Orthotellurated Derivatives of *N,N*-Dimethylbenzylamine: Crystal and Molecular Structures of [2-(Dimethylaminomethyl)phenyl]tellurium(IV) Tribromide and [2-(Butyldichlorotelluro)benzyl]dimethylammonium Chloride†

Harkesh B. Singh* and Narsimhan Sudha
Department of Chemistry, Indian Institute of Technology, Bombay 400 076, India
Antony A. West
Department of Chemical Engineering and Applied Chemistry, Aston University, Aston Triangle, Birmingham B4 7ET
Thomas A. Hamor*
Department of Chemistry, University of Birmingham, P.O. Box 363, Birmingham B15 2TT

The reaction of *o*-lithiobenzylamine with elemental tellurium followed by air oxidation furnished an ill defined 'tellurinic anhydride'. Halogenolysis reactions of this with bromine and sulphonyl chloride afforded the corresponding [2-(dimethylaminomethyl)phenyl]trihalogenotellurium(IV) derivatives. Reduction of the trihalides with excess of hydrazine hydrate gave novel [2-(dimethylaminomethyl)phenyl]halogenotellurium(II) derivatives. Metathesis of the chlorotellurium-(IV) and -(II) derivatives with sodium diethyldithiocarbamate resulted in the formation of dithiocarbamato derivatives. The crystal structure of [2-(dimethylaminomethyl)phenyl]tellurium(IV) tribromide is monoclinic, space group $P2_1/n$ with a = 9.226(6), b = 15.439(8), c = 9.618(5) Å, β = 94.94(5)°, Z = 4, and R = 0.0419 for 938 observed reflections. The co-ordination about Te approximates to octahedral with a vacant equatorial site: two Br atoms axial, the third Br and the organic ligand equatorial [Te–$Br_{(ax)}$ 2.758(2) and 2.633(3), Te–$Br_{(eq)}$ 2.632(2), Te–C 2.12(1), and Te–N 2.42(1) Å]. The compound is essentially monomeric, with a weak association between Te and a neighbouring bromine atom [3.896(2) Å]. [2-(Butyldichlorotelluro)benzyl]dimethylammonium chloride is monoclinic, space group $P2_1/n$ with a = 14.278(12), b = 8.349(5), c = 14.480(8) Å, β = 93.59(5)°, Z = 4, and R = 0.0288, for 2 245 observed reflections. The co-ordination about Te can also be considered as octahedral with a vacant equatorial site: two chlorines apical, and the chloride ion and two carbon atoms equatorial [Te–Cl 2.527(1) and 2.487(1), Te··· Cl 3.337(2), Te–C 2.134(4) and 2.154(4) Å]. The quaternary nitrogen atom is twisted away from the tellurium atom, Te···N 4.380(4) Å, forming a hydrogen bond with a chloride ion.

Cyclometallated compounds in which the metal–carbon σ bond is stabilized by a metal–donor atom bond have attracted considerable attention.[1–4] This is due partly to the compounds showing promise as powerful reagents for natural product synthesis[5] and as multidentate ligands for binding transition metals in a particular way.[6] Recently it has been shown that, among nitrogen donors, azobenzene,[7] Schiff bases,[8,9] and substituted pyridines[10] can be orthotellurated. In this paper we report some novel orthotellurated complexes of another important skeleton, *N,N*-dimethylbenzylamine. Emphasis has previously been placed on palladium(II) complexes[11,12] of this substrate because the Pd–C bonds in these particular compounds can undergo a large variety of insertion reactions. However such complexes are not so common with main-group elements.[13] We note an unsuccessful attempt to tellurate *N,N*-dimethylbenzylamine by Gysling *et al.*[14]

Following earlier structural studies of bis[2-(2-pyridyl)-phenyl] tritelluride,[15] [2-(2-pyridyl)phenyl]tellurium(IV) tribromide,[10] dimethyldithiocarbamato[2-(2-pyridyl)phenyl]tellurium(II),[10] and dimethyldithiocarbamato[2-(2-quinolinyl)-phenyl]tellurium(II)[16] in which short Te···N interactions of 2.244—2.554 Å were observed, we now report the crystal structures of [2-(dimethylaminomethyl)phenyl]tellurium(IV) tribromide and [2-(butyldichlorotelluro)benzyl]dimethylammonium chloride. We continue our examination of the effect on the Te··· N interaction of the ligand type *trans* to nitrogen and of protonating the nitrogen atom.

Results and Discussion

Gysling *et al.*[14] attempted telluration by the reaction of *o*-lithio-*N,N*-dimethylbenzylamine with tellurium tetrachloride in tetrahydrofuran (thf) at −78 °C. The work-up led to decomposition. We have now found that orthotellurated complexes are formed in good yield from *o*-lithio-*N,N*-dimethylbenzylamine and elemental tellurium. The light yellow solution of arenetellurolate could be easily obtained by the reaction of *o*-lithiobenzylamine with finely powdered tellurium which was consumed completely in 3 h (Scheme 1). The oxidative work-up, as expected, did not afford the ditelluride (**1**). Instead a yellowish white oxygenated product (**2**) was obtained. Compound (**2**) showed a broad absorption band in the i.r. around 600 cm^{-1} indicating the presence of a Te–O vibration.[17] The u.v.–visible absorption spectrum in dichloromethane exhibited a band at $\lambda_{max.}$ 382 nm; however it did not show a band at ≈ 400 nm characteristic[18] of Te–Te vibration. The mass spectrum showed $R_2Te_2^+$ at m/z = 524 as the highest peak. This is not surprising in view of the fact that the oxygenated tellurium derivatives pyrolyze and do not show the M^+ peak. It was not found possible, however, to assign a structure to compound (**2**) consistent with the C, H, and N analysis.

Compound (**2**) underwent facile halogenolysis with bromine and sulphonyl chloride to yield the corresponding trihalides (**3**)

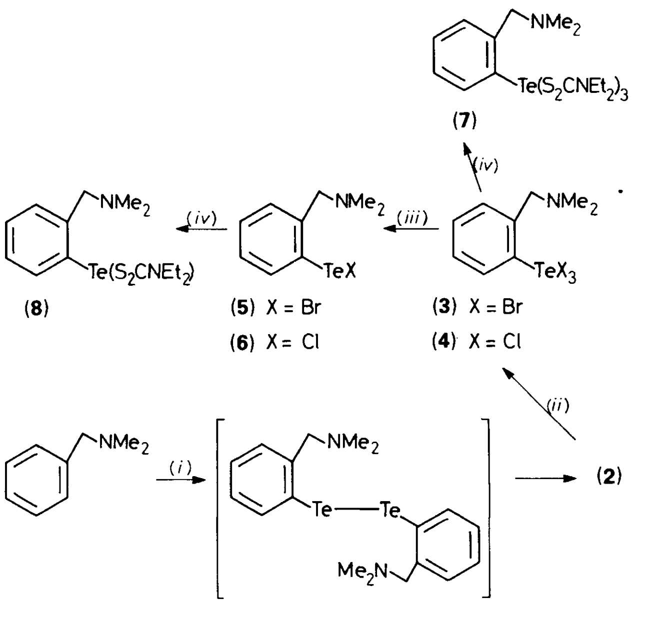
---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Table 1. Analytical data

Compound	M.p./°C	Yield/%	Colour	Analysis*/% C	H	N
(2)	160 (decomp.)	—	Yellowish white	34.2 ( )	4.65 ( )	4.20 ( )
(3)	200 (decomp.)	75	Yellowish orange	21.7 (21.5)	2.70 (2.40)	—
(4)	181	79	Pale yellow	29.0 (29.3)	3.20 (3.30)	3.75 (3.80)
(5)	124	64	Orange	29.3 (31.6)	3.00 (3.55)	3.70 (4.10)
(6)	121	62	Yellow	35.2 (36.3)	3.70 (4.05)	—
(7)	108—110	71	Yellowish orange	40.5 (40.7)	5.80 (6.00)	7.35 (7.90)
(8)	137—139	80	Yellow	41.3 (41.0)	5.45 (5.35)	6.65 (6.80)
(9)	166(decomp.)	39	White	33.8 (34.5)	4.25 (4.35)	3.70 (4.00)
(10)	140	40	White	36.4 (36.5)	4.35 (4.70)	3.85 (3.95)
(11)	143	32	White	36.4 (36.6)	5.05 (5.15)	—
(12)	178—180	51	White	29.5 (28.1)	3.00 (2.90)	—

* Calculated values in parentheses.



Scheme 1. (*i*) LiBu^n, Te°; (*ii*) SO_2Cl_2 or Br_2; (*iii*) $N_2H_4{\cdot}xH_2O$; (*iv*) $Na(S_2CNEt_2)$

and (**4**) in excellent yields. The structure of (**3**) has been established by *X*-ray crystallography. When reduction of the aryltellurium trihalides (**3**) and (**4**) with 0.5 equivalent of hydrazine hydrate in methanol was carried out, novel aryltellurium halides (**5**) and (**6**) were obtained in good yields. Metathetical reaction of the orthotellurated trichloride (**4**) and monochloride (**6**) with excess of sodium diethyldithiocarbamate afforded the corresponding dithiocarbamato derivatives (**7**) and (**8**).

Whilst ^1H and ^{13}C n.m.r. data in the case of HgR_2[13] and HgRCl ($R = C_6H_4CH_2NMe_2$) are not informative with regard to intramolecular Hg···N co-ordination, ^1H and ^{13}C n.m.r. data for tellurium compounds $RTeX_3$ and RTeX are significantly different from those for the free ligand. The N-methyl proton resonances of the free amine at about δ 2.2 are shifted downfield to 2.6—3.0 for the tellurium complexes indicating that nitrogen is co-ordinated through its unshared pair of electrons to the central atom, in agreement with the *X*-ray results for tribromide (**3**). In the case of dichloride (**11**), which was isolated as the hydrochloride salt, the *X*-ray results show that the nitrogen atom is not co-ordinated to tellurium and the downfield shift is due to protonation of the nitrogen atom. The downfield shift, as expected, is more pronounced in the case of aryltellurium trihalides where tellurium is bonded to the maximum number of electronegative groups. In contrast the proton resonances of the dithiocarbamato derivatives are shifted upfield.

The assignment of the carbon resonances was accomplished by taking into account the simple additivity relationship values for the monosubstituted benzene (128.5 p.p.m.)[19] as well as the chemical shift values of the analogous tellurium derivatives.[20] Inspection of the data reveals that telluration of the skeleton causes a downfield shift of *ca.* 18 p.p.m. indicative of telluration in the *ortho* position.

Arylmercury compounds containing *ortho* donor groups are known to undergo facile transmetallation reactions with tellurium tetrahalides and aryltellurium trihalides. This prompted us to study the transmetallation of $Hg(C_6H_4CH_2NMe_2\text{-}2)Cl$[13] with $TeBr_4$ and $EtOC_6H_4TeCl_3$ (Scheme 2). The reaction of $EtOC_6H_4TeCl_3$ with the mercury complex gave an insoluble white crystalline precipitate. Analytical data correspond to the adduct formula (**12**). Very recently McWhinnie and co-workers[10] have also observed similar adduct formation in the reaction of [2-(2-pyridyl)phenyl]mercury(II) chloride with organotellurium trihalides.

The lithium arenetellurolate also provided an opportunity to synthesize 'hybrid ligands' containing both hard N and soft Te. The reaction of the tellurolate with alkyl halides, *viz.* MeI, EtI, and Bu^{n}Br, afforded viscous tellurides which were characterized

Table 2. Proton n.m.r. chemical shifts relative to $SiMe_4$

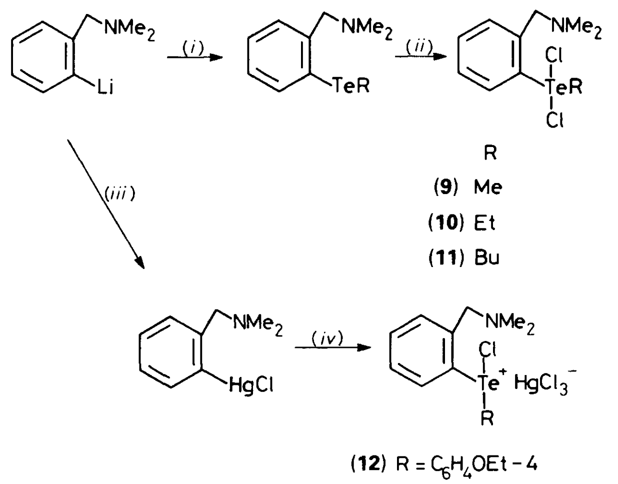
Compound	$N(CH_3)_2$	CH_2	Aryl protons	Others
$PhCH_2NMe_2$	2.25(s)	3.43(s)	7.2(m)	
(2)*	2.83(s)	4.0(s)	7.2—8.0(m)	
(3)*	3.0(s)	4.55(s)	7.3—8.0(m)	
(4)	2.97(s)	4.57(s)	7.48—7.96(m)	
(5)*	2.83(s)	4.00(s)	7.16—7.8(m)	
(6)*	2.86(s)	4.02(s)	7.14—7.8(m)	
(7)	2.6(s)	3.8(s)	7.1—7.7(m)	4.0(q), 1.2(t) $N(C_2H_5)_2$
(8)*	2.62(s)	3.82(s)	7.14—7.9(m)	4.08(q), 1.3(t) $N(C_2H_5)_2$
(9)	3.0(s)	4.55(s)	7.2—8.1(m)	3.48(s) Te–CH_3
(10)	2.87(s)	4.18(s)	7.2—8.0(m)	3.89(q), 1.74(t) Te–C_2H_5
(11)	2.81(s)	4.65(s)	7.3—8.0(m)	3.79, 2.0, 1.51, 1.0 Te–C_4H_9

* Recorded in $CDCl_3$.

Table 3. ^{13}C N.m.r. chemical shifts[a] for some orthotellurated complexes

	Aryl protons										
Compound	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	$N(CH_3)_2$	CH_2	$TeCH_3$	NCH_2CH_3	>C=S
$PhCH_2NMe_2$	128.4	138.4	128.4	127.6	126.4	127.6	63.8	44.7			
(3)	139.9	140.7	132.2	133.9	128.1	130.7	65.1	49.1			
	(11.5)	(2.3)	(3.8)	(6.3)	(1.7)	(3.1)	(1.3)	(4.4)			
(4)	146.7	140.0	131.3	132.1	128.0	130.4	64.3	47.5			
	(18.3)	(1.6)	(2.9)	(4.5)	(1.6)	(2.8)	(0.5)	(2.8)			
(6)	146.7	139.3	132.1	132.5	127.0	129.0	67.8	48.2			
	(18.3)	(0.9)	(3.7)	(4.9)	(0.6)	(1.4)	(4.0)	(3.5)			
(7)	135.1	140.6	128.0	128.6	126.8	n.o.	66.2	47.7		51.9[b]	191.3
	(6.7)	(2.2)	(−0.4)	(1.0)	(0.4)		(2.4)	(3.0)		13.7[c]	
(8)	135.1	140.7	128.0	128.7	126.9	n.o.	66.2	47.7		49.0[b]	191.3
	(6.7)	(2.3)	(−0.4)	(1.1)	(0.5)		(2.4)	(3.0)		13.2[c]	
(9)	138.7	139.9	131.3	132.7	126.4	128.4	67.3	47.7	59.8		
	(10.3)	(1.5)	(2.9)	(5.1)	(0)	(0.8)	(3.5)	(3.0)			

[a] In p.p.m. relative to $SiMe_4$; n.o. = not observed. Values in parentheses are differences in shifts relative to $PhCH_2NMe_2$. [b] Signal of NCH_2. [c] Signal of $NCCH_3$.



Scheme 2. (*i*) Te° then RX; (*ii*) SO_2Cl_2; (*iii*) $HgCl_2$; (*iv*) $4\text{-}EtOC_6H_4TeCl_3$

by derivatizing with SO_2Cl_2 [dichlorides **(9)**—**(11)**]. The structure of **(11)** was established by *X*-ray analysis. A similar reaction of the tellurolate with bromobenzene also gave a yellowish oily liquid. However, chlorination of this ligand resulted in formation of the trichloride $(2\text{-}Me_2NCH_2C_6H_4)TeCl_3$ instead of the expected dichloride. This is due to cleavage of the Te–C (aromatic) bond.[21]

The molecular diagram of [2-(dimethylaminomethyl)phenyl]tellurium(IV) tribromide [compound **(3)** in Scheme 1] is shown in Figure 1. The atomic co-ordinates are in Table 5, bond lengths and angles in Table 6. The axial Te–Br bond lengths [2.758(2) and 2.633(3) Å] span the value for the sum of the Pauling covalent radii (axial Te–Br 2.67 Å).[22,23] The shorter falls within the range commonly observed for this bond;[24–27] the longer, however, is significantly displaced from usual values. The Te–Br(3) bond [2.632(2) Å] is also elongated relative to the theoretical sum of the Pauling covalent radii (equatorial Te–Br 2.51 Å)[22,23] and to values commonly reported.[25–27] A similar pronounced difference in axial bond lengths occurs in 2-biphenylyltellurium tri-iodide.[28] Here the authors concluded that the structure had a tendency to form a telluronium salt of the type $[RI_2Te]^+I^-$. In the present structure there is a weak intermolecular interaction between tellurium and the bromine involved in the long Te–Br bond, Te ··· Br(1′) $(-x, 1-y, 1-z)$ 3.896(2) Å, with angles C(1)–Te ··· Br(1′) 162.7(4), N–Te ··· Br(1′) 87.1(3), and Br(1)–Te ··· Br(1′) 91.9(1)°. The Te ··· Br(1′) distance is, however, only slightly less than the sum of the van der Waals radii (3.91 Å),[29,30] and the molecules can be considered as essentially monomeric. This weak interaction may, however, be the reason for the relatively long Te–Br(1) bond distance.

The distance Te–C(1) [2.12(1) Å] is in good agreement with typical values found in tellurium(IV) complexes, which range from 2.11 to 2.16 Å[10,31] and with the mean value given by Allen *et al.*[32] (2.116 Å). The phenyl ring is planar (± 0.02 Å), and the bonds and angles are unexceptional.

The Te–N distance [2.42(1) Å] is significantly longer than the sum of the Pauling single-bond covalent radii[23] and a

Table 4. Crystal and experimental parameters

	(3)	(11)
Molecular formula	$C_9H_{12}Br_3NTe$	$[C_{13}H_{22}Cl_2NTe]^+Cl^-$
M	501.5	426.3
Crystal size (mm)	0.28 × 0.38 × 0.60	0.08 × 0.13 × 0.47
a/Å	9.226(6)	14.278(12)
b/Å	15.439(8)	8.349(5)
c/Å	9.618(5)	14.480(8)
β/°	94.94(5)	93.59(5)
U/Å^3	1 364.9	1 722.7
Space group	$P2_1/n$	$P2_1/n$
Z	4	4
F(000)	920	840
D_c/g cm^{-3}	2.441	1.644
μ/mm^{-1}	11.530	2.230
Data collection range, θ/°	2—25	2—25
Unique data measured	2 412	3 025
Significant data $[I > 2.5\sigma(I)]$	938	2 245
Least squares weights, K in $w = [\sigma^2(F) + KF^2]^{-1}$	0.011	0.000 55
Final *R*	0.0419	0.0288
Final *R′*	0.0561	0.0360

Table 5. Fractional atomic co-ordinates (× 10^4) with estimated standard deviations (e.s.d.s) in parentheses for compound (**3**)

Atom	*x*	*y*	*z*
Te	1 383(1)	3 822(1)	4 315(1)
Br(1)	−1 558(2)	3 743(1)	4 624(2)
Br(2)	4 195(3)	3 929(1)	4 050(3)
Br(3)	799(3)	3 836(1)	1 587(2)
N	1 713(15)	3 489(9)	6 782(14)
C(1)	1 523(16)	2 451(9)	4 374(17)
C(2)	1 788(19)	1 944(10)	3 231(18)
C(3)	1 843(21)	1 062(10)	3 352(22)
C(4)	1 707(23)	676(11)	4 615(22)
C(5)	1 415(22)	1 168(11)	5 811(23)
C(6)	1 310(19)	2 077(9)	5 675(20)
C(7)	1 008(20)	2 635(10)	6 891(18)
C(8)	3 300(21)	3 389(12)	7 295(24)
C(9)	1 069(28)	4 177(12)	7 569(20)

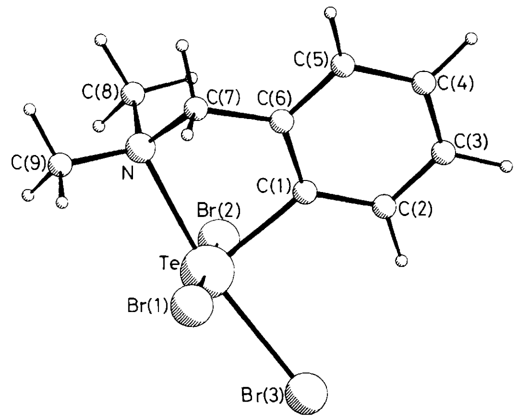


Figure 1. View of complex (**3**) showing the atom numbering

similar interaction in [2-(2-pyridyl)phenyl]tellurium(IV) tribromide [2.244(14) Å].[10] However, it is similar to that reported for (2,6-diacetylpyridine)tellurium trichloride [2.402(3) Å].[14]

If the Te ··· N interaction is considered to be significant, then the environment around tellurium can be considered to a first approximation as octahedral. In this representation the axial positions are occupied by Br(1) and Br(2), while C(1), N, Br(3), and the tellurium lone pair of electrons occupy the equatorial sites. The distortion from ideal octahedral geometry, particularly N–Te–Br(3) [167.4(3)°], can be explained in terms of the lone pair of electrons occupying an equatorial position between N and Br(3). Constraints imposed on the system by the five-membered ring cause the small value of the angle N–Te–C(1) [76.1(5)°]. These values are analogous to those found in the crystal structure of [2-(2-pyridyl)phenyl]tellurium(IV) tribromide.[10]

The structure of [2-(butyldichlorotelluro)benzyl]dimethylammonium chloride (**11**) is shown in Figure 2. Atomic co-ordinates are in Table 7 and bond lengths and angles in Table 8. The Te–Cl axial lengths, 2.487(1) and 2.527(1) Å, are in good agreement with the sum of covalent radii (axial Te–Cl 2.52 Å)[22,23] and may be compared with the values in a number of structures containing axial Te–Cl bonds,[33–35] which fall in the range 2.48—2.58 Å (average 2.52 Å). Within the asymmetric unit, there is a Te ··· Cl contact of 3.337(2) Å. This distance falls well within the sum of the van der Waals radii (3.81 Å),[30] and lies between tellurium–bridging chlorine distances found in triphenyltellurium chloride [3.142(1)—3.234(1) Å][36] and a secondary intermolecular contact identified in diethylammonium tetrachloro(*p*-phenoxyphenyl)tellurate (3.619 Å).[37]

There is no interaction between the protonated nitrogen and the tellurium atom, as the nitrogen is twisted away from the central tellurium atom [Te ··· N 4.380(4) Å]. The Te–C(1) length at 2.134(4) Å is similar to that of the corresponding bond in compound (**3**). The distance Te–C(10) [2.154(4) Å] is close to the theoretical value for the sum of the Pauling single-bond covalent radii for Te and C sp^3 and falls close to the average for Te–C sp^3 bonds.[32] The phenyl ring of the benzyldimethylammonium ligand is essentially planar (± 0.006 Å). The mean plane of the phenyl ring is oriented at an angle of 83.7(2)° to the mean plane of the butyl chain.

If the interaction between tellurium and the chloride ion is considered significant and the lone pair of electrons on tellurium is sterically active, then the geometry around tellurium may be considered as essentially octahedral. In this approximation C(1) lies approximately *trans* to the chloride ion [C(1)–Te ··· Cl(3) 173.3(2)°], and C(10) lies opposite the tellurium lone pair of electrons in the equatorial plane, with the two covalently bound chlorine atoms in the axial positions.

Table 6. Bond lengths (Å) and angles (°) with e.s.d.s in parentheses for compound (**3**)

Te–Br(1)	2.758(2)	C(1)–C(2)	1.39(2)
Te–Br(2)	2.633(3)	C(1)–C(6)	1.41(2)
Te–Br(3)	2.632(2)	C(2)–C(3)	1.37(2)
Te–N	2.42(1)	C(3)–C(4)	1.37(2)
Te–C(1)	2.12(1)	C(4)–C(5)	1.42(3)
N–C(7)	1.48(2)	C(5)–C(6)	1.41(2)
N–C(8)	1.51(2)	C(6)–C(7)	1.50(2)
N–C(9)	1.46(2)		
Br(1)–Te–Br(2)	178.7(1)	C(7)–N–C(9)	114(1)
Br(1)–Te–Br(3)	89.4(1)	C(8)–N–C(9)	109(2)
Br(2)–Te–Br(3)	91.3(1)	Te–C(1)–C(2)	124(1)
Br(1)–Te–N	85.8(3)	Te–C(1)–C(6)	115(1)
Br(2)–Te–N	93.8(3)	C(2)–C(1)–C(6)	121(1)
Br(3)–Te–N	167.4(3)	C(1)–C(2)–C(3)	120(2)
Br(1)–Te–C(1)	90.6(4)	C(2)–C(3)–C(4)	120(2)
Br(2)–Te–C(1)	90.4(4)	C(3)–C(4)–C(5)	121(2)
Br(3)–Te–C(1)	92.4(4)	C(4)–C(5)–C(6)	118(2)
N–Te–C(1)	76.1(5)	C(1)–C(6)–C(5)	118(2)
Te–N–C(7)	104(1)	C(1)–C(6)–C(7)	120(1)
Te–N–C(18)	112(1)	C(5)–C(6)–C(7)	121(2)
C(7)–N–C(8)	108(1)	N–C(7)–C(6)	110(1)
Te–N–C(9)	109(1)		

Table 7. Fractional atomic co-ordinates (× 10^5 for tellurium, × 10^4 for all other atoms) for compound (**11**)

Atom	*x*	*y*	*z*
Te	42 016(2)	15 017(4)	13 165(2)
Cl(1)	4 163(1)	−1 414(2)	848(1)
Cl(2)	3 995(1)	4 363(2)	1 734(1)
Cl(3)	6 343(1)	1 511(2)	2 381(1)
N	3 222(2)	3 237(5)	−1 431(2)
C(1)	2 773(3)	1 567(5)	788(3)
C(2)	2 064(3)	1 469(7)	1 408(3)
C(3)	1 134(3)	1 463(7)	1 088(4)
C(4)	907(3)	1 561(7)	150(4)
C(5)	1 605(3)	1 659(6)	−462(3)
C(6)	2 547(3)	1 681(5)	−158(3)
C(7)	3 271(3)	1 714(6)	−875(3)
C(8)	3 803(4)	3 103(8)	−2 256(3)
C(9)	3 506(4)	4 658(7)	−861(4)
C(10)	3 964(3)	625(7)	2 681(3)
C(11)	3 769(4)	1 819(6)	3 427(3)
C(12)	3 655(4)	968(7)	4 334(3)
C(13)	3 380(4)	2 074(9)	5 097(4)

The chloride ion is also involved in a hydrogen bond with the benzyldimethylammonium group, in the symmetry-related molecule (0.5 + *x*, 0.5 −*y*, 0.5 + *z*) [N ··· Cl 3.102(5), H ··· Cl 2.33 Å].

It has been noted previously[10,38] that no strong bonds are found *trans* to a Te–C bond in organotellurium complexes. It may be seen that in neither of the present compounds is there primary bonding *trans* to a covalent Te–C bond. When the potentially electron-donating nitrogen atom is protonated, no Te ··· N interaction occurs.

Table 8. Bond lengths (Å) and angles (°) with e.s.d.s in parentheses for compound (**11**)

Te–Cl(1)	2.527(1)	C(2)–C(3)	1.379(2)
Te–Cl(2)	2.487(1)	C(3)–C(4)	1.381(8)
Te–C(1)	2.134(4)	C(4)–C(5)	1.377(7)
Te–C(10)	2.154(4)	C(5)–C(6)	1.389(6)
N–C(7)	1.504(6)	C(6)–C(7)	1.511(6)
N–C(8)	1.500(6)	C(10)–C(11)	1.508(7)
N–C(9)	1.486(6)	C(11)–C(12)	1.509(7)
C(1)–C(2)	1.396(6)	C(12)–C(13)	1.511(8)
C(1)–C(6)	1.391(6)		
Cl(1)–Te–Cl(2)	171.9(1)	C(1)–C(2)–C(3)	120.4(4)
Cl(1)–Te–C(1)	85.6(1)	C(2)–C(3)–C(4)	119.5(4)
Cl(2)–Te–C(1)	86.4(1)	C(3)–C(4)–C(5)	120.2(4)
Cl(1)–Te–C(10)	85.2(1)	C(4)–C(5)–C(6)	121.5(4)
Cl(2)–Te–C(10)	94.3(1)	C(1)–C(6)–C(5)	118.1(4)
C(1)–Te–C(10)	97.8(2)	C(1)–C(6)–C(7)	123.5(4)
C(7)–N–C(8)	110.6(4)	C(5)–C(6)–C(7)	118.2(4)
C(7)–N–C(9)	112.1(4)	N–C(7)–C(6)	111.8(4)
C(8)–N–C(9)	111.0(4)	Te–C(10)–C(11)	118.6(4)
Te–C(1)–C(2)	118.9(3)	C(10)–C(11)–C(12)	110.3(4)
Te–C(1)–C(6)	120.8(3)	C(11)–C(12)–C(13)	113.3(5)
C(2)–C(1)–C(6)	120.3(4)		

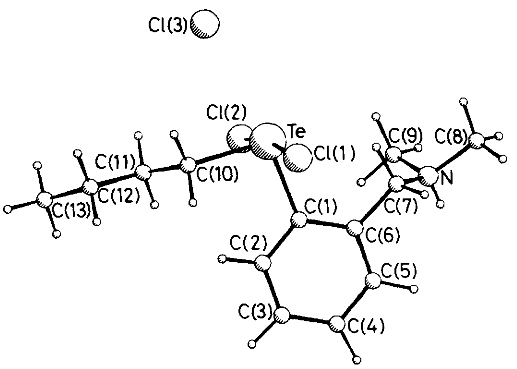


Figure 2. View of complex (**11**) showing the atom numbering

Experimental

Syntheses.—All reactions of 2-lithio-*N*,*N*-dimethylbenzylamine were carried out under argon in a three-necked flask (100 cm^3) fitted with a septum, glass stopper, and a reflux condenser connected to an argon/vacuum line. A commercial solution of n-butyl-lithium was syringed into the solution of the amine in dry diethyl ether in concentrations as specified below. Elemental tellurium was finely ground in a pestle and mortar and introduced under a brisk stream of argon to avoid any introduction of moisture or air.

Bis[*2-(dimethylaminomethyl)phenyl*] *ditelluride* (**1**) (*attempted*). n-Butyl-lithium (8 cm^3, 12.2 mmol) was added dropwise to a stirred solution of *N*,*N*-dimethylbenzylamine (1.53 cm^3, 10.2 mmol) in dry ether (30 cm^3) at room temperature. The solution was stirred for 24 h at this temperature after which elemental tellurium (1.30 g, 10.2 mmol) was added. On further stirring for 3 h all the tellurium dissolved. The resulting yellowish solution was poured into a beaker containing water (100 cm^3) and left overnight in an efficient fume hood to effect complete oxidation. The organic phase was separated and the aqueous phase was extracted with dichloromethane. The combined organic phases were dried over anhydrous magnesium sulphate. Evaporation of the solvent gave a yellowish compound. The product was recrystallized from ethanol to yield an off-white solid (**2**), yield 0.8 g, m.p. 160 °C, $\lambda_{max.}$ 382 nm.

[*2-(Dimethylaminomethyl)phenyl*]*tellurium*(IV) *tribromide* (**3**). A solution of compound (**2**) (0.8 g) in a mixture of chloroform (20 cm^3) and hexane (10 cm^3) was treated dropwise with a solution of bromine (0.27 cm^3, 5.3 mmol) in chloroform. After stirring for an additional 2 h the reaction mixture was filtered and washed with hexane to give a yellowish orange crystalline solid.

[2-(Dimethylaminomethyl)phenyl]tellurium(IV) *trichloride* (**4**). The yellowish white solid (**2**) (0.48 g) was dissolved in a mixture of chloroform (25 cm^3) and hexane (15 cm^3). Addition of excess of SO_2Cl_2 caused immediate precipitation. The light yellow precipitate was washed with ether and recrystallized from ethanol to give the desired product.

[2-(Dimethylaminomethyl)phenyl]tellurium(II) *bromide* (**5**). To a suspension of compound (**3**) (0.32 g, 0.64 mmol) in methanol (15 cm^3), hydrazine hydrate in methanol was added dropwise till the solution became clear; in the process the pale yellow solution became reddish orange. Some black precipitate was also formed and removed by filtration. The filtrate was concentrated and the resulting orange solid was recrystallized from chloroform.

[2-(Dimethylaminomethyl)phenyl]tellurium(II) *chloride* (**6**). The compound was synthesized by a similar method to that used for (**5**), but using (**4**) (0.26 g, 0.71 mmol) in methanol (15 cm^3). The resulting crude yellow solid was recrystallized from chloroform to yield a yellow crystalline solid.

Tris(diethyldithiocarbamato)[2-(dimethylaminomethyl)phenyl]tellurium(IV) (**7**). To a solution of compound (**4**) (0.30 g, 0.81 mmol) in acetone was added with stirring under argon a solution of sodium diethyldithiocarbamate (0.60 g, 3.5 mmol) in methanol (10 cm^3). The reaction mixture was stirred for 1 h and filtered. Concentration of the filtrate, followed by recrystallization from acetone, gave a yellowish orange crystalline solid.

(Diethyldithiocarbamato)[2-(dimethylaminomethyl)phenyl]tellurium(II) (**8**). A solution of sodium diethyldithiocarbamate (0.08 g, 0.5 mmol) in methanol (10 cm^3) was added to a solution of compound (**6**) (0.1 g, 0.3 mmol) in CH_2Cl_2 (15 cm^3) at room temperature. The reaction mixture was stirred for 1 h after which the solvent was removed on a rotary evaporator. The residue was stirred vigorously with CH_2Cl_2 and filtered to remove NaCl. The filtrate was concentrated to give a yellow crystalline solid.

[2-(Dimethylaminomethyl)phenyl]methyltellurium(IV) *dichloride* (**9**). To a solution of *N,N*-dimethylbenzylamine (0.90 g, 6.6 mmol) in dry ether (10 cm^3), n-butyl-lithium (5.3 cm^3, 8.6 mmol) was added dropwise. After stirring for 24 h at room temperature, tellurium powder (0.84 g, 6.6 mmol) was added and the reaction mixture stirred for an additional 3 h. When all the tellurium had been consumed, iodomethane (0.40 cm^3, 6.6 mmol) was syringed into the flask and the reaction mixture stirred for 30 min after which it was quenched with water (100 cm^3) and the organic phase separated. The aqueous phase was extracted with ether (2 × 50 cm^3). The combined organic phase was dried over anhydrous $CaCl_2$, filtered, and concentrated. The crude telluride obtained was converted into the solid dichloride (**9**) by addition of excess of SO_2Cl_2. Recrystallization from ethanol provided white crystals.

[2-(Dimethylaminomethyl)phenyl]ethyltellurium(IV) *dichloride* (**10**). To the aryl-lithium tellurolate prepared from *N,N*-dimethylbenzylamine (1.38 g, 10.2 mmol), n-butyl-lithium (8 cm^3, 12.2 mmol), and tellurium (1.30 g, 10.2 mmol) in dry ether (30 cm^3) was added iodoethane (1.59 g, 10.2 mmol) and the reaction mixture stirred for an additional 30 min. It was then quenched with water (100 cm^3), extracted with ether, and the organic phase dried over $CaCl_2$. Filtration followed by concentration gave an oily liquid which was converted into the corresponding dichloride by reaction with excess of SO_2Cl_2. The crude dichloride was purified by recrystallization from ethanol to afford white crystals.

Butyl[2-(dimethylaminomethyl)phenyl]tellurium(IV) *dichloride* (**11**). Into the lithium tellurolate solution was syringed bromobutane (1.39 g, 10.2 mmol). After stirring for an additional 30 min, the reaction was worked up as for compounds (**9**) and (**10**). The solid dichloride was recrystallized from ethanol as the hydrochloride salt.

[2-(Dimethylaminomethyl)phenyl]phenyltellurium(IV) *dichloride* (*attempted*). To the lithium tellurolate solution was added bromobenzene (1.60 g, 10.2 mmol) and the reaction mixture stirred for an additional 0.5 h. The usual work-up gave an oily residue which was treated with excess of sulphonyl chloride to give a yellowish white crystalline solid (**4**).

[2-(Dimethylaminomethyl)phenyl]mercury(II) *chloride*. This compound was prepared by a literature method.[13]

Reaction of [2-(Dimethylaminomethyl)phenyl]mercury(II) *Chloride with 4-Ethoxyphenyltellurium*(IV) *Trichloride*.—[2-(Dimethylaminomethyl)phenyl]mercury chloride (0.50 g, 1.3 mmol) and 4-ethoxyphenyltellurium(IV) trichloride (0.48 g, 1.3 mmol) were refluxed in dry 1,4-dioxane (20 cm^3) for 5 h. Upon cooling a white crystalline precipitate (**12**) was obtained.

Physical Measurements.—Melting points (uncorrected) were determined with a locally made instrument. Analysis for C, H, and N was by the Analytical Services, Regional Sophisticated Instrumentation Centre, Lucknow. Infrared spectra were recorded for KBr discs with a Perkin-Elmer 681 instrument, mass spectra at 70 eV (1.12×10^{-17}J) with a Varian MAT 1125 instrument, u.v.–visible spectra in solution with a Shimadzu UV 260 spectrophotometer, and ^1H and ^{13}C n.m.r. spectra on a Bruker WH-500 spectrometer with chemical shifts relative to $SiMe_4$. Thanks are also due to the National n.m.r. facility at Tata Institute of Fundamental Research Bombay for recording these spectra.

Reagents.—Tellurium powder, n-butyl-lithium, and *N,N*-dimethylbenzylamine were obtained from Fluka.

X-*Ray Structure Determinations*.—Cell dimensions and reflection intensities were measured with graphite-monochromated Mo-K_α radiation on an Enraf-Nonius CAD-4 diffractometer, operating in the ω—2θ scan mode. Three standard reflections were monitored at regular intervals to check the stability of the system. Lorentz and polarization factors were applied and also absorption corrections[39] for compound (**3**). Details of crystal and experimental parameters are given in Table 4.

The tellurium and bromine atoms of (**3**) were located by direct methods. For compound (**11**) the tellurium and many of the lighter atoms were located from a Patterson synthesis. In both structures the remaining non-hydrogen atoms were found by Fourier difference synthesis. With the exception of the hydrogen attached to the positively charged nitrogen atom in (**11**), hydrogens were placed in calculated positions (C–H 1.08 Å), and allowed to 'ride' on their respective carbon atoms in the subsequent least-squares calculations. Non-hydrogen atoms were refined with anisotropic thermal parameters.

Computations were carried out on the Birmingham University Honeywell computer and on the CDC 7600 at the University of Manchester Regional Computer Centre with DIFABS,[39] SHELXS 86,[40] SHELX 76,[41] and PLUTO.[42]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates and thermal parameters.

Acknowledgements

We thank Professor W. R. McWhinnie for his interest and critical reading of the manuscript. H. B. S. thanks Council of Scientific and Industrial Research New Delhi and Board of Research in Nuclear Sciences Department of Atomic Energy for financial support. A. A. W. thanks Aston University for a research studentship.

References

1 I. Omae, 'Organometallic Intramolecular Coordination Compounds,' Elsevier, Amsterdam, 1986.

2 V. V. Dunina, O. A. Zalevskaya, and V. M. Polapov, *Russ. Chem. Rev.*, 1988, **57**, 250.

3 A. A. H. van der Zeijden, G. van Koten, R. A. Nordemann, B. Kojic-Prodic, and A. L. Spek, *Organometallics*, 1988, **7**, 1957.

4 A. A. H. van der Zeijden, G. van Koten, R. Luijk, K. Vrieze, C. Slob, H. Krabbendam, and A. L. Spek, *Inorg. Chem.*, 1988, **27**, 1014.

5 N. Barr, S. F. Dyke, and S. N. Quessy, *J. Organomet. Chem.*, 1983, **253**, 391.

6 H. J. Gysling, in 'The Chemistry of Organic Selenium and Tellurium Compounds,' Wiley, New York, 1986, vol. 1, pp. 679—855.

7 M. A. K. Ahmed, A. E. MacCarthy, W. R. McWhinnie, and F. J. Berry, *J. Chem. Soc., Dalton Trans.*, 1986, 771; R. E. Cobbledick, F. W. B. Einstein, W. R. McWhinnie, and F. H. Musa, *J. Chem. Res.*, 1979, (*S*) 145.

8 H. B. Singh and W. R. McWhinnie, *J. Chem. Soc., Dalton Trans.*, 1985, 821; N. Al-Salim, T. A. Hamor, and W. R. McWhinnie, *J. Chem. Soc., Chem. Commun.*, 1986, 453.

9 V. I. Minkin, A. A. Maksimenko, G. K. Mehrotra, A. G. Maslakov, O. E. Kompan, and I. D. Sadekov, *J. Organomet. Chem.*, 1988, **348**, 63.

10 N. Al-Salim, A. A. West, W. R. McWhinnie, and T. A. Hamor, *J. Chem. Soc., Dalton Trans.*, 1988, 2363 and refs. therein.

11 A. D. Ryabov, *Synthesis*, 1985, 233.

12 J. Vicente, A. Arcas, M. V. Borrachero, and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1987, 1655.

13 A. F. M. J. van der Ploeg, C. E. M. van der Kolk, and G. van Koten, *J. Organomet. Chem.*, 1981, **212**, 283.

14 H. J. Gysling, H. R. Luss, and S. A. Gardner, *J. Organomet. Chem.*, 1980, **184**, 417.

15 T. A. Hamor, N. Al-Salim, A. A. West, and W. R. McWhinnie, *J. Organomet. Chem.*, 1986, **310**, C5.

16 A. A. West, W. R. McWhinnie, and T. A. Hamor, *J. Organomet. Chem.*, 1988, **356**, 159.

17 P. Granger, S. Chapelle, W. R. McWhinnie, and A. Al-Rubaie, *J. Organomet. Chem.*, 1981, **220**, 149.

18 R. T. Mehdi and J. D. Miller, *J. Chem. Soc., Dalton Trans.*, 1983, 1071.

19 D. F. Ewing, *Org. Magn. Reson.*, 1979, **12**, 499.

20 R. K. Chadha and J. M. Miller, *J. Chem. Soc., Dalton Trans.*, 1982, 117.

21 H. M. K. K. Pathirana and W. R. McWhinnie, *J. Chem. Soc., Dalton Trans.*, 1986, 2003.

22 L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, 1960.

23 W. R. McWhinnie and Z. Monsef-Mirzai, in 'Proceedings of the Fourth International Conference on the Organic Chemistry of Selenium and Tellurium,' eds. F. J. Berry and W. R. McWhinnie, The University of Aston in Birmingham, 1983, pp. 3—31.

24 C. Knobler and J. D. McCullough, *Inorg. Chem.*, 1977, **16**, 612.

25 M. R. Detty, H. R. Luss, J. M. McKelvey, and S. M. Geer, *J. Org. Chem.*, 1986, **51**, 1693.

26 T. S. Camerson, R. B. Amero, C. Chan, and R. E. Cordes, *Cryst. Struct. Commun.*, 1980, **9**, 543.

27 M. R. Detty and H. R. Luss, *J. Org. Chem.*, 1983, **48**, 5149.

28 J. D. McCullough and C. Knobler, *Inorg. Chem.*, 1976, **15**, 2728.

29 N. W. Alcock, *Adv. Inorg. Chem. Radiochem.*, 1972, **15**, 1.

30 A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441.

31 M. A. K. Ahmed, W. R. McWhinnie, and T. A. Hamor, *J. Organomet. Chem.*, 1985, **281**, 205.

32 F. H. Allen, D. G. Watson, L. Brammer, A. G. Orpen, and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1987, S1.

33 N. W. Alcock and W. D. Harrison, *J. Chem. Soc., Dalton Trans.*, 1982, 251.

34 R. K. Chadha, J. E. Drake, and M. A. Khan, *Acta Crystallogr., Sect. C*, 1983, **39**, 45.

35 R. H. Jones and T. A. Hamor, *J. Organomet. Chem.*, 1984, **262**, 151.

36 R. F. Ziolo and M. Extine, *Inorg. Chem.*, 1980, **19**, 2964.

37 R. K. Chadha, J. E. Drake, and M. A. Khan, *Can. J. Chem.*, 1984, **62**, 32.

38 O. Foss, *Pure Appl. Chem.*, 1970, **24**, 31.

39 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.

40 G. M. Sheldrick, SHELXS 86, Program for the solution of crystal structures, University of Göttingen, 1987.

41 G. M. Sheldrick, SHELX 76, Program for crystal structure determination, University of Cambridge, 1976.

42 W. D. S. Motherwell and W. Clegg, PLUTO, Program for drawing crystal and molecular structures, University of Cambridge, 1978.

Received 16*th May* 1989; *Paper* 9/02072A