Room-Temperature Insertion of Elemental Tellurium into the C_{sp^3}−Br and −I Bonds of α-Bromo- and α-Iodopinacolone

Ashok K. S. Chauhan,*,† Puspendra Singh,† Arun Kumar,† Ramesh C. Srivastava,† Ray J. Butcher,‡ and Andrew Duthie§

Department of Chemistry, University of Lucknow, Lucknow 226007, India, Department of Chemistry, Howard University, Washington, D.C. 20059, and School of Life and Environmental Sciences, Deakin University, Geelong 3217, Australia

Received December 18, 2006

Pinacolyltellurium(IV) dihalides, (t-BuCOCH$_2$)$_2$TeX$_2$ (X = Br (**1b**), I (**1c**)) and Ar(t-BuCOCH$_2$)TeCl$_2$ (Ar = 1-C$_{10}$H$_7$ (Np) (**2a**), 2,4,6-Me$_3$C$_6$H$_2$ (Mes) (**3a**)), are readily prepared at room temperature by the oxidative insertion of elemental tellurium into the C_{sp^3}−Br or −I bond of the α-halopinacolone and by the reaction of ArTeCl$_3$ with the pinacolone t-BuCOCH$_3$. The bromides Np(t-BuCOCH$_2$)TeBr$_2$ (**2b**) and Mes(t-BuCOCH$_2$)TeBr$_2$ (**3b**) can be prepared by the addition of bromine to the telluride Ar(t-BuCOCH$_2$)-Te or of α-bromopinacolone to ArTeBr. Variable-temperature ^{1}H and ^{13}C NMR of the separate signals for the o-Me groups in **3a**,**b** indicate a very high barrier to rotation about the Te−C(aryl) bond. Crystal diffraction data for **1c**, **2a**−**c**, and **3b** show that intramolecular 1,4-Te···O(C) secondary bonding interactions (SBIs) are retained even in the presence of bulky aryl groups and intermolecular Te···X SBIs are subject to electronic population and steric congestion around the Te(IV) center in the solid state.

Introduction

Available routes to functionalized organotelluriums involve prior protection of the functional group and/or the use of air-sensitive reagents. Oxidative insertion of Te into the C_{sp^3}−I bond offers a direct and simple route to dialkyltellurium(IV) diiodides. Analogous alkyl chlorides and bromides react only in the presence of NaI. In the recent past we achieved insertion of elemental Te into the C_{sp^3}−Br bond in the case of substituted benzoylmethyl bromides, (4-YC$_6$H$_4$COCH$_2$Br, Y = H, Me, OMe), but reaction temperatures of ∼50 °C were required.[1] Electronic effects of the 4-substituent were found to play a vital role in the ease of insertion.[2] In further work, we have now studied the oxidative insertion of Te into the C_{sp^3}−Br(I) bond of α-halopinacolone, t-BuCOCH$_2$X (X = Br, I). Electrophilic substitution of the parent ketone with ArTeCl$_3$ (Ar = Np, Mes) at ambient temperature, a reaction which affords unsymmetrical organotellurium(IV) dichlorides, has also been investigated.

Results and Discussion

Attempted reactions are represented in Scheme 1. Elemental Te inserts into the C_{sp^3}−X (X = Br, I) bond of freshly prepared α-halopinacolone at room temperature to give the crystalline bis(pinacolyl)tellurium dihalides (t-BuCOCH$_2$)$_2$TeX$_2$ (X = Br (**1b**), I (**1c**)). The dichloride analogue (t-BuCOCH$_2$)$_2$TeCl$_2$ (**1a**) has been prepared earlier[3] by the reaction of TeCl$_4$ with pinacolone but was characterized by elemental analysis only. Attempted reduction of **1** with Na$_2$S$_2$O$_5$ leads to the formation of tellurium powder. Reactions of ArTeCl$_3$ with pinacolone at room temperature afforded unsymmetrical aryl(alkyl)-tellurium(IV) dichlorides, Ar(t-BuCOCH$_2$)TeCl$_2$ (Ar = Np (**2a**), Mes (**3a**)). Reduction of **2a** and **3a** with Na$_2$S$_2$O$_5$ gives yellow solutions of the corresponding telluride, Ar(t-BuCOCH$_2$)Te. Oxidative addition of halogens to the labile unsymmetrical tellurides is achieved by adding CCl$_4$ solutions of SO$_2$Cl$_2$, Br$_2$, or I$_2$ to the freshly prepared dichloromethane solutions of tellurides, affording the crystalline dihalides Ar(t-BuCOCH$_2$)-TeX$_2$ (Ar = Np, X = Cl (**2a**), Br (**2b**), I (**2c**); Ar = Mes, X = Cl (**3a**), Br (**3b**)) in good yield. Mes(t-BuCOCH$_2$)TeI$_2$ (**3c**) is obtained by metathesis of **3a** with 2 equiv of KI. Bromides **2b** and **3b** could also be obtained by oxidative addition of α-bromopinacolone to aryltellurium(II) bromide (prepared in situ from Ar$_2$Te$_2$ and Br$_2$), while detelluration of **1b** by mesityltellurium bromide gave **3b**.

The ^{1}H and ^{13}C NMR spectra of the mesityl derivatives (**3**) are interesting, as they show two separate signals for each of the o-Me groups. Extrapolation of variable-temperature ^{1}H NMR data for **3a** in toluene-d$_8$ indicates a coalescence temperature, T_C, close to 210 °C (Supporting Information, Figure S1). The steric bulk of the t-Bu group of the pinacolyl ligand appears to be responsible for the restricted rotation around the Te−C(Mes) bond, as the analogous compounds Mes(4-YC$_6$H$_4$COCH$_2$)TeX$_2$ show only one singlet for the protons of both o-Me groups.[4] The ^{125}Te NMR of the symmetrical as well as the unsymmetrical pinacolyl derivatives **1**−**3** show the presence of only one Te-containing species in solution as well as, in the case of **1a** and **3a**, in the solid state.

Crystal Structures of Pinacolyltellurium(IV) Halides 1c, 2a−c, and 3b. Crystal data and structure refinement details for compounds **1c**, **2a**−**c**, and **3b** are given in Table 1. ORTEP views of their molecular structures are depicted in Figures 1−5.

* To whom correspondence should be addressed. E-mail: akschauhan2003@yahoo.co.in.
† University of Lucknow.
‡ Howard University.
§ Deakin University.

(1) Chauhan, A. K. S.; Kumar, A.; Srivastava, R. C.; Butcher, R. J. *J. Organomet. Chem.* **2002**, *658*, 169.
(2) Chauhan, A. K. S.; Kumar, A.; Srivastava, R. C.; Beckmann, J.; Duthie, A.; Butcher, R. J. *J. Organomet. Chem.* **2004**, *689*, 345.
(3) Morgan, G. T.; Elvins, O. C. *J. Chem. Soc.* **1925**, *127*, 2625.
(4) Chauhan, A. K. S.; Anamika; Kumar, A.; Srivastava, R. C.; Butcher, R. J.; Duthie, A. *J. Organomet. Chem.* **2006**, *691*, 5887.

10.1021/om061144a CCC: $37.00 © 2007 American Chemical Society
Publication on Web 03/17/2007

Scheme 1

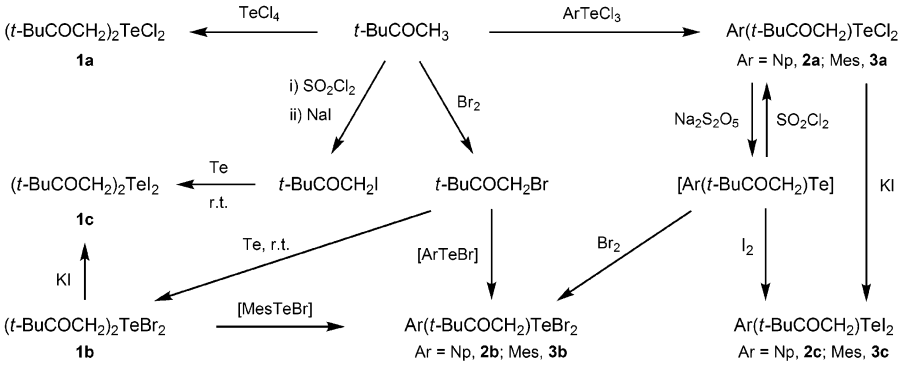

Table 1. Crystal Data and Structure Refinement Details of 1c, 2a−c, and 3b

	1c	2a	2b	2c	3b
empirical formula	$C_{12}H_{22}I_2O_2Te$	$C_{16}H_{18}Cl_2OTe$	$C_{16}H_{18}Br_2OTe$	$C_{16}H_{18}I_2OTe$	$C_{15}H_{22}Br_2OTe$
dormula mass (g mol^{-1})	579.70	424.80	513.72	607.70	505.75
temp (K)	293(2)	293(2)	93(2)	93(2)	93(2)
wavelength, λ (Å)	1.541 78	0.710 73	0.710 73	0.710 73	0.710 73
cryst syst	monoclinic	monoclinic	monoclinic	orthorhombic	triclinic
cryst size (mm^3)	0.88 × 0.12 × 0.08	0.50 × 0.20 × 0.15	0.95 × 0.25 × 0.10	0.30 × 0.20 × 0.04	0.78 × 0.65 × 0.14
space group	$P2_1/n$	$P2_1/c$	$P2_1/c$	$Pcab$	$P\bar{1}$
a (Å)	5.9353(8)	6.3922(3)	6.515(1)	9.344(2)	8.683(2)
b (Å)	18.965(2)	14.4621(7)	14.279(3)	18.924(4)	9.604(2)
c (Å)	16.687(4)	19.0730(9)	19.049(4)	20.531(4)	11.030(2)
α (deg)	90	90	90	90	72.785(3)
β (deg)	90.64(2)	94.477(1)	93.574(3)	90	81.713(6)
γ (deg)	90	90	90	90	85.755(6)
V (Å^3)	1878.2(6)	1757.8(1)	1768.6(6)	3630(1)	868.9(3)
Z	4	4	4	8	2
ρ_{calcd} (Mg m^{-3})	2.050	1.605	1.929	2.224	1.933
abs coeff (mm^{-1})	38.249	1.990	6.194	5.035	6.302
F(000)	1072	832	976	2240	484
θ range (deg)	3.53−56.04	1.77−27.99	1.78−27.50	1.98−24.73	1.95−25.00
index ranges	$-6 \le h \le 0$, $-20 \le k \le 0$, $-17 \le l \le 17$	$-8 \le h \le 8$, $-18 \le k \le 16$, $-23 \le l \le 25$	$-7 \le h \le 8$, $-18 \le k \le 18$, $-24 \le l \le 24$	$-10 \le h \le 9$, $-22 \le k \le 22$, $-24 \le l \le 24$	$-10 \le h \le 10$, $10 \le k \le 11$, $0 \le l \le 13$
no. of rflns collected	2667	13 646	13 112	18 500	2933
no. of indep rflns	2391 (R(int) = 0.0299)	4212 (R(int) = 0.0301)	4056 (R(int) = 0.0280)	3096 (R(int) = 0.1044)	3834 (R(int) = 0.0000)
completeness to θ_{max} (%)	97.6	99.2	99.6	99.8	95.5
abs cor			semiempirical from equivalents		
max, min transmissn	0.7737, 0.3583	1.000, 0.790	1.000, 0.639	1.000, 0.356	1.000, 0.356
refinement method			full-matrix least squares on F^2		
no. of data/restraints/params	2391/0/155	4212/31/309	4056/31/270	3096/0/181	2933/0/172
goodness of fit on F^2	1.089	1.053	1.001	1.031	1.008
final R indices ($I > 2\sigma(I)$)	R1 = 0.0785, wR2 = 0.2085	R1 = 0.0266, wR2 = 0.0634	R1 = 0.0330, wR2 = 0.0722	R1 = 0.0541, wR2 = 0.1354	R1 = 0.0561, wR2 = 0.1499
R indices (all data)	R1 = 0.0961, wR2 = 0.2345	R1 = 0.0398, wR2 = 0.0666	R1 = 0.0380, wR2 = 0.0742	R1 = 0.0896, wR2 = 0.1722	R1 = 0.0630, wR2 = 0.1536
largest diff peak/hole (e Å^{-3})	0.984/−1.048	0.698/−0.696	1.761/−2.348 (near Br)	1.863/−2.892 (near Te)	2.298/−3.147 (near Te)

The primary geometry around the Te(IV) atom in these diorganotellurium dihalides is ψ trigonal bipyramidal with a stereochemically active lone pair. Interatomic Te···O(carbonyl) distances (d(Te···O) range 2.811(3) Å in **2b** to 2.895(6) Å in **3b**) are short enough to imply the presence of attractive intramolecular 1,4-Te···O secondary bonding interactions.[5] In the symmetrical diorganotellurium(IV) compound **1c**, the small-bite chelating ligands adopt cisoidal conformations to give rise to two coplanar four-membered rings with a six-coordinate Te(IV) atom. The molecular geometry bears the butterfly shape (almost perfect C_{2v} symmetry). The crystal lattice is devoid of intermolecular Te···X SBIs, which substantiates our earlier observation[6] that intramolecular Te···O SBIs reduce the electrophilicity of the central Te atom among carbonyl-functionalized diorganotellurium(IV) dihalides to an extent that intermolecular Te···A interactions (A is an electron-rich atom) are discouraged.

The crystal structures of Np(*t*-BuCOCH$_2$)TeCl$_2$ (**2a**) and Np(*t*-BuCOCH$_2$)TeBr$_2$ (**2b**) exhibit statistical twofold disorder associated with the 1-naphthyl and *t*-Bu fragments. While the interatomic distances between the central Te(IV) and ligand atoms in **2a** compare well with those in the phenacyl analogue Np(PhCOCH$_2$)TeCl$_2$,[4] a larger C−Te−C angle (103.5(3)° in **2a** compared to 98.4(1)° in Np(PhCOCH$_2$)TeCl$_2$) is indicative of greater steric repulsion between the 1-naphthyl and pinacolyl ligands. As a consequence, the molecular association by means

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

(6) Chauhan, A. K. S.; Anamika; Kumar, A.; Srivastava, R. C.; Butcher, R. J. *J. Organomet. Chem.* **2005**, *690*, 313.

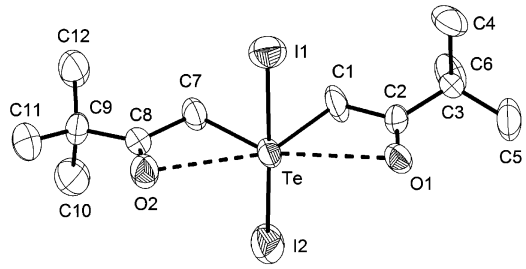

Figure 1. ORTEP diagram showing 30% probability displacement ellipsoids and crystallographic numbering scheme for **1c**. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Te−C1 = 2.17(2), Te−C7 = 2.11(2), Te−I1 = 2.896(2), Te−I2 = 2.889(2), Te···O1 = 2.87(1), Te···O2 = 2.85(1); C1−Te−C7 = 95.0(7), I1−Te−I2 = 173.50(7).

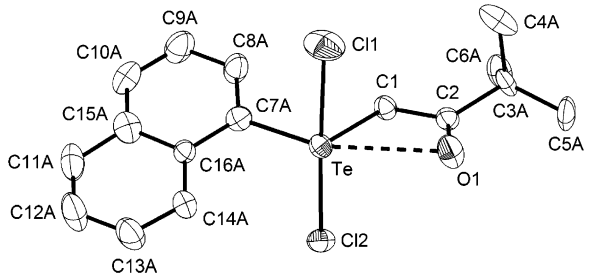

Figure 2. ORTEP diagram showing 30% probability displacement ellipsoids and the crystallographic numbering scheme for **2a**. Only one set of atoms for the disordered *t*-Bu and naphthyl groups is shown. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Te−C1 = 2.118(3), Te−C7A = 2.01(2), Te−Cl1 = 2.478(1), Te−Cl2 = 2.512(1), Te···O1 = 2.828(2); C1−Te−C7A = 103.5(3), Cl1−Te−Cl2 = 172.17(3).

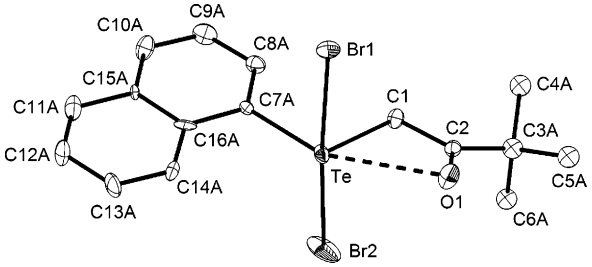

Figure 3. ORTEP diagram showing 50% probability displacement ellipsoids and the crystallographic numbering scheme for **2b**. Only one set of atoms for the disordered *t*-Bu and naphthyl groups is shown. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Te−C1 = 2.123(4), Te−C7A = 2.17(2), Te−Br1 = 2.668(1), Te−Br2 = 2.652(1), Te···O1 = 2.811(3); C1−Te−C7 = 97.0(3), Br1−Te−Br2 = 171.73(2).

of intermolecular Te···X SBIs that is commonplace in the solid-state structures of organotellurium(IV) halides[7] is not realized in the pinacolyl derivatives **2a**,**b**. Instead, C−H···X (X = Cl, Br) hydrogen bonds[8,9] involving Te(IV)-bound halogen atoms are observed in the crystalline state (Supporting Information, Figures S2 and S3). On the other hand, longer Te−I bonds in the diiodide analogue **2c** reduce steric repulsion between the equatorial ligands (∠C−Te−C = 96.2(5)°) and intermolecular Te···I SBIs (in addition to C−H···O H-bonding) appear to contribute significantly to the formation of centrosymmetric

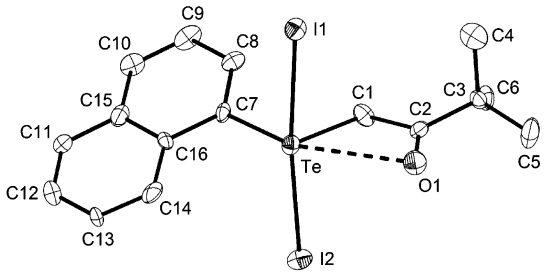

Figure 4. ORTEP diagram showing 50% probability displacement ellipsoids and the crystallographic numbering scheme for **2c**. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Te−C1 = 2.14(1), Te−C7 = 2.12(1), Te−I1 = 2.918(1), Te−I2 = 2.927(1), Te···O = 2.87(1); C1−Te−C7 = 96.2(5), I1−Te−I2 = 173.94(4).

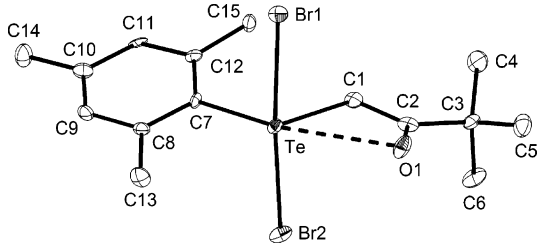

Figure 5. ORTEP diagram showing 50% probability displacement ellipsoids and the crystallographic numbering scheme for **3b**. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Te−C1 = 2.143(8), Te−C7 = 2.118(8), Te−Br1 = 2.667(1), Te−Br2 = 2.679(1), Te···O = 2.895(6); C1−Te−C7 = 107.7(3), Br1−Te−Br2 = 173.64(3).

dimer supermolecules in its crystalline state (Supporting Information, Figure S4).

The presence of the sterically more demanding mesityl and the chelating pinacolyl ligands further widens the C−Te−C angle to 107.64(3)° in (Mes)(*t*-BuCOCH$_2$)TeBr$_2$, (**3b**). Greater steric repulsion between the skeletal carbon atoms of mesityl and acyl ligands is also obvious from the larger interplanar angle of 25.1(2)° in **3b** as compared to 4.5(2)° in (Mes)(PhCOCH$_2$)-TeCl$_2$.[4] This impedes free rotation of the mesityl group about the Te−C(aryl) bond (as also indicated by ^{1}H and ^{13}C NMR data; vide supra). Steric hindrance of the mesityl group together with the intramolecular Te···O SBI results in an absence of intermolecular Te···X SBIs in the crystal structure of **3b**.

Experimental Section

General Considerations. Preparative work was performed under dry nitrogen. Melting points were recorded in capillary tubes and are uncorrected. The starting materials, pinacolone and α-bromopinacolone, were prepared by literature methods.[10,11] α-Chloropinacolone was prepared by chlorination of pinacolone in dichloromethane with sulfuryl chloride, while α-iodopinacolone was obtained by halide exchange of α-chloropinacolone with sodium iodide in acetone. 1-Naphthyltellurium and mesityltellurium trichlorides were prepared by the chlorination of their corresponding ditellurides. IR spectra were recorded as KBr pellets using a Perkin-Elmer RX1 spectrometer. The elctrospray mass spectra were recorded on a Micromass Quattro II triple quadrupole ESI spectrometer with capillary and cone voltages of 3.5 kV and 40 V, respectively. The data are averaged over six to eight scans. ^{1}H NMR spectra were recorded at 300.13 MHz in CDCl$_3$ on a Varian DRX

(7) Zukerman-Schpecter, J.; Haiduc, I. *Phosphorus, Sulfur Silicon Relat. Elem.* **2001**, *171*, 73.
(8) Aullón, G.; Bellamy, D.; Brammer, L.; Bruton, E. A.; Orpen, A. G. *Chem. Commun.* **1998**, 653.
(9) Thallapally, P. K.; Nangia, A. *Cryst. Eng. Commun.* **2001**, 114.
(10) Furniss, B. S.; Hannaford, A. J.; Smith, P. W. G.; Tatchell, A. R.; *Vogel's Text Book of Practical Organic Chemistry*, 5th ed.; Addison-Wesley: Reading, MA, 1989; p 527.
(11) Hill, G. A.; Kropa, E. L. *J. Am. Chem. Soc.* **1933**, *55*, 2509.

300 spectrometer using Me_4Si as the internal standard. Solution $^{13}C\{^1H\}$ (100.54 MHz) and $^{125}Te\{^1H\}$ NMR spectra (126.19 MHz) were recorded in $CDCl_3$ on a JEOL Eclipse Plus 400 NMR spectrometer, using Me_4Si and Me_2Te as internal standards. $^{125}Te\{^1H\}$ CP-MAS NMR spectra were obtained using the same spectrometer equipped with a 6 mm rotor operating at spinning frequencies between 8 and 10 kHz. A 10 s relaxation delay was used, and typically 5000−10 000 transitions were accumulated to obtain adequate signal-to-noise ratios. The isotropic chemical shifts δ_{iso} were determined by comparison of two acquisitions measured at sufficiently different spinning frequencies and were referenced against Me_2Te using solid $Te(OH)_6$ as the secondary reference (δ_{iso} 692.2/685.5).[12] Microanalyses were carried out using a Carlo Erba 1108 analyzer. Tellurium was estimated volumetrically and the halogen content gravimetrically as silver halide.

Preparation of $(t\text{-BuCOCH}_2)_2TeX_2$ (X = Cl (1a), Br (1b), I (1c)). (a) 1b. Freshly ground tellurium powder (0.64 g, 5.0 mmol) and α-bromopinacolone (1.79 g, 10.0 mmol) were stirred together at room temperature for 24 h. The resulting blackish solid was extracted with hot hexane (50 mL), and the extracts were cooled to give crude bis(pinacolyl)ltellurium dibromide (**1b**), which was recrystallized from hot CCl_4 as colorless needles. Yield: 1.60 g (66%). Mp: 195−196 °C. Anal. Calcd for $C_{12}H_{22}O_2Br_2Te$: C, 29.65; H, 4.53; Te, 26.27. Found: C, 29.70; H, 4.60; Te, 26.30. IR (cm^{-1}): 1686.2 ($\nu_{C=O}$). ^1H NMR: δ 1.26 (s, 9H, CMe_3), 4.96 (s, 2H, CH_2) ppm. $^{13}C\{^1H\}$ NMR: δ 26.43 (Me), 43.88 (C), 55.51 ($^1J(^{13}C-^{125}Te)$ = 110 Hz, CH_2), 208.54 (CO) ppm. $^{125}Te\{^1H\}$ NMR: δ 671.6 ppm. ESMS: *m/z* 427.2 $[M - 2Br + t\text{-BuCOCH}_2]^+$, 407.0 $[M - Br]^+$, 345.1 $[M - 2Br + OH]^+$.

(b) 1c. Yellow crystalline $(t\text{-BuCOCH}_2)_2TeI_2$ (**1c**) was prepared from iodopinacolone (2.26 g, 10.0 mmol) and tellurium powder (0.64 g, 5.0 mmol) using the method above for the preparation of **1b**. Yield: 1.45 g (50%). Mp: 164 °C. Anal. Calcd for $C_{12}H_{22}O_2I_2Te$: C, 24.84; H, 3.79; Te, 22.01. Found: C, 25.01; H, 3.85; Te, 22.40. IR (cm^{-1}): 1685.8 ($\nu_{C=O}$). ^1H NMR: δ 1.27 (s, 9H, CMe_3), 4.97 (s, 2H, CH_2) ppm. $^{13}C\{^1H\}$ NMR: δ 26.56 (Me), 43.64 (C), 52.04 ($^1J(^{13}C-^{125}Te)$ = 84 Hz, CH_2), 208.98 (CO) ppm. $^{125}Te\{^1H\}$ NMR: δ 569.2 ppm. The iodide **1c** is relatively less stable than the bromide **1b** or the chloride **1a**, as it changes color slowly with time. Elemental tellurium is obtained when **1c** is heated in methanol.

Alternatively, **1c** was prepared in higher yield when **1b** (0.49 g, 1.0 mmol) and KI (0.33 g, 2.0 mmol) were stirred together in chloroform (10 mL) for ∼3 h. Potassium halides were removed by filtration. Addition of petroleum ether and cooling afforded yellow crystals of **1c**. Yield: 0.43 g (74%).

(c) 1a. This compound was prepared according to the literature method[3] using $TeCl_4$ (3.45 g, 12.8 mmol) and pinacolone (2.92 g, 25.6 mmol). Yield: 1.27 g (25%). Mp: 191−192 °C. Anal. Calcd for $C_{12}H_{22}O_2Cl_2Te$: C, 36.30; H, 5.55; Cl, 17.90; Te, 32.17. Found: C, 36.13; H, 5.53; Cl, 18.50; Te, 32.40. IR (cm^{-1}): 1686.5 ($\nu_{C=O}$). ^1H NMR: δ 1.32 (s, 9H, CMe_3), 4.81 (s, 2H, CH_2) ppm. $^{13}C\{^1H\}$ NMR: δ 26.34 (Me), 43.99 (C), 57.30 ($^1J(^{13}C-^{125}Te)$ = 127 Hz, CH_2), 208.61 (CO) ppm. $^{125}Te\{^1H\}$ NMR: δ 743.5 ppm. $^{125}Te\{^1H\}$ CP-MAS: δ_{iso} 745.1 ppm.

Reaction of Pinocolone with $ArTeCl_3$ (Ar = Np, Mes). (a) 2a. A mixture of 1-naphthyltellurium trichloride (3.61 g, 10.0 mmol) and pinacolone (1.50 g, 15.0 mmol) was stirred slowly at room temperature under a flow of dry nitrogen (∼12 h). The resulting paste was washed with cold petroleum ether (3 × 10 mL), triturated with diethyl ether, and filtered to remove excess pinacolone. The residue was dissolved in chloroform and filtered through a short silica column. Concentration of the extract to about one-third of its original volume and addition of diethyl ether afforded a colorless solid, which was recrystallized from chloroform to give **2a** as rectangular crystals. Yield: 3.40 g (80%). Mp: 200 °C. Anal. Calcd for $C_{16}H_{18}OCl_2Te$: C, 45.24; H, 4.27; Cl, 16.69; Te, 30.04. Found: C, 45.26; H, 4.29; Cl, 17.80; Te, 29.80. IR (cm^{-1}): 1681.3 ($\nu_{C=O}$). ^1H NMR: δ 1.34 (s, 9H, CMe_3), 5.29 (s, 2H, CH_2), 7.59−8.19 (m, 7H, aryl) ppm. $^{13}C\{^1H\}$ NMR: δ 26.52 (Me), 43.37 (C), 66.35 ($^1J(^{13}C-^{125}Te)$ = 101 Hz, CH_2), 126.40, 126.81, 127.29, 128.20, 129.44, 131.98, 132.71, 132.92, 133.07, 134.22 (aryl C), 208.39 (CO) ppm. $^{125}Te\{^1H\}$ NMR: δ 762.6 ppm. ESMS: *m/z* 427.0 $[M - Cl + 2H_2O]^+$, 391.0 $[M - 2Cl + OH + H_2O]^+$, 373.0 $[M - 2Cl + OH]^+$.

(b) 3a. This compound was prepared from mesityltellurium trichloride (3.53 g, 10.0 mmol) and pinacolone (1.71 g, 15.0 mmol) at room temperature. Yield: 3.41 g (82%). Mp: 184 °C. Anal. Calcd for $C_{15}H_{22}OCl_2Te$: C, 43.22; H, 5.32; Cl, 17.01; Te, 30.61. Found: C, 43.24; H, 5.33; Cl, 17.0; Te, 30.50. IR (cm^{-1}): 1689.3 ($\nu_{C=O}$). ^1H NMR: δ 1.29 (s, 9H, CMe_3), 2.32 (s, 3H, *p*-Me), 2.70 (s, 3H, *o*-Me), 2.79 (s, 3H, *o*-Me), 5.21 (s, 2H, CH_2), 6.98 (s, 1H, aryl) 7.03 (s, 1H, aryl) ppm. $^{13}C\{^1H\}$ NMR: δ 21.00 (*p*-Me), 23.62 (*o*-Me), 24.08 (*o*-Me), 26.49 (CMe_3), 43.64 (C), 67.78 ($^1J(^{13}C-^{125}Te)$ = 120 Hz, CH_2), 130.35, 131.49, 134.19, 140.18, 141.09, 142.24 (aryl C), 208.48 (CO) ppm. $^{125}Te\{^1H\}$ NMR: δ 784.1 ppm. $^{125}Te\{^1H\}$ CP-MAS: δ_{iso} 814.5 ppm.

Oxidative Addition Reactions. A solution of **2a** (0.425 g, 1.00 mmol) in dichloromethane (∼40 mL) was shaken with an aqueous solution of $Na_2S_2O_5$ (0.57 g, 3.0 mmol) for ∼5 min. The yellow organic layer was quickly separated, washed with water (2 × 20 mL), and passed through anhydrous Na_2SO_4. To the resulting solution was added a solution of bromine (0.12 mL, 1.00 mmol) in carbon tetrachloride (5 mL) dropwise at room temperature. The volatiles were removed under reduced pressure, the residue was dissolved in dichloromethane, and this solution was passed through a short silica column. Concentration of the resulting solution and addition of petroleum ether afforded **2b** as yellow crystals: Yield: 0.45 g (88%). Mp: 194 °C. Anal. Calcd for $C_{16}H_{18}OBr_2Te$: C, 37.41; H, 3.53; Te, 24.84. Found: C, 37.45; H, 3.58; Te, 25.00. ^1H NMR: δ 1.35 (s, 9H, CMe_3), 5.45 (s, 2H, CH_2), 7.57−8.38 (m, 7H, aryl) ppm.

Under conditions similar to those above, reaction with I_2 (0.254 g, 1.00 mmol) afforded **2c**. Yield: 0.39 g (64%). Mp: 149 °C. Anal. Calcd for $C_{16}H_{18}OI_2Te$: C, 31.62; H, 2.99; I, 41.76; Te, 21.00. Found: C, 31.66; H, 3.01; I, 42.50; Te, 22.00. ^1H NMR: δ 1.37 (s, 9H, CMe_3), 5.49 (s, 2H, CH_2), 7.52−8.12 (m, 7H, aryl) ppm.

Compound **2c** was also prepared in higher yield when **2a** (0.426 g, 1.00 mmol) and KI (0.330 g, 2.0 mmol) were stirred together in chloroform (15 mL) for ∼3 h. Potassium halides were removed by filtration. Addition of petroleum ether and cooling afforded yellow crystals of **2c**. Yield: 0.455 g (77%).

Reduction of **2b** (0.514 g, 1.00 mmol) followed by addition of SO_2Cl_2 (0.57 g, 3.0 mmol) gave **2a**. Yield: 0.34 g (80%). Mp: 200 °C.

Reduction of **3a** (0.417 g, 1.00 mmol) using the above method for the reduction of **2a**, followed by addition of Br_2 (0.12 mL, 1.00 mmol), gave **3b**. Yield: 0.35 g (70%). Mp: 180 °C. Anal. Calcd for $C_{15}H_{22}OBr_2Te$: C, 35.62; H, 4.38; Te, 25.23. Found: C, 35.70; H, 4.45; Te, 25.70. IR (cm^{-1}): 1694.22 ($\nu_{C=O}$). ^1H NMR: δ 1.30 (s, 9H, CMe_3), 2.32 (s, 3H, *p*-Me), 2.67 (s, 3H, *o*-Me), 2.76 (s, 3H, *o*-Me), 5.38 (s, 2H, CH_2), 6.96 (s, 1H, aryl), 7.02 (s, 1H, aryl) ppm. ESMS: *m/z* 427.0 $[M - Br]^+$, 365.1 $[M - 2Br + OH]^+$.

Compound **3c** was prepared in good yield (80%) by metathesis of **3a** with KI in a way similar to that of **2b** (vide supra). Yield: 75%. Mp: 125−126 °C. Anal. Calcd for $C_{15}H_{22}OI_2Te$: C, 30.04; H, 3.70; Te, 21.28. Found: C, 30.24; H, 3.60; Te, 21.70. ^1H NMR: δ 1.33 (s, 9H, CMe_3), 2.33 (s, 3H, *p*-Me), 2.58 (s, 3H, *o*-Me), 2.66 (s, 3H, *o*-Me), 5.47 (s, 2H, CH_2), 6.93, 7.00 (2H, aryl) ppm. $^{13}C\{^1H\}$ NMR: δ 21.43 (*p*-Me), 23.80 (*o*-Me), 26.11 (*o*-Me), 27.09 (CMe_3), 44.60 (C), 60.86 (CH_2), 125.84, 132.09, 137.09, 139.66, 142.10, 142.45 (aryl C), 209.15 (CO) ppm.

(12) Collins, M. J.; Ripmeester, J. A.; Sawyer, J. F. *J. Am. Chem. Soc.* **1987**, *109*, 4113.

Alternative Procedures for Synthesis of 2b and 3b. (i) To a suspension of NpTeBr (prepared in situ from Np_2Te_2 (0.255 g, 0.50 mmol) and Br_2 (0.080 g, 0.50 mmol) in chloroform at 0 °C) was added a solution of α-bromopinacolone (0.179 g, 1.00 mmol) in the same solvent at room temperature. The reaction mixture was stirred for 24 h at room temperature and then heated at reflux for 2 h. The dark brown solid that formed was removed by filtration and the solvent removed under reduced pressure to give a dark brown paste that was washed twice with cold diethyl ether. The residue was dissolved in $CHCl_3$ and filtered through a short silica column. Removal of volatiles afforded **2b** as a light yellow solid. Yield: 0.15 g (29%). Mp: 194 °C.

Under similar conditions Mes_2Te_2 (0.247 g, 0.50 mmol) afforded **3b**. Yield: 0.15 g (30%). Mp: 180−181 °C.

(ii) To a suspension of MesTeBr (prepared in situ from Mes_2Te_2 (0.247 g, 0.50 mmol) and Br_2 (0.080 g, 0.50 mmol) in dichloromethane at 0 °C) was added a solution of **1b** (0.243 g, 0.50 mmol) in the same solvent at room temperature. Elemental tellurium began to appear after 2 h of stirring. The reaction mixture was stirred for 12 h before filtering to remove tellurium powder (0.057 g, 90% with respect to **1b**). Volatiles were distilled from the filtrate under reduced pressure to give a brown residue that was washed with diethyl ether to remove unreacted **1b** and dissolved in chloroform (10 mL), and this solution was passed through a short silica column. Addition of petroleum ether (40−60 °C) to the concentrated solution afforded **3b** on cooling, as a light yellow crystalline solid. Yield: 0.18 g (35%, with respect to Mes_2Te_2).

Crystallography. Single crystals of **1c**, **2a**−**c**, and **3b** suitable for X-ray crystallography were obtained by slow evaporation of their chloroform solutions. Intensity data were collected on a Bruker PS4 diffractometer with graphite-monochromated Mo Kα (1.547 18 Å for **1c** and 0.710 73 Å for **2a**−**c** and **3b**) radiation. Data were reduced and corrected for absorption using the programs SAINT and SADABS.[13] The structures were solved by direct methods and difference Fourier synthesis using SHELXS-97 implemented in the program WinGX 2002.[14] Full-matrix least-squares refinements on F^2, using all data, were carried out with anisotropic displacement parameters applied to all non-hydrogen atoms except the t-Bu carbons of **2b**, which were refined isotropically. Hydrogen atoms were included in geometrically calculated positions using a riding model and were refined isotropically. The *t*-Bu and naphthyl groups of compounds **2a**,**b** are disordered and were refined over two sites with occupancy factors of 0.46(2):0.54(2) and 0.489(4):0.511(4) for **2a** and 0.48(2):0.52(2) and 0.495(6):0.505(6) for **2b**, respectively.

Acknowledgment. Financial assistance by the Department of Science and Technology, Government of India, New Delhi, India, is gratefully acknowledged. P.S. thanks the CSIR, New Delhi, India, for a JRF.

Supporting Information Available: Figures summarizing variable-temperature ^{1}H NMR spectra for **3a** and intermolecular interactions for **2a**−**c** and CIF files containing crystal data for **1c**, **2a**−**c**, and **3b**. This material is available free of charge via the Internet at http://pubs.acs.org. The CIF files have also been deposited with the Cambridge Crystallographic Data Centre. CCDC numbers for **1c**, **2a**−**c**, and **3b** are 639550, 639551, 639552, 639553, and 639554, respectively. Copies of the data can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EX, U.K. (fax, +44-1223-336033; web, http://www.ccdc.cam.ac.uk/).

OM061144A

(13) SMART, SAINT and SADABS; Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1999.

(14) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837.