866 *Organometallics* 1989, *8*, 866–870

XPS and ^{125}Te NMR Studies of Organotellurium Compounds. 2. Oxatellurolylium Halides and Dioxatellurapentalenes and Their Products of Oxidative Halogen Addition

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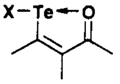
XPS (X-ray photoelectron spectroscopy or ESCA, electron spectroscopy for chemical analysis) analyses of oxatellurolylium halides **13** and dioxatellurapentalenes **14** have shown them to be tellurium(II) compounds when their Te(3d$_{5/2}$) binding energies are compared to those of tellurium(II) models. The oxatellurolylium trihalides **15** (and, by extension, the dioxatellurapentalene dihalides **16**) have Te(3d$_{5/2}$) binding energies consistent with a tellurium(IV) oxidation state when compared to tellurium(IV) models. Changes in the XPS binding energies, which result from substituent changes in the carbon π-framework, are similar in magnitude to changes from substitution in the electronegative ligands attached to tellurium. This makes quantitative assessment of the effect of higher order bonding on the electronic environment at tellurium difficult using the Te(3d$_{5/2}$) binding energies. The O(1s) electrons of **13–15** all have higher binding energies than model compounds **9**, **11**, and **12**, suggesting that partial bonding (linear, three-center, four-electron bonding) exists between the tellurium halide, the tellurium, and the enone oxygen (X–Te···O). While the XPS data show the oxygen atoms to be donating electrons in the three-center, four-electron bonds, the ^{125}Te NMR chemical shifts show deshielding as three-center, four-electron bonding increases. With dioxatellurapentalene **14a** as one limit with a symmetrical, strong three-center, four-electron bond and tellurapyranone **9** as the other limit with no bond between tellurium and oxygen, the ^{125}Te NMR chemical shift moves sequentially downfield from **9** to β-(phenyltelluro)butenoate ester **10** to the oxatellurolylium iodides to the oxatellurolylium bromides to the oxatellurolylium chlorides in the tellurium(II) series. This is exactly the trend to be expected if increasingly strong linear three-center, four-electron bonding, on net, deshields tellurium through increased ionic bonding. The compounds of this study are of AX_3E_2 and AX_5E types for tellurium(II) and tellurium(IV), respectively. The XPS and ^{125}Te NMR studies of these compounds are the first systematic studies of compounds of this type. The data suggest that ^{125}Te NMR chemical shifts are sensitive to the geometry of the complexes, the oxidation state of tellurium, and the electronic environment of tellurium.

The oxatellurolylium halides **1** and dioxatellurapentalenes **2** and their products of oxidative halogen addition, pertelluranes **3** and **4**, respectively, are organotellurium species in which the bonding to tellurium must account for more than eight electrons around the central atom.[2] Structures **1** and **2** are trigonal-bipyramidal (tbp) of the AX_3E_2 type to accommodate 10 electrons while structures **3** and **4** are octahedral of type AX_5E to accommodate 12 electrons.[3] To rationalize these features, the bonding to tellurium has been described in terms of linear three-center, four-electron bonds using only p orbitals[4] and, conversely, in terms using d orbitals as in the valence-shell electron-pair repulsion (VSEPR) treatment in which bonding is a combination of both covalent and ionic contributions.[5] The trans effect,[4] involving the two outer ligands, is illustrated in the two limits of the bonding schemes. One limit has two identical ligands to the central atom with a bond order of 0.5 between each outer ligand and the central atom. At this limit, the electronic field gradient along the three-center, four-electron bond is polarized toward the terminal atoms. From this limit, the bonding passes through the region, where one ligand is more strongly bonded than the other, to the other limit, where there is no bond trans to a strongly bound ligand. At this limit, there is one covalent ligand–central atom bond with no bonding contribution from the electrons of the other terminal atom. Spectroscopic techniques should be sensitive to the changes in ligand substitution of the central atom.



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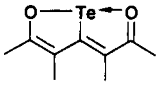

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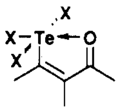

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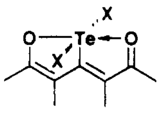

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In the preceding paper,[6] we examined a series of tellurapyran (**5**), tellurapyranone (**6**), and tellurapyrylium compounds (**7**), their tellurium(IV) analogues (**8**), and the

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[1] Division of Organic Chemistry of the American Chemical Society Fellow sponsored by the Rohm & Haas Company, 1986–1987. General Electric Fellow, 1985–1986.

[2] We are avoiding the use of the term "hypervalent" in the discussion of organotellurium compounds with three-center, four-electron bonds such as **1–4**. These compounds have been found not to "exceed the octet" and are, thus, not *hypervalent*. Gassman, P. G.; Callstrom, M. R.; Martin, J. C.; Rongione, J. C. *J. Am. Chem. Soc.*, in press.

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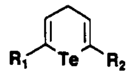
benzo analogues of 5–8 by ^{125}Te NMR and by X-ray photoelectron spectroscopy (XPS or ESCA, electron spectroscopy for chemical analysis). In these systems, charge delocalization and conjugation were primarily addressed. The oxatellurolylium halides 1 and dioxatellurapentalenes 2 are tellurium(II) compounds with markedly different geometries and bonding than the tellurium(II) compounds 5–7. The three ligand array in both 1 and 2 is T-shaped with a covalent tellurium–carbon bond and a linear three-center, four-electron bond involving the two more electronegative ligands and tellurium.[3] Compounds 1 and 2 both have a trigonal-bipyramidal geometry to accommodate the three ligands and two lone pairs of electrons.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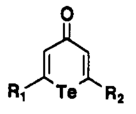
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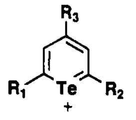
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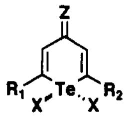
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The pertelluranes 3 and 4 are tellurium(IV) compounds with markedly different geometries and bonding than the tellurium(IV) compounds 8. Both 3 and 4 have two linear three-center, four-electron bonds involving the four electronegative ligands and a covalent tellurium–carbon bond.[3] A lone pair of electrons completes the octahedral geometry found in 3 and 4.

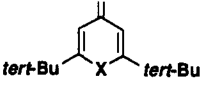
The organotellurium compounds that have been examined to date by ^{125}Te NMR[7] and XPS[8] have all been similar in structure to compounds 5–8. In conjunction with the preceding paper, a study of compounds 1–4 by ^{125}Te NMR spectroscopy and by XPS would allow the effects of geometry and bonding on ^{125}Te NMR chemical shifts and Te(3$d_{5/2}$) binding energies to be addressed.

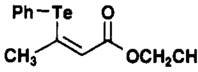
The effect of three-center, four-electron bonds on the electronic field gradient around tellurium has been measured experimentally from high-resolution X-ray intensity measurements on dimethyltellurium dichloride, a tbp AX_4E-type molecule.[9] The shape of the electron cloud along the Cl–Te–Cl bonds is polarized toward chlorine as is predicted by the bonding model where the electron demand of the ligands increases.[4,5]

Compounds of the type XSCH=CHCH=O with a cis configuration at the olefin and with X = F, OH, NH_2, CH_3, and SH were examined by the ab initio SCF-MO method.[10] The strength of the interaction between oxygen and sulfur in these systems was found to increase as the electronegativity of X increased. Furthermore, the net Mulliken charges at X, sulfur, and oxygen were found to increase with increasing electronegativity of X and increased sulfur–oxygen bonding. The increase in the net charges at these atoms is indicative of increased ionic bonding. Similar results should be obtained by replacing sulfur with tellurium in these systems. Theoretical treatment of structures 1–4 (R = H, X = Cl) with CNDO/2[3] has shown an increase in the net charges at tellurium and its ligands in comparing 1 with 2 and 3 with 4 as a chloride ligand is replaced with oxygen which is indicative of increased ionic bonding. Furthermore, the covalent bonding in 2 and 4 is symmetrical with approximately half of a covalent bond for each tellurium-oxygen interaction. Theoretical studies[3,10] suggest that the electron demand of the ligands attached to tellurium increases as three-center, four-electron bonding increases. Increasing electron demand by the ligands to tellurium in 1–4 should affect the electronic field gradient around tellurium. In addition to evaluating the effects of geometry on ^{125}Te NMR chemical shifts and Te(3$d_{5/2}$) binding energies in compounds 1–4, we were interested in the effects of changing the ligands about tellurium on both chemical shifts and binding energies. Herein, we report our results on ^{125}Te NMR chemical shifts and Te(3$d_{5/2}$) binding energies for the series of compounds 1–4.

Results and Discussion

In order to investigate the electronic environment at tellurium in the series 1–4, suitable models were needed that would incorporate some of the gross structural features of the molecules without promoting a strong three-center, four-electron bonding interaction between tellurium and oxygen. Tellurapyranone 9[6] was chosen as a model tellurium(II) compound for comparison with the oxatellurolylium halides 1 and dioxatellurapentalenes 2. Compound 9 is enone-like with the tellurium and carbonyl oxygen too far separated for nonbonded, intramolecular interaction. The (*Z*)-3-(phenyltelluro)but-2-enoate ester 10[11] was chosen as a second tellurium(II) model compound in which a weak trans interaction should be possible involving the aryl carbon–tellurium bond and the ester carbonyl oxygen.


9, X = Te
11, X = $TeCl_2$
12, X = $TeBr_2$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The dihalides 11 and 12[6] were chosen as model tellurium(IV) compounds that have the tellurium atom attached to an enone-like carbon framework that cannot have a tellurium interaction with the carbonyl oxygen in an intramolecular sense (model compounds 9 and 10 have a common complicating feature since carbonyl effects can be transmitted to tellurium in a conjugative sense).[6] The ^{125}Te NMR chemical shifts for the model compounds 9–12 as well as their Te(3$d_{5/2}$) and O(1s) binding energies as determined by XPS are compiled in Table I.

The oxatellurolylium halides 13[3,11] were chosen for study. As the halide changes from chloride to bromide to iodide in these systems, the electronegativity of the ligand decreases and approaches that of tellurium, and, as a consequence, the symmetry of the three-center, four-electron bonding involving the halide, tellurium, and oxygen should decrease as should the strength of the bond between tel-

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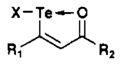
Table I. ^{125}Te NMR Chemical Shifts, Te(3d$_{5/2}$) Binding Energies, and O(1s) Binding Energies

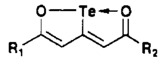
compd	chemical shift^a ^{125}Te, δ, ppm	binding energy,^{b} eV Te(3d$_{5/2}$) (±0.1 eV)	binding energy,^{b} eV O(1s) (±0.1 eV)
9	+445	574.1	531.7
10	+807	574.0	^{c}
11	+434	576.4	531.6
12	+363	576.0	531.7
13a	+1726	574.6	531.9
13b	+1697	574.2	531.8
13c	+1692	574.3	531.8
13d	+1672	574.5	531.9
13e	+1672		
13f	+1650	574.3	532.0
13g	+1501	574.0	531.7
13h	+1484	573.8	
14a	+1955	574.0	531.9
14b	+1967	574.5	531.9^c
14c	+1961	574.6	
15a	+1365	576.6	531.9
15b	+1359	576.5	531.8
15c	+1365	576.4	531.8
15d	+1386	576.4	531.9
15e	+1398	576.2	531.9
15f	+1416	576.2	531.9
16a	+1459		
16b	+1444		

^{a} Diphenyl telluride was used as an external standard; all spectra were measured in CD_2Cl_2. ^{b} All binding energies are calibrated vs C(1s) of polyethylene (284.6 eV). ^{c} The two oxygen signals were not resolved.

lurium and oxygen. The dioxatellurapentalene **14a**,[12] when compared with the oxatellurolylium halides **13**, has symmetrical three-center, four-electron bonding between the two oxygen ligands and the central tellurium atom. The bonding along the oxygen–tellurium–oxygen axis in this molecule is expected to be quite strong. However, dioxatellurapentalenes **14b**[12b] and **14c**[12b] break the symmetry of the ligand carbon framework which could influence the three-center, four-electron bonding to tellurium.

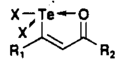


13a; X = Cl, R$_1$ = Me, R$_2$ = Ph
13b; X = Cl, R$_1$ = R$_2$ = Ph
13c; X = Cl, R$_1$ = Ph, R$_2$ = 1-Naph
13d; X = Br, R$_1$ = Me, R$_2$ = Ph
13e; X = Br, R$_1$ = R$_2$ = Ph
13f; X = Br, R$_1$ = Ph, R$_2$ = 1-Naph
13g; X = I, R$_1$ = R$_2$ = Ph
13h; X = I, R$_1$ = Ph, R$_2$ = 2,5-(MeO)$_2$C$_6$H$_3$

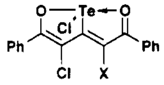


14a; R$_1$ = R$_2$ = Ph
14b; R$_1$ = Me, R$_2$ = Ph
14c; R$_1$ = 4-(F)C$_6$H$_4$, R$_2$, = 4-(O$_2$N)C$_6$H$_4$

Oxidative halogen addition to the oxatellurolylium halides **13** gives the oxatellurolylium trihalides **15**[3] while oxidative chlorine addition to dioxatellurapentalene **14a** gives tetrachloride **16a**[12b] and trichloride **16b**.[12a] The oxidative halogen addition increases the formal tellurium oxidation state by +2 and changes the coordination sphere around tellurium.



15a; X = Cl, R$_1$ = Me, R$_2$ = Ph
15b; X = Cl, R$_1$ = R$_2$ = Ph
15c; X = Cl, R$_1$ = Ph, R$_2$ = 1-Naph
15d; X = Br, R$_1$ = Me, R$_2$ = Ph
15e; X = Br, R$_1$ = Ph, R$_2$ = 4-(Me)C$_6$H$_4$
15f; X = Br, R$_1$ = Ph, R$_2$ = 1-Naph



16a, X = Cl
16b, X = H

The ^{125}Te NMR chemical shifts for compounds **13–16** are compiled in Table I. The dioxatellurapentalene dihalides **16**, in addition to being sparingly soluble for the NMR studies, were difficult to obtain in greater than 90–95% purity (contamination by unreacted starting material). As a consequence, XPS studies were not attempted with compounds **16**. The Te(3d$_{5/2}$) and O(1s) binding energies as determined by XPS for compounds **13–15** are compiled in Table I as well.

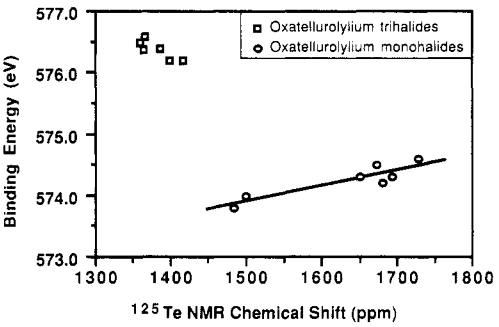


Figure 1. The Te(3d$_{5/2}$) binding energies versus ^{125}Te NMR chemical shifts for oxatellurolylium halides **13a–d**, **13f**, **13g**, and **13h** and trihalides **15a–f**.

(i) XPS Studies. The Te(3d$_{5/2}$) binding energies of compounds **13–15** are normal with respect to the expected values for tellurium(II) and tellurium(IV) as represented by the model compounds **9–12**. The Te(3d$_{5/2}$) binding energies for the oxatellurolylium halides **13** and dioxatellurapentalenes **14** fall in the range of 573.8–574.6 eV while the model tellurium(II) compounds **9** and **10** and the tellurium(II) compounds in the preceding paper[6] have Te(3d$_{5/2}$) binding energies in the range of 573.0–575.2 eV. Similarly, the Te(3d$_{5/2}$) binding energies for the oxatellurolylium trihalides **15** fall in the range of 576.2–576.6 eV while the model tellurium(IV) compounds **11** and **12** and the tellurium(IV) compounds in the preceding paper[6] fall in the range of 575.7–576.4 eV. Thus, the oxatellurolylium halides **13** and dioxatellurapentalenes **14** should be considered to be tellurium(II) compounds, and the oxatellurolylium trihalides **15** and dioxatellurapentalene dihalides **16** should be considered to be tellurium(IV) compounds.

Changes in the carbon π-framework lead to pronounced differences in Te(3d$_{5/2}$) binding energies. Comparing oxatellurolylium chlorides **13a** and **13b** gives a 0.4-eV difference in binding energies by changing substituents from methyl to phenyl while a comparison of the trichlorides **15a** and **15b** gives a 0.1-eV difference for the same change. Comparing oxatellurolylium iodides **13g** and **13h** gives a 0.2-eV difference in binding energies by replacing a phenyl substituent with a 2,5-dimethoxyphenyl substituent. Disrupting the symmetry of dioxatellurapentalene **14a** leads to binding energy differences of 0.5 and 0.6 eV with the unsymmetrical dioxatellurapentalenes **14b** and **14c**, respectively.

A general correlation was found between the Te(3d$_{5/2}$) binding energies and the ^{125}Te NMR chemical shift for the oxatellurolylium monohalides as shown in Figure 1 (least-squares correlation coefficient of 0.90). The relationship fails, however, upon examination of the dioxatellurapentalenes **14a–c** or the oxatellurolylium trihalides. However, all of the oxatellurolylium trihalides were found to fall within a fairly narrow range. Although final-state effects[13] in the XPS measurement could be responsible for the lack of a linear relationship between XPS binding energies and NMR chemical shifts for **14a–c**, changes in ligand substitution which result in dramatic changes in

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symmetry about tellurium are expected to affect both the diamagnetic and the paramagnetic shielding contributions to the NMR chemical shift. This results in the oxatellurolylium monohalides having a general correlation of XPS binding energy with NMR chemical shift and the oxatellurolylium trihalides binding energies all falling within a fairly narrow range. The dioxatellurapentalene compounds, which include the limits of symmetrical and nonsymmetrical three-center, four-electron bonding along the oxygen–tellurium–oxygen axis, demonstrate the most unusual behavior with a change in binding energy of 0.6 eV with a change of only 12 ppm in the ^{125}Te NMR chemical shift. Because of the inductive effects from the halide ligands and from the changes in the carbon π-framework with respect to the Te($3d_{5/2}$) binding energies, it is difficult to assess the effect of three-center, four-electron bonding on Te($3d_{5/2}$) binding energies in these systems.

A better measure of the strength of the bond between tellurium and oxygen is found upon comparison of the O(1s) electron binding energies in **13**–**16** and model compounds. Binding energies of the O(1s) electron for the model compounds **9**, **11**, and **12** are in the range of 531.6–531.7 eV. Compound **10** was excluded from this comparison since there are two different oxygen atoms in this molecule and the O(1s) signals were unresolvable. It was expected that **9** would have the complication of a resonance form, as shown for **7** with $R_3 = O^-$, involving separation of charge. Since **11** and **12** [tellurium(IV) compounds which do not have resonance forms such as **7**] have O(1s) binding energies (531.6 and 531.7 eV, respectively) that are the same (within experimental error) as **9** (531.7 eV), the resonance forms in which electron density resides at carbons 3 and 5 must contribute little to the electronic description of **9**. Binding energies of the O(1s) electron for the chlorides, bromides, and dioxatellurapentalenes are in the range 531.8–532.0 eV. While the XPS experiments do not distinguish the strength of the three-center, four-electron bonds in compounds **13**–**15** (experimental error of ±0.1 eV, which corresponds to ±10% bond order),[14,15] the data suggest that a bonding interaction exists between tellurium and oxygen. Oxatellurolylium iodide **13g**, which should have one of the weakest tellurium–oxygen bonds, has an O(1s) binding energy of 531.7 eV. This value is indistinguishable, within experimental error, from the O(1s) binding energies of the model compounds suggesting little, if any, bonding between tellurium and oxygen in the oxatellurolylium iodide.

(ii) ^{125}Te NMR Studies. The ^{125}Te NMR chemical shifts of organotellurium compounds cover a range of several thousand ppm and are quite sensitive to the oxidation state and electronic environment at tellurium.[6,7] It has been shown that the electronic factors, which contribute to XPS chemical shifts in binding energy and are inductive in nature, are not the only factors that contribute to NMR chemical shifts. Although correlations of XPS binding energies with NMR chemical shifts have been made for narrow families of compounds,[6,16] a general correlation with a nucleus such as ^{125}Te that has a very broad range of chemical shifts is not expected.

The organotellurium compounds of this study are the first that have been studied by ^{125}Te NMR where the tellurium(II) compounds are trigonal-bipyramidal (AX_3E_2-type) and the tellurium(IV) compounds are octahedral (AX_5E-type). The effect of complex geometry with respect to ^{125}Te NMR chemical shifts has not been addressed systematically in the literature. Different geometries with different bonding hybridizations, as well as coordination numbers, would be expected to affect the electronic field gradient around tellurium.

If only inductive effects are considered for ^{125}Te NMR chemical shifts, one might expect a downfield chemical shift of the octahedral complexes relative to the tbp complexes as the octahedral complexes have more electron density on the ligands. The ^{125}Te NMR chemical shifts of the oxatellurolylium trihalides **15** and the dioxatellurapentalenes dihalides **16**, in the range of δ 1359–1459, are quite similar to the ^{125}Te NMR chemical shift of H_2TeCl_6 (δ 1403).[7a] The latter complex contains the octahedral $TeCl_6^{-2}$ group with a tellurium(IV) central atom. As a compairson, the tbp tellurium(IV) complexes $TeCl_4$, Ph_2TeCl_2, Me_2TeCl_2, and **11** have ^{125}Te NMR chemical shifts of δ 1138, 981, 749, and 434, respectively,[7a] which are significantly upfield from those of octahedral tellurium(IV). The octahedral tellurium(IV) complexes have one more three-center, four-electron bond than the tbp tellurium(IV) complexes.

The ^{125}Te NMR chemical shifts of the tbp tellurium(II) complexes **13** and **14** are a thousand parts per million or more downfield from those of two-coordinate tellurium(II) complexes such as **9** (δ 445), diphenyl telluride (δ 688),[7a] and dimethyl telluride (δ 0.0).[7a] It is expected that paramagnetic shielding contributions in these compounds play a major role in the dramatic differences that are observed in their ^{125}Te NMR chemical shifts. In the two-coordinate complexes, the tellurium lone pairs of electrons have considerable s character[17] and the tellurium-ligand bonds are highly covalent. In the tbp tellurium(II) complexes, the lone pairs of electrons have more p character (sp^2) as equatorial ligands and one covalent tellurium–ligand bond has been replaced by the three-center, four-electron bonding of tellurium with two highly electronegative ligands involving an essentially pure p orbital on tellurium.

In the tbp complexes, the changes in the electronic field gradient around tellurium with respect to both three-center, four-electron bonding and the spatial orientation of the lone pairs of electrons could contribute to the remarkable downfield shifts in the ^{125}Te NMR spectra of **13** and **14** relative to other organotellurium(II) compounds.

In the tellurium(II) compounds **9**, **10**, **13**, and **14**, the ^{125}Te NMR chemical shifts follow, in general, the trends expected as the strength of the tellurium–oxygen bonding interaction increases.[4,5,9,10] The formation of a three-center, four-electron bond increases the electron density at the ligands relative to the central atom in that bond.[4,5,9,10] The oxatellurolylium halides **13** show sequential downfield shifts as the electronegativity of the halide increases. Thus, oxatellurolylium iodides **13g** and **13h** have ^{125}Te NMR chemical shifts of δ 1501 and 1484, respectively; oxatellurolylium bromides **13d**–**f** have shifts in the range of δ 1650–1672; and oxatellurolylium chlorides **13a** and **13b** have chemical shifts of δ 1726 and 1692, respectively. The dioxatellurapentalenes **14**, with the most symmetrical three-center, four-electron bonding, have ^{125}Te NMR chemical shifts that are even further downfield in the range δ 1955–1967.

The ^{125}Te NMR chemical shifts in **13** and **14** are far more dependent on the atoms involved in the three-center, four-electron bonding than on changes in substituents

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[14] This estimation is based on the relationship of a change in binding energy of approximately 1 eV for a change of 1 in oxidation state.[15]

[15] Feltham, R. D.; Brant, P. *J. Am. Chem. Soc.* **1982**, *104*, 641.

[16] (a) Gassman, P. G.; Campbell, W. H.; Macomber, D. W. *Organometallics* **1984**, *3*, 385. (b) Gassman, P. G.; Macomber, D. W.; Hershberger, J. W. *Organometallics* **1983**, *2*, 1470.

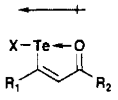
[17] Shustorovich, E. *Inorg. Chem.* **1979**, *18*, 2108.

attached to carbon on the carbon π-framework. While 20–30 ppm shifts are observed with ligand changes involving the substituents attached to carbon on the carbon backbone, ligand changes in the electronegative elements involved in bonding to tellurium cover a range of over 500 ppm. Comparison to the XPS binding energies of the same compounds finds that both changes (substituents attached to the carbon backbone and the electronegative ligands involved in three-center, four-electron bonding) are equally important for XPS. The NMR upfield chemical shift shown in Figure 1, observed upon oxidative addition of halogen to the complexes of this study, may, in part, be a function of changing the effective shielding of the tellurium nucleus by having different geometries for these tellurium(II) and tellurium(IV) complexes than the geometries of two-coordinate tellurium(II) and tbp tellurium(IV) species of similar studies.[6,7] It is difficult to assess the effect of halogen substitution on the ^{125}Te NMR chemical shifts in the oxatellurolylium trihalides **15** and dioxatellurapentalene dihalides **16**. Since the mixed oxatellurolylium trihalides are unknown,[3] the effect of substituting all three halides at once must be separated from the effect of substituting only the halide involved in the three-center, four-electron bonding with oxygen.

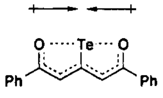
Conclusion

The XPS binding energy changes are a measure of the changes in electron density (inductive effects) at the atom center. The changes observed in the NMR chemical shifts, like XPS, are influenced by inductive effects but are also strongly influenced by changes in structure. The changes in structure affect the symmetry of the electron distribution about the atoms and, hence, the paramagnetic shielding term.

Three-center, four-electron bonding with oxygen, tellurium, and a halide should involve electron donation from oxygen to tellurium. The O(1s) binding energies of **13–15** relative to model compounds **9**, **11**, and **12** show that the oxygen is electron-deficient when involved in three-center, four-electron bonding. The ^{125}Te NMR chemical shifts and Te(3$d_{5/2}$) binding energies of oxatellurolylium monohalides **13** indicate that, as the halide becomes more electron-withdrawing (increasing the three-center, four-electron bonding interaction), the tellurium also becomes more electron-deficient. This suggests that the net bonding interaction may be represented by **17a**. Conversely, the polarization of the electron density for the symmetrical dioxatellurapentalene **14a** is shown as **17b**. The ionic contribution has also been predicted by computational studies.[3,10]



17a



17b

Experimental Section

The NMR solvent was CD_2Cl_2 which was used as received from Aldrich Chemical Co. ^{125}Te NMR spectra were recorded on a Varian Automated XL 300 NMR spectrometer at 94.704 MHz with a 5-mm broad-band probe (25–150 mg of sample/0.5 mL of solvent, probe temperature of 22 °C); samples were referenced to $^{125}TePh_2$ (at δ 688 relative to $^{125}TeMe_2$ at δ 0.0), as an external standard run as a neat liquid. The spectra were collected over 100–5000 transients by using a 100 000 Hz sweep width, a pulse time of 10 μs, and a delay time of 1.0 s. The spectra were proton decoupled with WALTZ decoupling by using 1.5 W of power centered at 5 ppm in the proton window. The ESCA analyses were carried out with a Physical Electronics Industries, Inc., ESCA-Auger-SIMS Model 555 spectrometer equipped with a Model 15-770 specimen introduction/reaction chamber. All reported values are ±0.1 eV. Both Mg Kα and Al Kα radiation were used. Samples were run with a polyethylene backing, allowing an internal calibration against the C(1s) binding energy (284.6 eV). The samples used in this study have been reported previously.[3,11,12]

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Registry No. **9**, 86029-92-7; **10**, 119244-03-0; **11**, 103817-94-3; **12**, 107144-04-7; **13a**, 87761-66-8; **13b**, 82531-84-8; **13c**, 82531-95-1; **13d**, 84281-13-0; **13e**, 99654-55-4; **13f**, 119244-04-1; **13g**, 82531-87-1; **13h**, 119244-05-2; **14a**, 87761-67-9; **14b**, 91412-32-7; **14c**, 91412-38-3; **15a**, 99654-57-6; **15b**, 99654-53-2; **15c**, 119244-06-3; **15d**, 99654-58-7; **15e**, 119244-07-4; **15f**, 119272-68-3; **16a**, 91412-55-4; **16b**, 87761-71-5.