_2C_6H_4$	$CDCl_3$		373[a]	1204[a]	1630 (**12**)

[a] Previously reported; values obtained during our study. [b] The shift of 320 ppm in ref 8 is most probably erroneous.

monomeric tellurenyl iodide. The overall geometry found in the crystal structure of **10** is nicely reproduced by density functional geometry optimizations from an idealized starting geometry (vide infra).

Tellurenyl Azides. To investigate the stability of tellurenyl azides in general, three types of tellurenyl iodides stable toward rapid dismutation were reacted with silver azide in toluene/MeCN solution: the extremely bulky alkanetellurenyl iodides TpsiTeI (**3**) and TsiTeI[9] and the sterically encumbered arenetellurenyl iodides TripTeI, Mes*TeI,[8] and 2,6-$Trip_2C_6H_3TeI$ (**10**), as well as the coordinatively stabilized benzenetellurenyl iodide 2-$Me_2NCH_2C_6H_4TeI$.[11] In all cases complete conversion into the corresponding tellurenyl azides $TpsiTeN_3$ (**4**), $TsiTeN_3$,[6] $TripTeN_3$ (**7**), Mes*TeN_3 (**8**), 2,6-$Trip_2C_6H_3TeN_3$ (**11**), and 2-$Me_2NCH_2C_6H_4TeN_3$ (**12**) could be observed (see eq 2). By rapid one-pot reactions of $(PhTe)_2$ and $(MesTe)_2$ (Mes = 2,4,6-$Me_3C_6H_2$) with I_2 and subsequently with AgN_3, it was found that these less bulky substituted tellurenyl azide species are not stable toward reductive decomposition; i.e., the corresponding ditellanes were obtained.

$$1/2\ (RTe)_2 + 1/2\ I_2 \xrightarrow{\text{toluene}} RTeI + AgN_3 \xrightarrow[-AgI]{\text{toluene/MeCN}} RTeN_3 \qquad (2)$$

R = Tpsi (**2**), Trip, Mes*, 2,6-$Trip_2C_6H_3$ (**9**), 2-$Me_2NCH_2C_6H_4$

R = Tpsi (**3**), Trip, Mes*, 2,6-$Trip_2C_6H_3$ (**10**), 2-$Me_2NCH_2C_6H_4$

R = Tpsi (**4**), Trip (**7**), Mes* (**8**), 2,6-$Trip_2C_6H_3$ (**11**), 2-$Me_2NCH_2C_6H_4$ (**12**)

As a slightly bulkier alternative to the Tsi substituent with a hopefully better propensity to crystallize, the Tesi (=$(EtMe_2Si)_3C$) ligand was also probed for the purpose of stabilizing tellurenyl iodides and azides. However, the synthesis of $(TesiTe)_2Te$, TesiTeI (**5**), and $TesiTeN_3$ (**6**) similar to the efficient procedures as described in the following for the 2,6-$Trip_2C_6H_3$ substituent was hampered by ill-defined side reactions which only allowed for the ^{125}Te NMR spectroscopic characterization of the crude products (see Table 1).

While Mes*TeN_3 (**8**) can be stored at −25 °C for 1 year in solution without reductive decomposition taking place, $TripTeN_3$ (**7**) is completely converted into $(TripTe)_2$ under the same conditions. Even more stable than **8** is 2,6-$Trip_2C_6H_3TeN_3$ (**11**), which can be kept at ambient temperature without decomposition. In the ^{125}Te NMR spectra of the tellurenyl azides, sharp resonances between 2235 and 1630 ppm with significant deshielding compared to the corresponding iodides (δ 2235 (**7**) vs 842 (TripTeI) ppm, δ 1630 (**12**) vs 1204 (**8**) ppm) were observed. For **7**, the extreme downfield shift caused by substitution of iodide for azide is exceptional (see Table 1). The covalent nature of these new arenetellurenyl azides was confirmed by ^{14}N NMR spectroscopy, which revealed the typical three resonances. Of all the Te(II) azides reported in this study, **12** has the smallest ^{125}Te NMR downfield shift (δ 1630 ppm), most likely because all other species are monomeric in solution and the tellurium atom in **12** is less deshielded due to the strong coordination to the amino nitrogen atom.

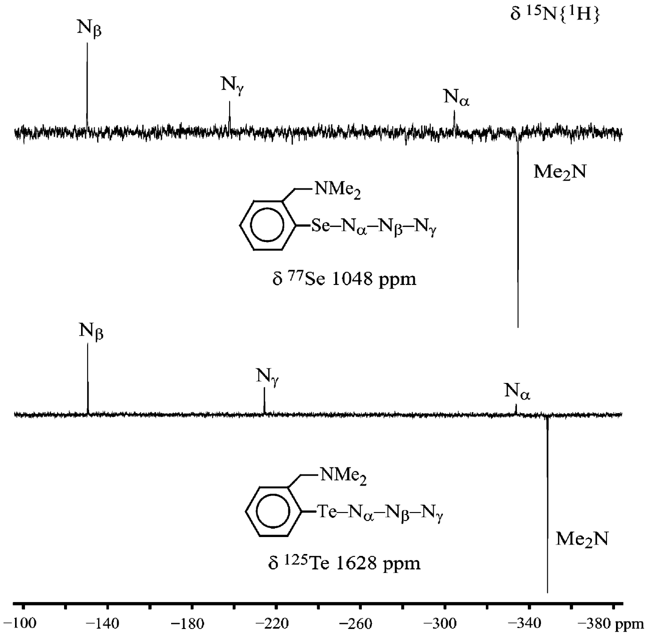


Figure 4. $^{15}N\{^1H\}$ NMR spectra of 2-$Me_2NCH_2C_6H_4SeN_3$ (top, ref 32) and **12** (bottom) in $CDCl_3$ at 25 °C. The resonances of the Me_2N groups appear with opposite sign due to a large NOE effect compared to the nitrogen atoms of the azide groups.

The high solubility of **12** and the analogous selenenyl azide 2-$Me_2NCH_2C_6H_4SeN_3$ allowed for the first time a direct comparison of the ^{15}N NMR spectra of two corresponding chalcogen azides (see Figure 4). While in the ^{14}N NMR spectra of covalent tellurium azides the resonances for N_α and N_γ are always more or less broadened, and often that of N_α remains almost indistinguishable from underground noise or the N_γ resonance (see Figure 2 of ref 5), for **12** and 2-$Me_2NCH_2C_6H_4SeN_3$ all four ^{15}N nuclei are found as sharp resonances. The substitution of selenium by tellurium causes weaker deshielding of all nitrogen nuclei in **12**, except practically identical values for N_β; the $\delta(^{125}Te)/\delta(^{77}Se)$ ratio is approximately 1.55 and thus close to the values observed for many other equivalent compounds of selenium and tellurium (1.6−1.8).[31]

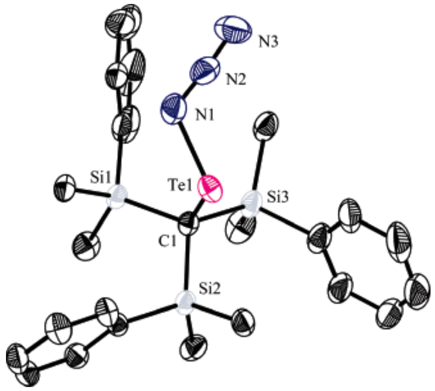


Figure 5. Molecular structure of $TpsiTeN_3$ (**4**) with hydrogen atoms omitted. Selected bond lengths (Å) and angles (deg): Te1−N1 2.064(8), N1−N2 1.18(1), N2−N3 1.17(1), C1−Te1 2.181(7), Si1−C1 1.885(8), Si2−C1 1.902(7), Si3−C1 1.909(7); C1−Te1−N1 103.5(3), Te1−N1−N2 115.7(6), N1−N2−N3 175.4(9), Te1−C1−Si1 111.8(3), Te1−C1−Si2 100.1(3), Te1−C1−Si3 104.6(3), Si1−C1−Si2 111.4(3), Si1−C1−Si3 114.3(3), Si2−C1−Si3 113.6(4).

The claret red solutions of the alkanetellurenyl azide **4** tend to slow decomposition back to the ditellane within days at ambient temperature. To compare and confirm its spectroscopic properties, we also prepared $TsiTeN_3$,[6] which is of stability very similar to that for **4**. In sharp contrast to $TsiTeN_3$, from solutions of **4** in benzene/MeCN pale red needles suitable for X-ray crystallography could be obtained after several months at −25 °C, which crystallized in the orthorhombic system, space group *Pbca*, $Z = 4$ with one molecule benzene as solvate. Again, as found for **1** and **2**, the extreme bulkiness of the Tpsi substituent causes a completely different structure of **4** in the crystal, compared to the tetrameric benzenetellurenyl halide $(PhTeI)_4$.[12] While in $(PhTeI)_4$ four PhTeI units built up an almost perfect square and together with long-range secondary interactions form a planar $[Te_4I_4]_n$ network, the alkanetellurenyl azide $TpsiTeN_3$ (**4**) is monomeric (see Figure 5). Though Te···N secondary bonding is well established for all structurally characterized tellurium(IV) azides, increasing the effective coordination around the tellurium center, the tellurium atom in **4** is only 2-fold coordinated. Therefore, the structural parameters of the Te(II)−N_3 unit in the alkanetellurenyl azide **4** are comparable to those of the organotellurium(VI) azide $(biphen)_2Te(N_3)_2$, which is also devoid of Te···N secondary interactions and undoubtedly covalent.[5] In tellurium(IV) azides, Te−N distances between 2.0 and 2.2 Å were found;[2,3] thus, the Te−N bond length in **4** is situated at the lower end of this range (2.063(7) Å). While the Te1−N1−N2 angle of 115.7(6)° very much resembles those found in $[Te(N_3)_5]^-$ and $(biphen)_2Te(N_3)_2$,[3,5] the almost identical $N_\alpha-N_\beta$ and $N_\beta-N_\gamma$ distances are somewhat puzzling (N1−N2 1.177(12) Å, N2−N3 1.168(12) Å), since the N1−N2−N3 angle is typical for covalent azides (175.4(9)°).

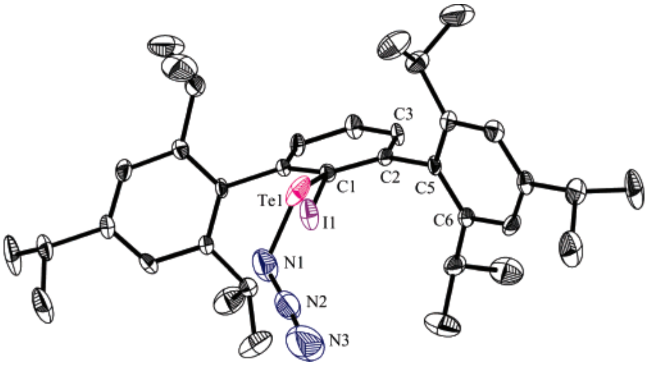


Figure 6. Molecular structure of 2,6-$Trip_2C_6H_3TeN_3$ (**11**) with hydrogen atoms and second, symmetry-generated Te−N_3 moiety omitted. The crystals contain approximately 25% of the contaminant 2,6-$Trip_2C_6H_3I$. Selected bond lengths (Å) and angles (deg): Te1−N1 2.00(1), Te1−C1 2.134(4), N1−N2 1.20(1), N2−N3 1.14(1); N1−Te1−C1 102.2(3), Te1−N1−N2 Te1 114.0(7), N1−N2−N3 175(1), Te1−C1−C2−C3 167.5(3), C1−C2−C5−C6 91.3(4).

In contrast to the alkanetellurenyl azide **4**, neither crystallization of **7** nor **8** was successful. However, the structural characterization of the arenetellurenyl azide 2,6-$Trip_2C_6H_3TeN_3$ (**11**) was possible due to its increased stability. By cooling of a saturated solution of **11** in hexane, dark brown blocks crystallized in the orthorhombic system, space group *Pbcm*, with $Z = 4$ (see Figure 6). Very similar to the corresponding arenetellurenyl iodide **10**, also for the azide **11** a disorder over the crystallographic mirror plane is found during refinement. Moreover, the crystal structure of **11** is even more complicated, since traces of 2,6-$Trip_2C_6H_3I$ present as a contaminant even after chromatographic purification of the precursor $(2,6\text{-}Trip_2C_6H_3Te)_2$ (**9**) were enriched to approximately 25% in the individual crystal measured. The position of the iodine atom lies on a special position on the mirror plane and as well in the plane of the central terphenyl ring (C1−I1 2.088(5) Å vs 2.102(6) Å in 2,6-$Trip_2C_6H_3I$[33]). This cocrystallization demonstrates the remarkably small differences between all the terphenyl-substituted molecules in this study. Again, as for the structure of the tellurenyl iodide **10**, the *i*-Pr groups of the adjacent Trip substituents are oriented away from the tellurium atom; a similar tilting of the ring planes away from the Te−N_3 moiety is observed. Since neither the tellurium nor the nitrogen atoms show intermolecular secondary interactions, **11** displays another example of a monomeric tellurenyl azide besides $TpsiTeN_3$ (**4**).

Along with $TsiTeN_3$,[6] the second tellurenyl azide reported prior to this study is the donor-stabilized 2-azidotellurenylbenzal-4′-methylaniline,[34] which was prepared by a halide exchange reaction and is thermally stable due to its intramolecular Te···N coordination. Very recently, with a similar approach, the isolation and characterization of the first covalent selenium azide, 2-$Me_2NCH_2C_6H_4SeN_3$, including X-ray crystal structure determination was accomplished.[32] These results allowed structural comparison of the equivalent covalent selenium and tellurium azides 2-$Me_2NCH_2C_6H_4SeN_3$ and 2-$Me_2NCH_2C_6H_4TeN_3$ (**12**), complementing the structural comparison of the ionic

---

(31) Mason, J. *Multinuclear NMR*, 2nd ed.; Plenum Press: New York, 1989.

(32) Klapötke, T. M.; Krumm, B.; Polborn, K. *J. Am. Chem. Soc.* **2004**, *126*, 710−711.

(33) Twamley, B.; Hardman, N. J.; Power, P. P. *Acta Crystallogr.* **2000**, *C56*, 514−515.

(34) Sadekov, I. D.; Maksimenko, A. A.; Maslakov, A. G.; Minkin, V. I. *J. Organomet. Chem.* **1990**, *391*, 179−188.

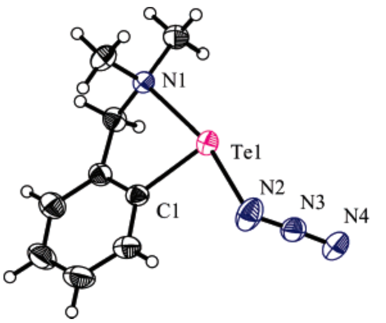


Figure 7. Molecular structure of 2-$Me_2NCH_2C_6H_4TeN_3$ (**12**). Selected bond lengths (Å) and angles (deg): Te1−N1 2.355(3), Te1−N2 2.241(4), C1−Te1 2.112(4), N2−N3 1.198(6), N3−N4 1.145(6); C1−Te1−N1 76.4(1), C1−Te1−N2 90.0(2), N1−Te1−N2 166.0(2), Te1−N2−N3 114.5(3), N2−N3−N4 176.6(5), N3−N2−Te1−N1 130.20(2).

$[Ph_3E]N_3$ and $[Me_3E]N_3$ (E = Se, Te) chalcogenonium azides.[35] The tellurenyl azide **12** was synthesized by reaction of 2-$Me_2NCH_2C_6H_4TeI$ with AgN_3. The latter tellurenyl iodide is conveniently available by iodination of the corresponding ditellane (2-$Me_2NCH_2C_6H_4Te)_2$, however, was previously obtained and characterized as a byproduct during the synthesis of 2-$Me_2NCH_2C_6H_4TeMe$.[11] An alternative route to prepare **12** by reaction of Me_3SiN_3 with 2-$Me_2NCH_2C_6H_4TeF$ (^{19}F NMR (CD_3CN) δ −238.3 ppm; ^{125}Te NMR (CD_3CN) δ 1960 ppm, $^{1}J_{Te-F} = 1616$ Hz), which can be obtained by reaction of the tellurenyl iodide with AgF, is not feasible due to dismutation and sensitivity of the tellurenyl fluoride. Yellow crystals of **12** are stable at room temperature and toward hydrolysis in moist air. The tellurenyl azide **12** in general is more stable than the selenenyl azide 2-$Me_2NCH_2C_6H_4SeN_3$[32] and similar to the properties found for the analogous tellurenyl fluoride 2-$Me_2NCH_2C_6H_4TeF$ and selenenyl fluoride 2-$Me_2NCH_2C_6H_4SeF$.[36] The azide **12** crystallizes isotypically in the orthorhombic system, space group *Pbca*, with $Z = 8$ (with *Pbca*, Figure 7). The structural parameters of both compounds are quite similar, except that in **12** significantly shorter Te···Te contacts of 4.004 Å compared to 2-$Me_2NCH_2C_6H_4SeN_3$ (Se···Se 4.213 Å) occur. As for the latter, the expected coordination of the aminomethyl nitrogen atom to tellurium is found, leading to a five-membered heterocycle with a T-shaped 3-coordinated tellurium atom and a 4-coordinated amine moiety. The Me_2N−Te distance in **12** is very similar to that in 2-$Me_2NCH_2C_6H_4TeCl/I$[11,37] (2.355(3) vs 2.362(3)/2.366(4) Å), but the Te−C1 distance is shorter (2.112(4) vs 2.120(3)/2.127(4) Å). The coordination around tellurium is analogous to those in 2-$Me_2NCH_2C_6H_4TeCl/I$,[11,37] regarding the C1−Te1−N2 (90.0(2) vs 91.40(9)/95.6(1)°) and N1−Te1−N2 angles (166.0(2) vs 167.91(8)/172.08(8)°). Compared to the undisturbed 2c−2e system **4**, the Te−N_3 bond length, for Te(IV) and Te(VI) azides between 2.0 and 2.2 Å,[2−4] is elongated due to the additional Me_2N−Te coordination in **12** (2.241(4) Å vs 2.064(8) Å), while the Te1−N2−N3 angle is not affected (114.5(3) vs 115.7(6)°). In contrast to the structure of $Me_2NCH_2C_6H_4SeN_3$,[32] in **12** the N2−N3 and N3−N4 distances differ more significantly from each other ($N_\alpha-N_\beta$ 1.198(6), $N_\beta-N_\gamma$ 1.145(6) Å), as expected for a covalently bound azido group ($N_\alpha-N_\beta-N_\gamma$ angle 176.6(5)°).

The EI mass spectra of the tellurenyl azides $RTeN_3$ reflect the increasing stability of these species depending on the substituent R. While for Mes*TeN_3 (**8**) the molecular ion peak is observed with low intensity and accompanied by the peak of the ditellane, for 2,6-$Trip_2C_6H_3TeN_3$ (**11**) [M^+] as well as [$M^+ - N_2$] are detected at *m/z* 653 (30%) and 625 (15%), respectively. In the case of 2-$Me_2NCH_2C_6H_4TeN_3$ (**12**) as well, the [M^+] is found at *m/z* 306 with 10% intensity. The vibrational spectra of $TpsiTeN_3$ (**4**) and **11** show the asymmetric stretching vibration of the azide group at 2069 and 2052 cm^{-1}, respectively; the donor-stabilized tellurenyl azide **12** is found at slightly lower frequency, 2039 cm^{-1}. The Te−N stretching vibrations for **4** and **11** are located in the Raman spectra at 425 and 417 cm^{-1}. The $\nu_{as}(N_3)$ vibrations appear in regions similar to those of the two known organotellurium(VI) azides Ph_5TeN_3 and biphen$_2Te(N_3)_2$,[5] which also exhibit no intermolecular coordination in the solid state.

Calculated Structures of TpsiTeLi (1), $(TsiTe)_2$, $TpsiTeN_3$ (4), 2,6-$Trip_2C_6H_3TeI$ (10), and 2-$Me_2NCH_2C_6H_4TeN_3$ (12). To compare the experimentally obtained X-ray structures of the tellurolate **1**, the ditellane **2**, and the tellurenyl iodide **10**, as well as the tellurenyl azides **4** and **12**, with calculated structures, quantum chemical calculations at different levels of theory were performed (see Experimental Section for details). The use of reliable approximations (MARI-*J* and RI-MP2) rendered geometry optimizations and vibrational analyses possible even for the relatively large ditellanes. However, the computational effort into theoretical treatment of $(TpsiTe)_2$ (**2**, 124 atoms) produced only narrow differences between **2** and the less demanding $(TsiTe)_2$ (82 atoms) molecule. Therefore, the latter was investigated to gain insight into the conformational behavior of such bulky dialkyl ditellanes in the gas phase; the structures of **1**, **4**, **10**, and **12** are less difficult. Table 2 gives an overview of the calculations.

For $(TsiTe)_2$, several minima regarding the conformation of the R_3C−Te−Te−CR_3 moiety were found. While optimization of $(TsiTe)_2$ at the BP86/SV(P) level led to a minimum (NIMAG = 0) with torsion angle 180°, i.e., an antiperiplanar conformation (C_i) as found in the X-ray structure of **2**, subsequent optimization starting from this geometry with TZVP basis sets broke C_i symmetry (negative mode with symmetry A_u) and ended at slightly different geometries with torsion angles between 158 and 166°, depending on the distortion along the negative mode. Manual distortion of the C_i molecular geometry to torsion angles of 170 and 160°, respectively, yielded a minimum structure with torsion angle 161.40° (see Supporting Information).

The calculated structures of the azides **4** and **12** are in good agreement with the experimental parameters determined

---

[35] Klapötke, T. M.; Krumm, B.; Mayer, P.; Piotrowski, H.; Schwab, I.; Vogt, M. *Eur. J. Inorg. Chem.* **2002**, 2701−2709. Klapötke, T. M.; Krumm, B.; Mayer, P.; Piotrowski, H.; Polborn, K.; Schwab, I. *Z. Anorg. Allg. Chem.* **2002**, *628*, 1831−1834.

[36] Klapötke, T. M.; Krumm, B.; Schwab, I. Unpublished results.

[37] Engman, L.; Wojton, A.; Oleksyn, B. J.; Sliwinski, K. *Phosphorus, Sulfur, Silicon* **2004**, *179*, 285−292.

Table 2. Energies (hartrees), ZPE Corrections (kJ/mol), and Bonding Parameters of **1**, **2**, **4**, **10**, and **12** at Different Levels of Theory

molecule	method	E	d(C−Si)	d(C−Te)	d(Te−N/I)
TpsiTe$^-$ (**1**)	expt		1.866(5)−1.884(5)	2.270(4)	
	MARIJ-BP86/TZVP	−1849.7422	1.924−1.929	2.290	
TpsiTeN$_3$ (**4**, C_1)	expt		1.885(7)−1.909(7)	2.180(6)	2.064(8)
	MARIJ-BP86/TZVP	−2013.9283	1.955−1.972	2.226	2.131
	MARIJ-BP86/TZVPP	−2014.0142	1.948−1.960	2.210	2.107
	B3YLP/TZVPP	−2012.9646	1.949−1.963	2.216	2.087
2,6-Trip$_2$C$_6$H$_3$TeI (**10**, C_1)	expt			2.136(6)	2.617(1)
	MARIJ-BP86/TZVP	−1421.4556		2.166	2.784
	MARIJ-BP86/TZVPP	−1421.5240		2.140	2.740
2-Me$_2$NCH$_2$C$_6$H$_4$TeN$_3$ (**12**, C_1)	expt			2.112(4)	2.241(4)/2.355(3)
	MARIJ-BP86/TZVP	−577.4671		2.141	2.193/2.550
	MARIJ-BP86/TZVPP	−577.5040		2.129	2.162/2.568
	B3YLP/TZVPP	−577.0190		2.137	2.163/2.606
	RI-MP2/TZVP	−575.6324		2.125	2.163/2.470
	RI-MP2/TZVPP	−576.0123		2.107	2.139/2.440

by X-ray diffraction. Comparison of the Te−C and Te−N bond lengths in **12** shows that the description of the Te···N interaction by density functional theory is problematic, as expected. Correlated methods (RI-MP2), however, lead to a significant shortening of the Te···N distance and a very accurate calculated geometry in general.

The molecular structure of the tellurenyl iodide **10** was optimized from an idealized C_s input geometry first, because at this time no experimental data were available. It was found that by shifting along a remaining imaginary frequency, symmetry broke to C_1. The resulting structure reflects the same trend for the C−Te−I moiety as found later in the crystal structure: the tellurium atom sits slightly above the plane of the central aromatic ring, while the Te−I bond is not perpendicular to this plane anymore. The orientation of the *i*-Pr groups and the tilting angle of the 2,6-Trip substituents are very similar.

Conclusion

The use of sterically encumbering alkyl and aryl substituents during this study provides insight into the stability and structural features of extremely bulky tellurolates, ditellanes, tellurenyl iodides, and tellurenyl azides. Such a stabilization of organotellurenyl(II) iodides and azides enables a thorough examination of these species, including spectroscopic characterization. Furthermore, our report complements the research on organotellurium azides and, in more general, broadens the knowledge of tellurenyl (pseudo)halides. In addition to these kinetically stabilized species, the synthesis of an *ortho*-amino-substituted tellurenyl azide provides a direct comparison of two covalent chalcogen azides REN$_3$ (E = Se, Te) for the first time. Other than monomeric tellurenyl azides are unlikely to be isolated, because the kinetical stabilization required for their existence causes a steric hindrance, which prevents additional coordination by Te···N secondary bonding.

X-ray crystallographic studies on TpsiTeLi(THF)$_4$, (TpsiTe)$_2$, TpsiTeN$_3$, 2,6-Trip$_2$C$_6$H$_3$TeI, 2,6-Trip$_2$C$_6$H$_3$TeN$_3$, and 2-Me$_2$NCH$_2$C$_6$H$_4$TeN$_3$ show structures without secondary interactions which feature monomeric molecular units. This study provides classification and comparison for Te(II) azides in the context of the only covalent selenenyl azide hitherto known, as well as Te(IV) and Te(VI) azides.

Computational studies including geometry optimization and frequency analysis of the TpsiTeLi(THF)$_4$, (TpsiTe)$_2$, TpsiTeN$_3$, 2,6-Trip$_2$C$_6$H$_3$TeI, and 2-Me$_2$NCH$_2$C$_6$H$_4$TeN$_3$ molecules confirmed the experimental data.

General Procedures. All manipulations of air- and moisture-sensitive materials were performed under an inert atmosphere of dry argon using flame-dried glass vessels and Schlenk techniques;[38] ethers and hydrocarbons were freshly distilled from sodium/benzophenone, and CH$_2$Cl$_2$ and CH$_3$CN, from P$_4$O$_{10}$ under N$_2$. The compounds AgN$_3$,[39] PhMe$_2$SiCl,[40] (PhMe$_2$Si)$_3$CH (=TpsiH),[17] (EtMe$_2$Si)$_3$CH (=TesiH),[41] 2,6-Trip$_2$C$_6$H$_3$I,[18] ((Me$_3$Si)$_3$CTe)$_2$ (=(TsiTe)$_2$),[7] TsiTeI,[9] TsiTeN$_3$,[6] (TripTe)$_2$, and (Mes*Te)$_2$[8] were prepared according to literature procedures. Commercially available bromoform was destabilized by repeated extraction with water, distilled in vacuo, and stored at 4 °C in the dark under argon. MeLi in Et$_2$O (1.6 M, Chemetall), *n*-BuLi in hexanes (2.5 M, Aldrich), Li[BEt$_3$H] in THF (1 M, Aldrich), EtMe$_2$SiCl (ABCR), and I$_2$ (Acros) were used as received. Elemental tellurium was purchased from Aldrich (200 mesh) and activated 24 h in boiling toluene with 5 mol % Ph$_3$P, washed with cold toluene, dried in vacuo, and stored under argon.[42] Infrared spectra were recorded on Perkin-Elmer Spektrum One FT-IR or Nicolet 520 FT-IR spectrometers (as KBr pellets or between KBr plates), and Raman spectra, on a Perkin-Elmer 2000 NIR FT spectrometer fitted with a Nd:YAG laser (1064 nm). NMR spectra were recorded on a JEOL Eclipse 400 instrument at 25 °C, and chemical shifts were determined with respect to external Me$_4$Si (^{1}H, 399.8 MHz; ^{13}C, 100.5 MHz; ^{29}Si, 79.5 MHz), MeNO$_2$ (^{14}N/^{15}N, 28.9/40.6 MHz), CFCl$_3$ (^{19}F, 376.1 MHz), Me$_2$Te (^{125}Te, 126.1 MHz), and Me$_2$Hg (^{199}Hg, 71.7 MHz). Mass spectra were recorded on a JEOL MStation JMS 700 spectrometer; tellurium-containing fragments refer to ^{130}Te. Elemental analyses: Analytical Service LMU.

---

(38) Shriver, D. F.; Drezdzon, M. A. *The manipulation of air-sensitive compounds*; Wiley: New York, 1986.

(39) Gmelin, L.; Meyer, J.; Pietsch, E. H. E.; Kotowski, A.; Becke-Goehring, M. *Gmelin Handbook of Inorganic Chemistry*, 8th ed.; Springer-Verlag: Berlin, 1978.

(40) Lehnert, R.; Porzel, A.; Rühlmann, K. *Z. Chem.* **1988**, *5*, 190−192.

(41) Uhl, W.; Jantschak, A. *J. Organomet. Chem.* **1998**, *555*, 263−269.

(42) Erker, G.; Hock, R. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 179−180.

Table 3. Crystal and Structure Refinement Data

	TpsiTeLi·4THF (**1**)	TpsiTeTeTpsi (**2**)	$TpsiTeN_3 \cdot C_6H_6$ (**4**)	$2,6\text{-}Trip_2C_6H_3TeI$ (**10**)	$2,6\text{-}Trip_2C_6H_3TeN_3$ (**11**)	$2\text{-}Me_2NCH_2C_6H_4TeN_3$ (**12**)
empirical formula	$C_{41}H_{65}LiO_4Si_3Te$	$C_{50}H_{66}Si_6Te_2$	$C_{28}H_{36}N_3Si_3Te$	$C_{36}H_{49}ITe$	$C_{36}H_{49}N_3Te$	$C_9H_{12}N_4Te$
formula mass	840.74	1090.77	626.47	736.25	651.38	303.83
temp (K)	193(2)	193(2)	193(2)	200(3)	200(3)	295(2)
cryst size (mm)	0.15 × 0.15 × 0.10	0.20 × 0.15 × 0.10	0.12 × 0.18 × 0.30	0.33 × 0.21 × 0.06	0.43 × 0.31 × 0.20	0.17 × 0.33 × 0.53
cryst descriptn	orange prism	green prism	pale red needle	dark blue platelet	brown block	yellow block
cryst system	monoclinic	monoclinic	monoclinic	orthorhombic	orthorhombic	orthorhombic
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	*Pnma*	*Pbcm*	*Pbca*
a (Å)	14.039(2)	13.5963(9)	15.719(3)	12.0621(8)	10.9540(8)	9.268(2)
b (Å)	18.740(2)	14.8897(9)	10.579(2)	25.666(2)	12.0599(8)	11.039(1)
c (Å)	16.900(2)	13.9463(9)	20.952(4)	10.965(1)	25.553(2)	22.333(5)
β (deg)	91.287(2)	114.390(1)	110.38(3)	90	90	90
V [Å^3]	4445.1(9)	2571.4(3)	3266(1)	3394.5(5)	3376(1)	2284.8(8)
Z	4	2	4	4	4	8
ρ_{calc} (g cm^{-3})	1.256	1.409	1.274	1.441	1.282	1.767
μ (mm^{-1})	0.786	1.306	1.040	1.807	0.908	2.573
F(000)	1760	1108	1276	1480	1352	1168
θ range (deg)	3.24−49.42	3.28−46.50	2.82−58.72	2.02−23.99	1.59−24.02	2.86−23.96
index ranges	$-15 \le h \le 16$, $-21 \le k \le 21$, $-19 \le l \le 19$	$-15 \le h \le 15$, $-16 \le k \le 16$, $-15 \le l \le 15$	$-19 \le h \le 18$, $-7 \le k \le 14$, $-27 \le l \le 25$	$-13 \le h \le 13$, $-27 \le k \le 29$, $-12 \le l \le 12$	$-12 \le h \le 12$, $-13 \le k \le 13$, $-26 \le l \le 29$	$0 \le h \le 10$, $-12 \le k \le 0$, $0 \le l \le 25$
reflcns collcd	22 388	11 321	9427	18 748	18 450	1795
reflcns obsd	3531	3062	3239	1792	2015	1586
reflcns unique	7352 ($R_{int} = 0.0629$)	3602 ($R_{int} = 0.0330$)	3748 ($R_{int} = 0.0342$)	2718 ($R_{int} = 0.1105$)	2721 ($R_{int} = 0.0928$)	1794 ($R_{int} = 0.0114$)
R1, wR2 (2σ data)	0.0447, 0.0930	0.0273, 0.0647	0.0558, 0.1721	0.0448, 0.0984	0.0419, 0.1011	0.0246, 0.0660
R1, wR2 (all data)	0.1023, 0.0998	0.0359, 0.0675	0.0650, 0.1838	0.0741, 0.1070	0.0618, 0.1072	0.0287, 0.0683
max/min transm	0.9132/0.7463	0.8240/0.7378	1.000/0.3470	0.7497/0.4403	0.7655/0.8420	0.9990/0.7942
data/restr/params	7352/0/457	3602/0/268	3748/0/316	2718/0/190	2721/18/212	1794/0/129
GOF on F^2	0.804	1.009	0.998	0.909	0.999	1.110
larg diff peak/hole (e/Å^3)	1.184/−0.566	0.502/−0.337	1.269/−0.583	0.974/−0.711	0.689/−0.425	0.595/−0.507

Caution! *Silver azide is potentially explosive. This necessitates meticulous safety precautions during its preparation and handling; please see ref 3.*

X-ray Crystallography. For compounds **1**, **2**, and **4** a Siemens P4 diffractometer with CCD area detector, for compounds **10** and **11** a STOE IPDS area detector device, and for **12** a Nonius CAD4 device were employed for data collection using Mo Kα radiation. The structures were solved using direct methods (SHELXS[43]), refined by full-matrix least-squares on F^2 (SHELXL[43]), and displayed with thermal ellipsoids at 40% probability (Table 3). During initial refinement of **10** iodine and tellurium atoms were located on a mirror plane. Further anisotropic refinement of all non-hydrogen atoms led to unusual large temperature factor components for the iodine atom, indicating disorder around the special position. The effect was smaller concerning tellurium but visible. In a first step both atoms were shifted marginally from the special position using a damping factor of 2000. Once convergence of the positions occurred, the damping factor was reduced stepwise and finally removed for the final runs. The site occupation factor (SOF) was fixed at a value of 0.5 for iodine and tellurium.

(Trisilylmethyl)tellurium Derivatives. Lithium (Tris(phenyldimethylsilyl)methyl)tellurolate, TpsiTeLi (1). Into a solution of 5.0 g (12.0 mmol) of $(PhMe_2Si)_3CH$ (sublimed at 90 °C/10^{-3} mbar) in 85 mL of THF was added 9.3 mL (13.0 mmol) of a freshly filtered solution of MeLi in Et_2O (1.6 M). After removal of the Et_2O by fractional distillation, the slightly yellow solution was refluxed for 4 h and then cooled to 25 °C, and 12.1 mmol of finely ground tellurium powder was added. After the sample was stirred for 3 h at room temperature, almost all tellurium was consumed; the dark-brown solution was filtered through a glass frit, and 50 mL of *n*-heptane was added as supernatant. After the mixture was cooled for 1 h at −20 °C, TpsiTeLi·4 THF (**1**) crystallized as orange prisms. $^{125}Te\{^1H\}$ NMR (THF): δ −141 ppm.

Bis(tris(phenyldimethylsilyl)methyl) Ditellane, (TpsiTe)$_2$ (2). A freshly prepared solution of 7.4 mmol of TpsiTeLi (**1**) in 30 mL of THF was slowly added to a solution of 0.94 g (3.7 mmol) of iodine in 60 mL of *n*-pentane. After the solution was stirred for 1 h at 25 °C, all volatile materials were removed in vacuo. The brownish residue was extracted with acetone; then the same volume of water was added, and a greenish precipitate was separated by filtration and washed with MeOH and *n*-pentane until the brown color of the extracts faded. Further purification of this crude product could be achieved by flash chromatography with methylene chloride over silica gel (Merck 60, 70−230 mesh). Rapid evaporation of these solutions at room temperature yielded **2** as green prisms. (37% yield; mp 140 °C (dec), air-stable, decomposition in solution at 25 °C). Products are invariably contaminated by TpsiH and traces of the tritellane $(TpsiTe)_2Te$. Therefore elemental analyses were not reproducible. Raman: strong fluorescence. IR (KBr): 3068 m, 3046 m, 3028 m, 3014 m, 2985 m, 2956 m, 2896 m, 1948 w, 1879 w, 1814 w, 1588 w, 1565 w, 1486 m, 1425 s, 1403 m, 1307 w, 1253 s, 1245 s, 1191 w, 1155 w, 1104 s, 1069 w, 999 w, 820 vs, 813 vs, 781 s, 736 s, 724 s, 699 vs, 659 s, 637 m, 581, 472 m cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.74−7.24 (Ar), 0.44 (Me) ppm. ^{13}C NMR ($CDCl_3$): δ 140.0/136.3/129.1/127.3 (Ar), 4.1 (Me, $^1J_{C-29Si} = 54.2$ Hz), −2.3 (Si_3C) ppm. ^{29}Si NMR ($CDCl_3$): δ −2.0 ppm. $^{125}Te\{^1H\}$ NMR ($CDCl_3$): δ 442 ppm. MS (D-EI) {*m*/*e* (intensity) [species]}: 1094 (0.1) [M$^+$], 959 (0.1) [M$^+$ − $PhMe_2Si$], 824 (0.1) [M$^+$ − $2PhMe_2Si$].

---

(43) Sheldrick, G. M. *SHELX-97*; University of Göttingen, Göttingen, Germany, 1997.

Tris(phenyldimethylsilyl)methanetellurenyl Iodide, TpsiTeI (3). Into a solution of 0.25 g (0.28 mmol) of $(TpsiTe)_2$ in 10 mL of benzene was added 0.058 g (0.23 mmol) of iodine in portions. After the sample was stirred for 1 h at ambient temperature, the color of the solution changed from green to dark blue-green. Evaporation of this solution yielded **3** as dark green solid and small amounts of TpsiI and tellurium (partly as a mirror). Therefore, the yield, melting point, and elemental analysis were not reproducible. Raman: strong fluorescence. IR (KBr): 3068 w, 3025 w, 2957 w, 2896 w, 1953 br, 1886 br, 1818 br, 1618 br, 1585 w, 1486 w, 1425 s, 1308 w, 1249 vs, 1193 w, 1157 w, 1106 s, 1096 s, 1070 m, 998 w, 919 w, 838 vs, 805 vs, 778 s, 735 s, 723 s, 700 s, 661 m, 638 m, 581 m, 473 m, 465 m cm^{-1}. $_1$H NMR ($CDCl_3$): δ 7.54−7.21 (Ar), 0.55 (Me) ppm. ^{13}C NMR ($CDCl_3$): δ 138.1/136.4/135.3/129.4/127.5 (Ar), 3.6 (Me, $^1J_{C-29Si} = 54.6$ Hz), −1.9 (Si_3C, $^1J_{C-29Si} = 31.5$ Hz) ppm. ^{29}Si NMR ($CDCl_3$): δ −0.1 ppm. ^{125}Te{^{1}H} NMR ($CDCl_3$): δ 1199 ppm.

Tris(phenyldimethylsilyl)methanetellurenyl Azide, $TpsiTeN_3$ (4). Into a freshly prepared solution of **3** from 0.25 g (0.28 mmol) of $(TpsiTe)_2$ and 0.058 g (0.23 mmol) of iodine in 10 mL of benzene (see above) were added 10 mL of MeCN and 0.10 g of AgN_3 (0.67 mmol). After being stirring for 3 h, the claret red solution was filtered through a glass frit (G4) under argon and all volatile materials were removed in vacuo. Raman: 3055 (48), 2967 (15), 2903 (32), 2069 (12, $\nu_{as}(N_3)$), 1590 (23), 1567 (12), 1193 (10), 1110 (7), 1031 (27), 1001 (100), 787 (15), 659 (55), 621 (17), 597 (11), 473 (11), 425 (35, ν(TeN)), 326 (30), 219 (31), 158 (33) cm^{-1}. IR (KBr): 3070 w, 2958 w, 2068 vs ($\nu_{as}(N_3)$), 1938 m, 1618 m, 1486 w, 1425 w, 1384 w, 1309 br, 1248 m, 1225 m, 1154 w, 999 w, 838 s, 810 s, 784 m, 739 m, 721 m, 701 m, 656 w, 635 w, 595 w, 471 w cm^{-1}. ^{1}H NMR (C_6D_6): δ 7.48−7.05 (Ar), 0.46 (Me) ppm. ^{13}C NMR (C_6D_6): δ 138.0/136.3/129.7/127.7 (Ar), 8.2 (Si_3C, $^1J_{C-29Si} = 32.3$ Hz), 3.1 (Me, $^1J_{C-29Si} = 54.6$ Hz) ppm. ^{14}N NMR [C_6D_6, $\Delta\nu_{1/2}$ (Hz)]: δ −129 (N_β, 260 Hz), −189 (N_γ, 650 Hz), (N_α not visible) ppm. ^{29}Si NMR (C_6D_6): δ −2.8 ppm. ^{125}Te{^{1}H} NMR (C_6D_6): δ 1952 ppm.

Tris(ethyldimethylsilyl)methanetellurenyl Iodide, TesiTeI (5). Into a solution of 0.55 g (2.0 mmol) of $(EtMe_2Si)_3CH$ in 20 mL of THF was added 2.2 mL (2.4 mmol) of a freshly filtered solution of MeLi in Et_2O (1.1 M). After the solution was refluxed for 8 h, an additional amount of 0.7 mL (0.8 mmol) of MeLi was added. The solution was refluxed for another 2 h and then cooled to 0 °C, and 0.36 g (2.8 mmol) of activated tellurium powder was added. After the mixture was stirred for 4 h at room temperature, almost all the tellurium was consumed, and moist air was allowed to enter the vessel for 1 day under vigorous stirring. From the dark-brown mixture all volatile materials were removed during 16 h in vacuo; the residue was extracted with Et_2O and dried with $MgSO_4$. This ethereal solution of the tritellane $(TesiTe)_2Te$ (^{125}Te NMR: δ 498, 352 ppm) was titrated with a saturated solution of iodine in Et_2O until the color of the solution turned from blue to brownish (excess iodine). The solution was then separated from precipitated tellurium powder by filtration and washed twice with a saturated solution of $NaHSO_3$ in water. The green ethereal extracts were dried over $MgSO_4$ and evaporated to yield TesiTeI (**5**) as a dark green oily residue (yield approximately 50%). The purity of these products was low in all cases; according to thin-layer chromatography, up to five different substances were formed, which did not permit separation of neat **5**. ^{125}Te{^{1}H} NMR (C_6D_6): δ 1195 ppm.

Tris(ethyldimethylsilyl)methanetellurenyl Azide, $TesiTeN_3$ (6). Into a freshly prepared solution of 0.25 g (0.5 mmol) of **5** in 3 mL of toluene were added 3 mL of MeCN and 0.10 g of AgN_3 (0.67 mmol). After being stirred for 3 h, the red solution was filtered through a glass frit (G4) under argon and all volatile materials were removed in vacuo. ^{1}H NMR (C_6D_6): δ 0.87 (t, CH_3CH_2, $^3J_{H-H} = 8.2$ Hz), 0.71 (q, CH_3CH_2), 0.17 (CH_3Si) ppm. ^{14}N NMR [C_6D_6, $\Delta\nu_{1/2}$ (Hz)]: δ −127 (N_β, 64 Hz), −192 (N_γ, 255 Hz), −372 (N_α, 800 Hz) ppm. ^{125}Te{^{1}H} NMR (C_6D_6): δ 2031 ppm.

Tellurium Phenyl and Terphenyl Derivatives. 2,4,6-Triisopropylbenzenetellurenyl Azide, $TripTeN_3$ (7). Into a solution of 0.4 g (0.6 mmol) of $(TripTe)_2$ in 10 mL of toluene was slowly added 0.15 g (0.6 mmol) of iodine in 10 mL of toluene at room temperature under vigorous stirring. After 1 h, the green solution was concentrated in vacuo to approximately 10 mL and 0.18 g (1.2 mmol) of AgN_3 and 10 mL of MeCN were added. After 3 h the silver salts were removed by passing the deep red solution through a glass frit (G4) under argon. Evaporation of this solution gave **7** as deep red oily residue, invariably contaminated with traces of $(TripTe)_2$. The relatively rapid decomposition of **7** allowed for NMR spectroscopic characterization only. ^{125}Te{^{1}H} NMR (C_6D_6): δ 2235 ppm.

2,4,6-Tri-*tert*-butylbenzenetellurenyl Azide, Mes*TeN_3 (8). Into a solution of 0.25 g (0.33 mmol) of (Mes*Te)$_2$ in 25 mL of toluene was slowly added 0.085 g (0.33 mmol) of iodine in 10 mL of toluene at room temperature under vigorous stirring. After 1 h, the green solution was concentrated in vacuo to approximately 10 mL and 0.1 g (0.67 mmol) of AgN_3 and 10 mL of MeCN were added. After 3 h the silver salts were removed by passing the deep red solution through a glass frit (G4) under argon. Evaporation of this solution gave **8** as dark purple residue, invariably contaminated with traces of (Mes*Te)$_2$. ^{1}H NMR (C_6D_6): δ 7.63 (2H, Ar-*H*), 1.59 (18 H, *o*-C*Me*$_3$), 1.21 (9 H, *p*-C*Me*$_3$). ^{13}C NMR (C_6D_6): δ 159.1 (*o*-C), 153.3 (*p*-C), 122.9 (*m*-C), 115.6 (*i*-C, $^1J_{C-^{125}Te} = 336$ Hz), 40.5 (*o*-*C*Me$_3$), 35.3 (*p*-*C*Me$_3$), 34.5 (*o*-C*Me*$_3$), 31.3 (*p*-C*Me*$_3$) ppm. ^{14}N NMR [C_6D_6, $\Delta\nu_{1/2}$ (Hz)]: δ −130 (N_β, 50 Hz), −204 (N_γ, 1200 Hz), −335 (N_α, >1200 Hz) ppm. ^{125}Te{^{1}H} NMR (C_6D_6): δ 1981 ppm. MS (D-EI) {*m*/*e* (intensity) [species]}: 750 (1) [(Mes*Te)$_2$], 417 (2) [M^+], 375 (2) [$M^+ - N_3$], 319 (3) [$M^+ - N_3 -$ *t*-Bu], 245 (80) [Mes*$^+$].

Bis(2,6-bis(2,4,6-triisopropylphenyl)phenyl Ditellane (2,6-$Trip_2C_6H_3Te)_2$ (9). Into a suspension of 9.12 g (15 mmol) of 2,6-$Trip_2C_6H_3I$ in 90 mL of *n*-hexane and 20 mL of Et_2O was added 6.4 mL (16 mmol) of *n*-BuLi (2.5 M in hexanes) under vigorous stirring at ambient temperature. After 24 h, from the cleared up solution all volatile materials were removed in vacuo. The remaining residue was dissolved in 60 mL of Et_2O, and 1.92 g (15 mmol) of activated tellurium powder was added. After a further 8 h, moist air was allowed to enter the dark brown reaction mixture for 16 h. Subsequently, the mixture was washed three times with water and the resulting dark red ethereal solution was titrated with a saturated solution of iodine in Et_2O until the color of the solution turned from blue to brownish (excess iodine). The solution was then separated from precipitated tellurium powder by filtration and washed twice with a saturated solution of $NaHSO_3$ in water. The blue ethereal extracts were dried over $MgSO_4$ and evaporated. From the remaining crude blue solid, 1 g was dissolved in 20 mL of THF and 2.7 mL (2.7 mmol) of a 1 M solution of Li[BEt_3H] in THF was added at room temperature into the teal blue solution. After the effervescence of hydrogen stopped, the solution was stirred for 1 h, and then all volatile materials were removed in vacuo. The remaining residue was extracted several times with *n*-pentane and filtered. The now clear blue solution is evaporated and separated from 2,6-$Trip_2C_6H_3I$ by column chromatography on silica gel (Merck 60, 70−230 mesh) with a mixture of 1:10 CH_2Cl_2/pentane as eluent. Rapid evaporation of these solutions gave **9** as violet prisms, probably a CH_2Cl_2 solvate. Recrystallization from 2-propanol yielded neat **9** as green crystals (20−30% yield dependent on chromatography; mp 252−254 °C). Raman: 3038 (25), 2959 (60), 2905 (61), 2865 (47), 1606 (49), 1563 (34), 1461 (36), 1292 (45), 1249 (14), 1171 (18), 1107 (25), 1057 (15), 1005 (31), 956 (14), 884 (40), 599 (23), 501 (28), 199 (100, ν(TeTe)), 147 (27) cm^{-1}. IR (KBr): 3046 w, 2957 vs, 2924 s, 2864 m, 1605 m, 1563 m, 1458 m, 1380 m, 1360 m, 1315 w, 1168 w, 1099 w, 1068 w, 1050 w, 1002 w, 939 w, 873 m, 799 m, 739 w, 648 w cm^{-1}. ^1H NMR (C_6D_6): δ 7.14 (4H, *m*-Trip*H*), 7.135 (2H, *m*-Ar*H*), 6.89 (m, 1H, *p*-Ar*H*), 2.90 (sept, 4H, *p*-C*H*(CH_3)$_2$, $^3J_{HH}$ = 6.8 Hz), 2.73 (sept, 4H, *o*-C*H*(CH_3)$_2$, $^3J_{HH}$ = 6.8 Hz), 1.35 (d, 12H, *p*-CH(C*H*$_3$)$_2$), 1.30 (d, 12H, *o*-CH(C*H*$_3$)$_2$), 1.06 (d, 12H, *o*-CH(C*H*$_3$)$_2$) ppm. ^{13}C NMR (C_6D_6): δ 148.7, 147.1, 147.0, 139.2, 129.8, 126.2, 122.1 (*C*−Te), 121.5, 34.6 (*p*-*C*H(CH_3)$_2$), 31.2 (*o*-*C*H(CH_3)$_2$), 25.9 (CH(*C*H$_3$)$_2$), 24.33 (CH(*C*H$_3$)$_2$), 24.28 (CH(*C*H$_3$)$_2$) ppm. $^{125}Te\{^1H\}$ NMR (C_6D_6): δ 332 ppm. MS (D-EI) {*m*/*e* (intensity) [species]}: 1222 (100) [M^+], 611 (30) [M^+ − *i*-Pr], 568 (40) [M^+ − 2*i*-Pr]. Anal. Calcd for $C_{72}H_{98}Te_2$: C, 70.7; H, 8.0. Found: C, 70.9; H, 8.1.

2,6-Bis(2,4,6-triisopropylphenyl)benzenetellurenyl Iodide, 2,6-$Trip_2C_6H_3TeI$ (10). Into a solution of 0.12 g (0.10 mmol) of **9** in Et_2O was added 0.025 g (0.10 mmol) of iodine. After being stirred for 0.5 h at room temperature, the solution was washed twice with a saturated solution of $NaHSO_3$ in water and dried over $MgSO_4$. Evaporation yielded **10** as a blue powder (80−90% yield; mp >180 °C (dec)). Raman: 3043 (20), 2957 (43), 2927 (40), 2865 (32), 1606 (28), 1564 (19), 1459 (21), 1382 (10), 1293 (20), 1552 (10), 1172 (9), 1104 (14), 1056 (19), 883 (17), 602 (10), 544 (7), 497 (15), 202 (100, ν(TeI)), 145 (12) cm^{-1}. IR (KBr): 3049 w, 2955 vs, 2924 s, 2864 s, 1637 br, 1606 m, 1564 w, 1457 m, 1379 m, 1361 m, 1314 m, 1101 m, 1068 w, 1051 w, 1004 w, 940 w, 875 m, 798 m, 734 w, 649 w cm^{-1}. ^1H NMR (C_6D_6): δ 7.165 (2H, *m*-Ar*H*), 7.15 (4H, *m*-Trip*H*), 6.98 (m, 1H, *p*-Ar*H*), 2.94 (sept, 4H, *p*-C*H*(CH_3)$_2$, $^3J_{HH}$ = 6.8 Hz), 2.84 (sept, 4H, *o*-C*H*(CH_3)$_2$, $^3J_{HH}$ = 7.0 Hz), 1.49 (d, 12H, *p*-CH(C*H*$_3$)$_2$) ppm), 1.25 (d, 12H, *o*-CH(C*H*$_3$)$_2$), 1.12 (d, 12H, *o*-CH(C*H*$_3$)$_2$) ppm. ^{13}C NMR (C_6D_6): δ 150.5, 148.1, 144.8, 135.9, 129.7, 127.1, 121.5, 113.7 (*C*−Te, $^1J_{C-^{125}Te}$ = 358.6 Hz), 34.9 (*p*-*C*H(CH_3)$_2$), 31.3 (*o*-*C*H(CH_3)$_2$), 25.5 (CH(*C*H$_3$)$_2$), 24.3 (CH(*C*H$_3$)$_2$), 24.0 (CH(*C*H$_3$)$_2$) ppm. $^{125}Te\{^1H\}$ NMR (C_6D_6): δ 944 ppm. MS (D-EI) {*m*/*e* (intensity) [species]}: 738 (90) [M^+], 611 (55) [M^+ − I], 568 (85) [M^+ − I − *i*-Pr], 478 (55) [M^+ − TeI]. Anal. Calcd for $C_{36}H_{49}ITe$: C, 58.7; H, 6.7; I, 17.2. Found: C, 59.0; H, 6.9; I, 17.6.

2,6-Bis(2,4,6-triisopropylphenyl)benzenetellurenyl Azide, 2,6-$Trip_2C_6H_3TeN_3$ (11). To a solution of 0.055 g (0.075 mmol) of **10** in toluene was added 0.020 g (0.10 mmol) of AgN_3. After the solution was stirred for 3 h at room temperature, the color changed from blue to orange. Filtration through a glass frit (G4) under argon followed by evaporation yielded **11** as brown solid (75−80% yield; >135 °C dec into **9**). Raman: 3047 (13), 3022 (11), 2957 (38), 2906 (36), 2688 (29), 2709 (6), 2052 (16, $\nu_{as}N_3$), 1608 (31), 1566 (19), 1460 (22), 1382 (9), 1294 (23), 1252 (8), 1173 (9), 1105 (15), 1056 (12), 1006 (14), 946 (11), 883 (28), 657 (13), 498 (20), 417 (100, νTeN), 273 (18), 250 (16), 190 (28), 175 (27), 142 (20) cm^{-1}. IR (KBr): 3049 w, 2955 vs, 2924 s, 2864 s, 2054 vs ($\nu_{as}(N_3)$), 1638 br, 1606 m, 1564 w, 1457 m, 1379 m, 1361 m, 1313 m, 1260 w, 1212 m, 1101 m, 1068 w, 1051 w, 940 w, 875 m, 798 m, 738 w, 649 w, 493 w cm^{-1}. ^1H NMR (C_6D_6): δ 7.16 (4H, *m*-Trip*H*), 7.04−6.96 (m, 3H, *m*/*p*-Ar*H*), 2.92 (sept, 4H, *p*-C*H*(CH_3)$_2$, $^3J_{HH}$ = 6.8 Hz), 2.85 (sept, 4H, *o*-C*H*(CH_3)$_2$, $^3J_{HH}$ = 7.0 Hz), 1.41 (d, 12H, *p*-CH(C*H*$_3$)$_2$) ppm), 1.27 (d, 12H, *o*-CH(C*H*$_3$)$_2$), 1.11 (d, 12H, *o*-CH(C*H*$_3$)$_2$) ppm. ^{13}C NMR (C_6D_6): δ 150.1, 147.5, 143.6, 134.0, 130.5, 127.5, 126.6 (*C*−Te), 121.7, 34.9 (*p*-*C*H(CH_3)$_2$), 31.3 (*o*-*C*H(CH_3)$_2$), 25.5 (CH(*C*H$_3$)$_2$), 24.3 (CH(*C*H$_3$)$_2$), 24.0 (CH(*C*H$_3$)$_2$) ppm. ^{14}N NMR [C_6D_6, $\Delta\nu_{1/2}$ (Hz)]: δ −127 (N_β, 330 Hz), −188 (N_γ, 1150 Hz), (N_α not visible) ppm. ^{15}N NMR (C_6D_6): δ −127.0 (N_β), −186.7 (N_γ), −355.3 (N_α) ppm. $^{125}Te\{^1H\}$ NMR (C_6D_6): δ 1860 ppm. MS (D-EI) {*m*/*e* (intensity) [species]}: 653 (30) [M^+], 625 (15) [$M^+ - N_2$], 611 (55) [$M^+ - N_3$], v, 568 (85) [$M^+ - N_2$ − *i*-Pr]. Anal. Calcd for $C_{36}H_{49}N_3Te$: C, 66.2; H, 7.5; N, 6.4. Found: C, 65.5; H, 7.7; N, 5.6.

2-((Dimethylamino)methyl)benzenetellurenyl Iodide, 2-$Me_2NCH_2C_6H_4TeI$. Into a solution of 4.1 g (30.6 mmol) of *N*,*N*-dimethylbenzylamine in 150 mL of diethyl ether was added 14.4 mL (36 mmol) of *n*-BuLi at 25 °C.[19] After being stirred for 16 h, the yellow solution was decanted from a colorless precipitate. The precipitate was washed twice with 10 mL of diethyl ether, and then 3.9 g (30.6 mmol) of tellurium powder was added with vigorous stirring. After 16 h, for 10 min dry oxygen was passed through the now red solution. Then, moist air was allowed to enter the reaction vessel. After 1 h, the solution was washed twice with water, dried over Na_2SO_4, and evaporated. The red oil obtained was dissolved in CH_2Cl_2 and titrated with iodine in hexane until a darker red color remained and iodine began to separate as oil. The solution was stirred for 15 h, and then all volatile materials were removed in vacuo. The remaining residue is fractionally sublimed at 55 °C/10^{-3} mbar to remove $(2\text{-}Me_2NCH_2C_6H_4)_2Te$. At 80 °C, pure **8** was obtained as a dark-orange powder (70% yield, mp 158 °C). The ^1H and ^{13}C NMR spectra as well as MS data are in accord with ref 11. $^{125}Te\{^1H\}$ NMR ($CDCl_3$): δ 1204 ppm.

2-((Dimethylamino)methyl)benzenetellurenyl Azide, $2\text{-}Me_2NCH_2C_6H_4TeN_3$ (12). Into a dark-orange solution of 0.78 g (2 mmol) of **8** in 10 mL of 1:1 toluene/MeCN was added 0.30 g (1 mmol) of AgN_3 at ambient temperature under vigorous stirring in the dark. After 4 h, the now bright yellow solution over a yellow precipitate (AgI) was decanted. The residue was extracted twice with toluene, and the combined extracts were evaporated in vacuo to yield **12** as a yellow solid (95% yield, mp 58 °C). Raman: strong fluorescence. IR (KBr): 3058 w, 3000 w, 2970 w, 2910 br, 2838 w, 2039 vs ($\nu_{as}(N_3)$), 1989 w, 1628 br, 1584 m, 1458 s, 1439 m, 1408 w, 1354 w, 1313 m, 1297 w, 1260 m, 1205 w, 1177 w, 1154 w, 1146 w, 1101 w, 1026 m, 1002 m, 973 w, 838 s, 746 s, 501 w, 461 m cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.72 (d, 1H, Ar-H), 7.26−7.10 (m, 3H, Ar-H), 3.80 (2H, CH_2), 2.61 (6H, Me_2N) ppm. ^{13}C NMR ($CDCl_3$): δ 137.3, 131.3, 128.6, 126.7, 126.6, 125.9 (*C*−Te, $^1J_{C-^{125}Te} = 328.2$ Hz), 66.8 (CH_2, $^3J_{C-^{125}Te} = 14.6$ Hz), 46.7 (Me_2N) ppm. ^{14}N NMR [$CDCl_3$, $\Delta\nu_{1/2}$ (Hz)]: δ −131 (N_β, 64 Hz), −214 (N_γ, 190 Hz), −329 (N_α, 1150 Hz) ppm, Me_2N not visible. ^{15}N NMR ($CDCl_3$): δ −130.5 (N_β), −214.3 (N_γ), −334.0 (N_α), −348.7 (Me_2N) ppm. $^{125}Te\{^1H\}$ NMR ($CDCl_3$): δ 1630 ppm. MS (D-EI) {*m*/*e* (intensity) [species]}: 306 (10) [M^+], 264 (45) [$M^+ - N_3$], 202 (5) [$C_7H_6Te^+$]. Anal. Calcd for $C_9H_{12}N_4Te$: C, 35.3; H, 3.9; N, 18.3. Found: C, 35.6; H, 4.0; N, 18.3.

Computational Details. The electronic structures of **1** (anion), $(TsiTe)_2$, **4**, **10**, and **12** were calculated with TURBOMOLE V5-7[44] using a density functional (Becke-Perdew86 or B3LYP functionals,[45] m4 grid) partly with the multipole accelerated resolution of the identity (MARI-*J*) approximation[46,47] for DFT employing Ahlrich's SV(P), TZVP, and TZVPP basis sets[48] for Te atoms together with the large-core MWB46 ECP[49] for tellurium (see Table 2). All structures were optimized in internal redundant coordinates[50] (SCF convergence to $\leq 10^{-7}$ au, total energy converged to $\leq 1 \times 10^{-6}$ au, and maximum norm of BP86 energy gradient converged to $\leq 1 \times 10^{-3}$ au; C_1 symmetry unless noted otherwise) with SV(P) basis sets and the MARI-*J* approximation initially. Subsequent analytical LES (lowest eigenvalue search for each irrep) for the lowest Hessian eigenvalues (harmonic approximation, quadrature weights included) was carried out with the AOFORCE module,[51] and the optimization was repeated until the number of imaginary frequencies (NIMAG) became zero. Subsequently, these geometries were taken as starting points for MARI-*J*/BP86 optimizations with TZVP and TZVPP basis sets. To check the influence of the MARI-*J* approximation and the density functional chosen, for **4** and **12** also MPI-parallel B3LYP/TZVPP geometry optimizations (m4 grid, 16 Intel Xeon CPUs) with TURBOMOLE V5-6 were carried out.[47] Furthermore, MP2 calculations employing the resolution of the identity (RI) approximation were performed with TZVP bases for **12**.[52]

Acknowledgment. Financial support of this work by the University of Munich and the Fonds der Chemischen Industrie is gratefully acknowledged. We are indebted to the Leibniz-Rechenzentrum (LRZ), Munich, Germany, for generous allocation of computing time on their IA32 (Pentium 4) Linux cluster and Dr. F. Weigend, Institut für Nanotechnologie, Forschungszentrum Karlsruhe, for modified versions of the TURBOMOLE RI-MP2[52] module. We wish to thank the research student Mr. M. Scherr for his strong commitment during the preparation of some compounds presented in this study and DDipl.-Ing. F. Schönborn, Leopold-Franzens-Universität, Innsbruck, Austria, for his help with a literature enquiry.

Supporting Information Available: X-ray crystallographic files for compounds **1**, **2**, **4**, **10**, **11**, and **12** (CIF) and Cartesian coordinates and figures for the optimized structures of the molecules (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

IC048219S

---

(44) Ahlrichs, R.; Bär, M.; Häser, M.; Horn, H.; Kölmel, C. *Chem. Phys. Lett.* **1989**, *162*, 165−169.

(45) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822−8824. Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098−3100. Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785−789.

(46) Treutler, O.; Ahlrichs, R. *J. Chem. Phys.* **1995**, *102*, 346−354. Eichkorn, K.; Treutler, O.; Öhm, H.; Häser, M.; Ahlrichs, R. *Chem. Phys. Lett.* **1995**, *240*, 283−290. Eichkorn, K.; Treutler, O.; Öhm, H.; Häser, M.; Ahlrichs, R. *Chem. Phys. Lett.* **1995**, *242*, 652−660. Eichkorn, K.; Weigend, F.; Treutler, O.; Ahlrichs, R. *Theor. Chem. Acc.* **1997**, *97*, 119−124. Sierka, M.; Hogekamp, A.; Ahlrichs, R. *J. Chem. Phys.* **2003**, *118*, 9136−9148.

(47) v. Arnim, M.; Ahlrichs, R. *J. Comput. Chem.* **1998**, *19*, 1746−1757.

(48) Schäfer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys.* **1992**, *97*, 2571−2577. Schäfer, A.; Huber, C.; Ahlrichs, R. *J. Chem. Phys.* **1994**, *100*, 5829−5835.

(49) Bergner, A.; Dolg, M.; Küchle, W.; Stoll, H.; Preuss, H. *Mol. Phys.* **1993**, *80*, 1431−1441.

(50) v. Arnim, M.; Ahlrichs, R. *J. Chem. Phys.* **1999**, *111*, 9183−9190.

(51) Horn, H.; Weiss, H.; Häser, M.; Ehrig, M.; Ahlrichs, R. *J. Comput. Chem.* **1991**, *12*, 1058−1064. Deglmann, P.; Furche, F.; Ahlrichs, R. *Chem. Phys. Lett.* **2002**, *362*, 511−518. Deglmann, P.; Furche, F. *J. Chem. Phys.* **2002**, *117*, 9535−9538.

(52) Weigend, F.; Häser, M. *Theor. Chem. Acc.* **1997**, *97*, 331−340. Weigend, F.; Häser, M.; Patzelt, H.; Ahlrichs, R. *Chem. Phys. Lett.* **1998**, *294*, 143−152.