GC or by silica gel chromatography with hexane eluent as a pure substance, mp 168–169 °C (lit.[43] 171–173 °C), but the two isomers $C_{20}H_{14}S_2$ could not be separated. The mixture had the following: ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.85–7.00 (m); a GCMS consistent with those of **5** and **6**; MS (mixture) calcd for $C_{20}H_{14}S_2$ 318.053699, found 318.05355; GCMS, m/e (relative intensity) 320 (11), 318 (M$^+$, 100), 285 (20), 284 (25), 241 (36), 240 (67), 208 (29), 165 (25); IR (neat) 3043 (s), 1593 (w), 1576 (s), 1470 (s), 1448 (s), 1433 (s), 1422 (s), 1075 (m), 1063 (m), 1015 (s), 740 (s), 680 (s) cm^{-1}.

Irradiation of PhC$\equiv$CSPh with PhSH at 350 nm for 25 h yielded a mixture of **3** (E and Z isomers) and **4**. 2,2-Bis(phenylthio)-1-phenylethene (**4**)[44] was isolated by silica gel chromatography with hexane eluent: ^{1}H NMR (CDCl$_3$) δ 7.61 (m), 7.4–7.1 (m), 6.89 (s); GCMS (relative intensity) 322 (5), 320 (M$^+$, 45), 211 (97), 209 (40), 179 (23), 178 (100); IR (neat) 3062 (w), 1582 (m), 1479 (s), 1440 (s), 1025 (m), 738 (s), 688 (s) cm^{-1}. 1,2-Bis(phenylthio)phenylethene[45] (mixture of E and Z isomers): ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.65–7.10 (m); GCMS, m/e (relative intensity) 322 (5), 320 (M$^+$, 45), 211 (96), 210 (40), 179 (23), 178 (100); IR (neat) 3067 (m), 1587 (s), 1545 (m), 1485 (s), 1445 (s), 1030 (m), 740 (s), 680 (s). Compounds **3** and **4** were not significant products in the reaction of (PhC$\equiv$C)$_2$Hg with (PhS)$_2$Hg or PhSSPh. Compound **7** had the same retention time as PhC$\equiv$CSnBu$_3$ (7% OV-3, $^1/_8$ in. × 10 ft) and was not analyzed as a reaction product with PhC$\equiv$CSnBu$_3$ as the substrate.

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Registry No. (Z)-**3**, 41424-40-2; (E)-**3**, 41424-41-3; **4**, 35550-81-3; **5**, 108344-94-1; **6**, 77128-61-1; **7**, 1207-95-0; CH$_2$=CHSPh, 1822-73-7; (CH$_3$)$_2$C=CHSPh, 13640-71-6; (E)-PhCH=CHSPh, 7214-53-1; Ph$_2$C=CHSPh, 13112-46-4; CH$_2$=CHSCH$_2$Ph, 1822-76-0; (CH$_3$)$_2$C=CHSCH$_2$Ph, 63196-87-2; (E)-PhCH=CHSCH$_2$Ph, 13294-33-2; CH$_2$=CHSO$_2$Ph, 5535-48-8; (CH$_3$)$_2$C=CHSO$_2$Ph, 54897-35-7; (E)-PhCH=CHSO$_2$Ph, 16212-06-9; (Z)-PhCH=CHSO$_2$Ph, 32291-77-3; (E)-PhCH=CHSO$_2$CCl$_3$, 108344-83-8; Ph$_2$C=CHSO$_2$Ph, 26189-62-8; (E)-PhCH=CHSePh, 60466-40-2; (Z)-PhCH=CHSePh, 60466-30-0; (E)-MeO$_2$CCH=CHSPh, 49833-37-6; (Z)-MeO$_2$CCH=CHSPh, 49833-38-7; (E)-MeO$_2$CCH=CHSO$_2$Ph, 1865-13-0; (Z)-MeO$_2$CCH=CHSO$_2$Ph, 91077-67-7; CH$_2$=CHSePh, 35167-28-3; (E)-t-BuCH=CHSBu-n, 70127-58-1; (Z)-t-BuCH=CHSBu-n, 64228-42-8; (E)-t-BuCH=CHSPh, 53847-74-8; (Z)-t-BuCH=CHSPh, 58431-67-7; (E)-t-BuCH=CHSePh, 63831-89-0; (Z)-t-BuCH=CHSePh, 108344-84-9; (E)-t-BuCH=CHTePh, 75924-68-4; (Z)-t-BuCH=CHTePh, 108344-85-0; (E)-t-BuCH=CHSO$_2$Ph, 68969-27-7; (Z)-t-BuCH=CHSO$_2$Ph, 108344-86-1; (E)-t-BuCH=CHSO$_2$C$_6$H$_4$-p-Me, 74829-77-9; (Z)-t-BuCH=CHSO$_2$C$_6$H$_4$-p-Me, 108344-87-2; (E)-t-BuCH=CHSO$_2$Me, 108344-88-3; (Z)-t-BuCH=CHSO$_2$Me, 108344-89-4; Ph$_2$C=CHSMe, 15096-10-3; Ph$_2$C=CHSPr-i, 108344-90-7; (E)-ClCH=CHSPh, 26620-11-1; (Z)-ClCH=CHSPh, 60785-27-5; (Z)-PhCH=CHSPh, 7214-56-4; Ph$_2$C=CHSePh, 108365-51-1; (CH$_3$)$_2$C=CHSePh, 77461-45-1; Ph$_2$C=CHP(O)(OEt)$_2$, 78462-91-6; (E)-PhCH=CHP(O)(OEt)$_2$, 20408-33-7; (Z)-PhCH=CNP(O)(OEt)$_2$, 25362-01-0; (E)-t-BuCH=CHP(O)(OEt)$_2$, 75924-69-5; (Z)-t-BuCH=CHP(O)(OEt)$_2$, 108344-91-8; (CH$_3$)$_2$C=CHP(O)(OEt)$_2$, 58142-40-8; PhC$\equiv$CP(O)(OEt)$_2$, 3450-67-7; PhC$\equiv$CSPh, 35460-31-2; CH$_2$=CHSnBu$_3$, 7486-35-3; (CH$_3$)$_2$C=CHSnBu$_3$, 66680-86-2; (E)-PhCH=CHSnBu$_3$, 66680-88-4; Ph$_2$C=CHSnBu$_3$, 91083-76-0; (E)-MeO$_2$CCH=CHSnBu$_3$, 82101-74-4; (Z)-MeO$_2$CCH=CHSnBu$_3$, 82101-75-5; CH$_2$=CHHgCl, 762-55-0; (E)-t-BuCH=CHHgCl, 36525-02-7; (E)-PhCh=CHHgCl, 36525-03-8; Ph$_2$C=CHHgCl, 24522-19-8; (E)-ClCH=CHHgCl, 1190-78-9; (Z)-ClCH=CHHgCl, 2350-34-7; Ph$_2$C=CHHgBr, 67341-86-0; (E)-t-BuCH=CHHgBr, 108344-92-9; (CH$_3$)$_2$C=CHHgBr, 23010-28-8; Cl$_3$CSO$_2$-Cl, 2547-61-7; PhSeSO$_2$C$_6$H$_4$CH$_3$-p, 68819-94-3; Hg(SePh)$_2$, 21514-25-0; Hg(SO$_2$H)$_2$, 15220-40-3; [(EtO)$_2$P(O)]$_2$Hg, 29105-14-4; (EtO)$_2$P(O)HgCl, 29120-01-2; Ph$_2$C=CHI, 19997-66-1; PhC$\equiv$CI, 932-88-7; (Z)-PhCH=CHSO$_2$CCl$_3$, 108344-93-0; (E)-PhSCH=CHSPh, 18893-63-5; (Z)-PhSCH=CHSPh, 18893-62-4; PhS—SPh, 882-33-7; PhCH$_2$S—SCH$_2$Ph, 150-60-7; PhSO$_2$—Cl, 98-09-9; PhSe—SePh, 1666-13-3; n-BuS—SBu-n, 629-45-8; PhTe—TePh, 32294-60-3; p-MeC$_6$H$_4$SO$_2$—Cl, 98-59-9; MeSO$_2$—Cl, 124-63-0; MeS—SMe, 624-92-0; i-PrS—SPr-i, 4253-89-8; Hg(SPh)$_2$, 21514-24-9; (PhC$\equiv$C)$_2$Hg, 6077-10-7; PhC$\equiv$CSnBu$_3$, 3757-88-8.

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^{125}Te NMR and Mössbauer Spectroscopy of Tellurium–Phosphine Complexes and the Tellurocyanates

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The nature of the bonding to tellurium in the phosphine complexes R$_3$PTe and (R$_2$P)$_2$Te and in the tellurocyanates TeCN$^-$, ArTeCN, ArCH$_2$TeCN, and ArTe(X)CN$^-$ (X = Cl, Br, I) has been studied by ^{125}Te solution NMR spectroscopy at ambient temperature and by ^{125}Te Mössbauer spectroscopy at 4.2 K. No evidence was found for multiple bonding to tellurium in either solution or the solid state. The phosphine complexes R$_3$PTe give ^{125}Te NMR shifts of −837 to −495 ppm (Me$_2$Te) and ^{125}Te quadrupole splittings of 10–12 mm s^{-1}. The TeCN$^-$ ion has a ^{125}Te NMR shift of −509 to −569 ppm dependent on solvent and counterion, ArTeCN and ArCH$_2$TeCN shifts of +570–580 ppm, and the halide derivatives ArCH$_2$Te(X)CN$^-$ shifts of −586 to −604 ppm. The ^{125}Te Mössbauer quadrupole splitting of TeCN$^-$ is 12 mm s^{-1}, of ArTeCN and ArCH$_2$TeCN is 13.7–14.1 mm s^{-1}, of ArCH$_2$Te(X)CN, X = Cl, is 14.5 mm s^{-1}, of ArCH$_2$Te(X)CN, X = Br, is 13.8 mm s^{-1}, and of ArCH$_2$Te(X)CN, X = I, is 14.0 mm s^{-1}.

Introduction

The application of ^{125}Te NMR and Mössbauer spectroscopy in the study of organotellurium compounds has attracted considerable attention in recent years. However, relatively little work has been reported on tellurium–phosphine complexes or on the tellurocyanates. Du Mont and Kroth[1] have reported ^{125}Te NMR data for (t-Bu)$_3$PTe, (n-Bu)$_3$PTe, and Te[P(t-Bu)$_2$]$_2$, while the tellurocyanates have not been studied to date.

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Table I. ^{125}Te NMR Data for Phosphine Tellurides

	δ^a	$^1J(^{125}\text{Te}-^{31}\text{P})$, Hz
Ph_3PTe	-491.8	
n-Bu_3PTe	-803.2 (-55)	1732
t-Bu_3PTe	-836.5 (-86)	1663
(morpholine)$_3$PTe	-812.6	2153
$(Me_2N)_3PTe$	-821.7	2095
(*t*-$Bu_2P)_2Te$	-151.3 (-148)	451 (451)

[a] δ measured in C_6H_6/C_6D_6 with respect to Me_2Te (neat) at ambient temperature Negative shifts are to high field. Values in parentheses are taken from ref 1.

These compounds are of some interest because of the possible presence of multiple bonding to tellurium. This can be represented in terms of the resonance forms:

$$R_3P{=}Te \qquad Te^{-}{-}C{\equiv}N$$

$$R_3P^{+} - Te^{-} \qquad Te{=}C{=}N^{-}$$

Thus, vibrational spectroscopy of Me_3PTe indicates the presence of a Te–P force constant, which is approximately an average of the single- and double-bond values.[2] The X-ray crystal structures of several phosphine tellurides[3-5] indicate the presence of Te–P bonds which appear to be shorter than that expected for a single bond. The ^{125}Te NMR chemical shifts reported by Du Mont and Kroth[1] for *t*-BuP_3Te and *n*-BuP_3Te were considerably more positive than might have been expected on the basis of ^{77}Se NMR data of similar selenium compounds,[6] and this could also be taken as evidence for some P═Te double-bond character in these complexes.

Bonding in the tellurocyanates has previously been investigated by a wide variety of techniques[7] including IR and Raman spectroscopy, ESCA, and ^{14}N NMR and NQR spectroscopy, while the X-ray crystal structures of PNP^+TeCN^- [8] and of *p*-nitrobenzyl tellurocyanate[9] and its halide derivatives[10] have all been reported. These measurements have suggested the presence of some π-character in the Te–C bond; e.g., the Te–C bond lengths in the $TeCN^-$ ion and in *p*-$NO_2C_6H_4CH_2TeCN$ are again shorter than the anticipated single-bond length.

In the present work we have measured the ^{125}Te solution NMR and solid-state Mössbauer spectra of a range of tellurium–phosphine and tellurocyanate complexes in an attempt to further explore the nature of the bonding to tellurium in both solution and the solid state.

Results

The ^{125}Te NMR chemical shifts relative to neat Me_2Te and, where appropriate, the $^1J(^{125}\text{Te}-^{31}\text{P})$ coupling constants are reported in Table I. The spectra of the phosphine tellurides were recorded in C_6H_6/C_6D_6 solution and the tellurocyanates primarily in Me_2SO or CH_3CN. All spectra were recorded at ambient temperature.

The phosphine tellurides yielded negative chemical shifts ranging from -151.3 to -836.5 ppm. The spectra of all but $(Ph_3P)Te$ and (*t*-$Bu_2P)_2Te$ were well-resolved doublets, indicating the presence of coupling to ^{31}P. Triphenylphosphine telluride is known[5] to crystallize as $(Ph_3P)_2Te$ in which a second molecule of phosphine is weakly bound to tellurium. The presence of excess phosphine in a solution of this compound cannot be avoided, and rapid exchange between the Ph_3P groups results in the absence of a tellurium–phosphorus coupling at ambient temperature. Indeed, in the presence of excess of the appropriate phosphine, the spectra of *n*-Bu_3PTe, *t*-Bu_3PTe, and $(Me_2N)_3PTe$ also collapse from a well-resolved doublet into a broad single line, indicative of rapid exchange between the phosphine ligands. The ^{125}Te spectra of ref 1 were evidently recorded in the presence of excess ligand and showed only a broad resonance and no Te–P couplings. Sample NMR spectra recorded in the present work are given in Figure 1.

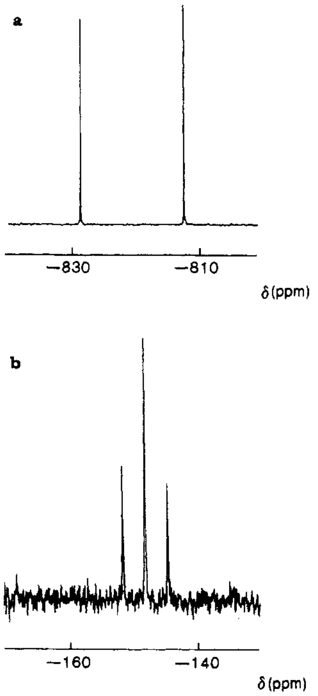

Figure 1. Tellurium-125 NMR spectra of (a) $(Me_2N)_3PTe$ and (b) (*t*-$Bu_2P)_2Te$ in C_6H_6/C_6D_6 at ambient temperature. Chemical shifts are relative to neat Me_2Te.

Table II. ^{125}Te NMR Chemical Shifts of Tellurocyanates

	δ^a	solv
KTeCN	-509.2	Me_2SO
$((C_6H_5)_4As)TeCN$	-511.1	Me_2SO
(PNP)TeCN	-568.8	CH_3CN
C_6H_5TeCN	+652.5	CH_3CN
p-$O_2NC_6H_4TeCN$	+679.66	Me_2SO
p-$O_2NC_6H_4CH_2TeCN$	+679.79	CH_3CN
p-$O_2NC_6H_4CH_2TeCN$	+692.19	acetone
$((C_6H_5)_4As)C_6H_5Te(Cl)CN$	+576.1	CH_3CN
$((C_6H_5)_4As)$*p*-$O_2NC_6H_4CH_2Te(Cl)CN$	+588.4	CH_3CN
$((C_6H_5)_4As)C_6H_4CH_2Te(Br)CN$	+574.7	CH_3CN
(PNP)*p*-$O_2NC_6H_4CH_2Te(Cl)CN$	+586.3	CH_3CN
(PNP)*p*-$O_2NC_6H_4CH_2Te(Br)CN$	+595.6	CH_3CN
(PNP)*p*-$O_2NC_6H_4CH_2Te(I)CN$	+603.5	CH_3CN

[a] δ with respect to Me_2Te (neat) at ambient temperature. Negative shifts are to high field. PNP = bis(triphenylphosphine)nitrogen(1+) cation, $(Ph_3P)_2N^+$.

In the compound (*t*-$Bu_2P)_2Te$, two phosphine ligands are covalently bound to tellurium and the ^{125}Te spectrum yields a well-resolved triplet.

For the tellurocyanates (Table II) the chemical shifts range from -569 for PNP^+TeCN^- in CH_3CN to +692 ppm for *p*-$O_2NC_6H_4CH_2TeCN$ acetone. For the $TeCN^-$ ion some influence was observed of the counterion and/or

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Table III. ^{125}Te Mössbauer Data (mm s^{-1})

	δ,^{a} ±0.08	Δ, ±0.1	Γ
Ph_3PTe	0.08	12.5	5.9
n-Bu_3PTe	−0.11	10.1	6.2
t-Bu_3PTe	0.02	10.3	6.5
(morpholine)$_3$PTe	−0.13	10.2	5.9
$(Me_2N)_3PTe$	−0.12	10.2	6.0
$(t\text{-}Bu_2P)_2Te$	0.23	9.1	6.1
(PNP)TeCN	0.08	12.0	5.5
$((C_6H_5)_4As)TeCN$	0.15	12.2	5.7
C_6H_5TeCN	0.43	14.1	6.1
$C_6H_5CH_2TeCN$	0.37	14.1	6.2
p-$O_2NC_6H_4CH_2TeCN$	0.31	13.7	6.1
(PNP)p-$O_2NC_6H_4CH_2Te(Cl)CN$	0.42	14.5	5.4
(PNP)p-$O_2NC_6H_4CH_2Te(Br)CN$	0.38	13.8	5.5
(PNP)p-$O_2NC_6H_4CH_2Te(I)CN$	0.43	14.0	6.2

^{a} δ, Mössbauer chemical shift, with respect to I/Cu, source and absorbers at 4.2 K. PNP = bis(triphenylphosphine) nitrogen(1+) cation, $(Ph_3P)_2N^+$.

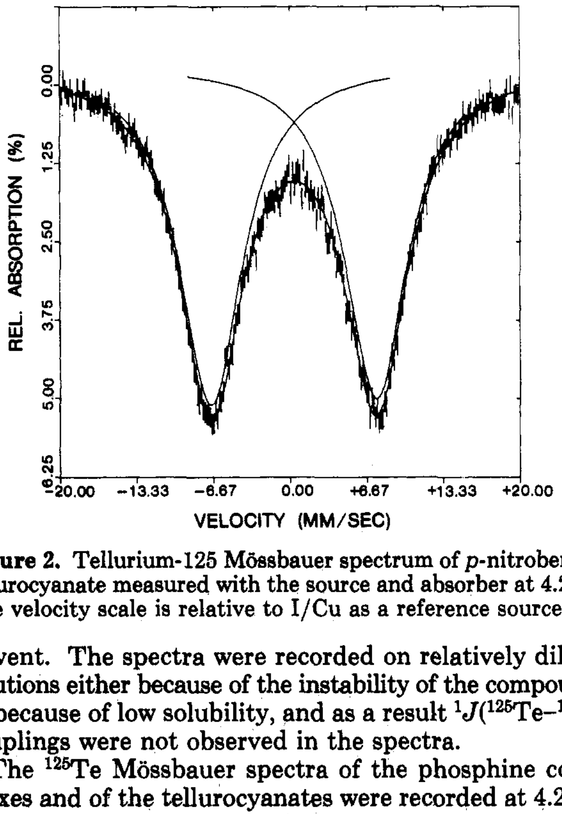

Figure 2. Tellurium-125 Mössbauer spectrum of p-nitrobenzyl tellurocyanate measured with the source and absorber at 4.2 K. The velocity scale is relative to I/Cu as a reference source.

solvent. The spectra were recorded on relatively dilute solutions either because of the instability of the compound or because of low solubility, and as a result $^1J(^{125}Te–^{13}C)$ couplings were not observed in the spectra.

The ^{125}Te Mössbauer spectra of the phosphine complexes and of the tellurocyanates were recorded at 4.2 K, and the data are given in Table III. A sample spectrum is shown in Figure 2, and in general excellent percent resonance absorptions were observed together with relatively narrow line widths.

Discussion

Phosphine Complexes. The chemical shifts reported here for t-Bu_3PTe (−836.5 ppm) and n-Bu_3PTe (−803.2 ppm) are not in agreement with those of Du Mont and Kroth (−55 and −86 ppm, respectively, with respect to Me_2Te) although the $^1J(^{125}Te–^{31}P)$ values agree reasonably well. On the other hand the chemical shift and coupling constant for $(t\text{-}Bu_2P)_2Te$ agree well with their values.[1]

A comparison of the present data with that reported earlier for phosphine selenides is possible noting that $\delta(^{125}Te)/\delta(^{77}Se) \approx 1.8$.[11] Triphenylphosphine selenide yielded a shift of −275 ppm[12] corresponding to a value of −495 ppm for the telluride, in good agreement with our observed value. The selenides Me_3PSe (−235 ppm) and $(MeO)_3PSe$ (−396 ppm)[13] give values for the corresponding tellurides of −423 and −712 ppm in a similar range to the shifts observed here.

Thus, the ^{125}Te chemical shifts of the phosphine tellurides of the form R_3PTe all exhibit substantial negative shifts with respect to Me_2Te, indicating the presence of considerable shielding at the tellurium nucleus. It has been noted that the C=Se double bond yields ^{77}Se chemical shifts of +600 to +2000 ppm with respect to Me_2Se.[14] With the assumption that the correlation between ^{77}Se and ^{125}Te NMR chemical shifts is applicable over such a wide range, this would correspond to ^{125}Te chemical shifts of ca. +1100 to +3600 ppm for the C=Te bond. The negative chemical shifts observed here, as for R_3PSe, would appear to indicate the predominance of the $R_3P^+–Te^-$ resonance form, since this would place greater electron density on the tellurium, leading to a greater shielding at the nucleus.[13]

The compound $(t\text{-}Bu_2P)_2Te$ exhibits a much more positive chemical shift than the R_3PTe complexes. The presence of two phosphorus ligands bonded to tellurium leads to a greater deshielding of the tellurium nucleus. This is consistent with the data for Me_3PSe (−235 ppm)[13] and Me_2PSeMe (+58 ppm),[15] where the coordination of a second ligand to selenium results in a substantially more positive shift.

The compounds R_3PTe exhibit large $^1J(^{125}Te–^{31}P)$ coupling constants of 1660–2120 Hz in agreement with literature values, indicating the presence of significant s character in the Te–P bond. This contrasts with the small coupling constant in $(t\text{-}Bu_2P)_2Te$ (451.1 Hz) and the apparent predominance in the latter of p bonding to tellurium.

The basicity toward tellurium of a number of the phosphine ligands studied here has been measured by Rømming et al. Triphenylphosphine is the weakest base, followed by (morpholine)$_3$P, n-Bu_3P, and finally $(Me_2N)_3P$. The more positive chemical shift of −492 ppm for Ph_3PTe is consistent with less electron donation to the tellurium by the ligand. However all the other complexes yield very similar chemical shifts. Moreover, the chemical shifts do not appear to be correlated with the $^1J(^{125}Te–^{31}P)$ values. The tellurium chemical shifts are generally taken to be dominated by the Ramsey paramagnetic shielding, σ_p,[16] and this is dependent on several factors, including the mean electronic excitation energy ΔE, which may mask any simple dependence on the basicity of the ligand.

Taken together the solution NMR data suggest that the Te–P bond has significant s character in the R_3PTe complexes but that there is little evidence for extensive π-bonding to tellurium.

The ^{125}Te Mössbauer data (Table II) indicate the presence of small isomer shifts (with respect to I/Cu as a reference standard) and relatively large nuclear quadrupole coupling constants. The latter indicates the presence of a considerable p-orbital imbalance in the tellurium 5p valence orbital populations in each of these compounds. This in itself suggests that in the solid state there is little π-bonding to tellurium. The presence of $Te(p\pi) \rightarrow P(d\pi)$

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bonding would be expected to substantially reduce the quadrupole splitting at tellurium, and this is not observed. The quadrupole splitting corresponding to one 5p hole in the tellurium valence shell would be ca. 12 mm s^{-1},[17] and the splittings observed here approach this value.

The quadrupole splitting in $(Ph_3P)Te$ is significantly larger than that in the other R_3PTe complexes. As noted earlier the X-ray crystal structure of this compound[5] shows the presence of a second molecule of phosphine and a trans P–Te···P arrangement with a short P–Te bond length of 238.8 pm, which compares with 248 pm for a single P–Te bond, and a long P···Te bond of 341.2 pm. In comparison $(morpholine)_3PTe$ has only one P–Te bond length of 235.7 pm.[3] The larger quadrupole splitting and hence p-orbital imbalance in $(Ph_3P)_2Te$ appear to be related to the peculiar stereochemistry about tellurium and the albeit weak coordination of a second phosphine ligand.

McFarlane and Rycroft[13] had suggested that the more positive ^{77}Se chemical shift of −275 ppm observed for Ph_3PSe was consistent with a somewhat greater π-character in the P–Se bond compared to that in $(MeO)_3PSe$ (δ −396) for example. However Ph_3PTe also exhibits a relatively positive ^{125}Te chemical shift of −495 ppm (cf. $(Me_2N)_3PTe$, δ −821), while the Mössbauer quadrupole splitting of 12 mm s^{-1} for Ph_3PTe is the largest observed for the phosphine tellurides. Since $Te(d\pi)\rightarrow P(p\pi)$ bonding should decrease the electric field gradient at the tellurium, the large Δ value for Ph_3PTe is quite inconsistent with greater π-bonding in $Ph_3P–Te$.

The ^{125}Te Mössbauer isomer shifts of the R_3PTe complexes are small in comparison with the reference standard. This is quite consistent with the presence of significant s character in the Te–P bond. While the removal of tellurium 5p electron density tends to increase the nuclear s-electron density and hence the isomer shift through deshielding of the 5s electrons from the nucleus, the removal of 5s electrons directly decreases the isomer shift, the latter being far more important than the former. The large nuclear quadrupole coupling constants in these compounds indicates the removal of very considerable p-electron density from the tellurium along the Te–P σ-bond. The small isomer shift indicates significant s character in the Te–P bond and that this offsets the 5p orbital vacancy to a significant extent.

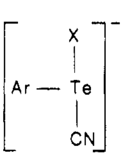
In $(t\text{-}Bu_2P)_2Te$ the isomer shift is somewhat more positive than that in the R_3PTe complexes. The coordination of a second phosphorus ligand to tellurium leads to a small overall increase in the s-electron density at the nucleus. The p-orbital vacancy on tellurium predominates over the s-orbital participation in the Te–P bonds, leading to a small net increase in the nuclear s-electron density.

While the P–Te bond lengths observed in $(Ph_3P)_2Te$ (238.8 pm), $(morpholine)_3PTe$ (235.7 pm) and *cis*-$(t\text{-}BuPN(Me))_2Te_2$ (232.7–230.5 pm) are relatively short in comparison with the anticipated single Te–P bond length of 248 pm, neither the NMR chemical shifts in solution nor the solid Mssbauer quadupole splitting are consistent with the presence of π-bonding.

Tellurocyanates. A picture similar to the above emerges for the tellurocyanates. The $TeCN^-$ ion exhibits an NMR chemical shift of −509 to −568 ppm depending on the cation and/or solvent. These values are in good agreement with that expected on the basis of the ^{77}Se chemical shift of −322 ppm for $KSeCN$[18] and a $\delta(^{125}Te)/\delta(^{77}Se)$ ratio of 1.8. The large negative shift again implies extensive shielding at the tellurium and supports the formulation as $^-Te–CN$ rather than the presence of Te–CN π-bonding.

On coordinating a second ligand to the tellurium, as in C_6H_5TeCN, there is a substantial increase in the ^{125}Te chemical shifts and values ranging from +652 to +692 ppm are now observed consistent with that expected from the ^{77}Se chemical shift of +288 ppm for $C_6H_5CH_2SeCN$.[18] The ^{125}Te chemical shifts are very similar regardless of whether the organic ligand is phenyl, benzyl, or *p*-nitrobenzyl. The more positive shifts again indicate that the tellurium has become deshielded, and this is analogous to the situation for $t\text{-}Bu_3PTe$ (−836 ppm) and $(t\text{-}Bu_2P)_2Te$ (−151 ppm).

The negatively charged halide ions $p\text{-}O_2NC_6H_4CH_2Te(X)CN^-$ (X = Cl, Br, I), as in the tetraphenylarsonium or PNP^+ (bis(triphenylphosphine)nitrogen(1+)) salts, have chemical shifts which are less positive but quite similar to the parent organotellurocyanate. These anions are T-shaped, and the halogen is coordinated trans to the cyanide group:


$$\left[Ar - \overset{X}{\underset{CN}{Te}} \right]^-$$

The bonding in the X–Te–CN linkage may be viewed as 3c–2e, and the X-ray crystal structures suggest that the Te–CN bond in the ions $p\text{-}O_2NC_6H_4Te(X)CN^-$ is significantly longer (2.13–2.14 Å)[10] than that in $p\text{-}O_2NC_6H_4CH_2TeCN$ (2.06 Å)[9] or $TeCN^-$ (2.02 Å); i.e., as the halogen becomes coordinated to the tellurium, the Te–CN bond lengthens. However, the net shielding about the tellurium, as reflected in the chemical shifts, remains much the same. Again, there is little evidence for Te–CN multiple-bond character in the organotellurocyanates, since in $p\text{-}O_2NC_6H_4CH_2Te(X)CN^-$ there cannot be any Te–CN double-bond character and yet the NMR chemical shifts for the anion and for the parent organotellurocyanate are the same.

The ^{125}Te Mössbauer data for the $TeCN^-$ ion (Table III) show the presence of a large nuclear quadrupole coupling constant. Since the presence of Te–C π-bonding would reduce the magnitude of the nuclear quadrupole coupling significantly, the very large value of Δ observed again suggests that π-bonding to tellurium must be minimal.

It is of interest to compare the ^{125}Te Mössbauer data for $TeCN^-$ with the iodine Mössbauer data for ICN since these two species are isoelectronic and isostructural. The ^{129}I Mössbauer isomer shift and nuclear quadrupole coupling constant for ^{129}ICN have been interpreted as demonstrating that the I–CN bond is σ in character and that there is no π-bonding present.[19] The iodine nuclear quadrupole coupling constant in ICN of 2640 MHz (η = 0) expressed in terms of the ground state for ^{127}I (the reference for NQR data) corresponds to a splitting expressed in velocity units of 56.8 mm s^{-1}. Thus assuming that the asymmetry parameters for $TeCN^-$ is also zero, i.e., that the Te–CN bond has axial symmetry

$$\frac{|e^2qQ(^{125}Te)|}{|e^2qQ(^{127}I)|} = 0.21$$

Noting that the ratio of the unit field gradients for one 5p hole on tellurium and iodine is 0.85, and that $|eQgnd(^{127}I)|$, the magnitude of the ground-state nuclear quadrupole moment for ^{127}I, is 0.79 barn,[19] the above suggests that

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quadrupole moment of the nuclear excited state for ^{125}Te is ca. 0.2 barn. This agrees well with previous estimates of this parameter,[19] suggesting that as in ICN there is little evidence for π-bonding in $TeCN^-$.

The Mössbauer quadrupole splittings of *p*-$O_2NC_6H_4CH_2TeCN$ and its halide derivatives span a small range from 13.8 to 14.5 mm s^{-1} (Table III). The very large quadrupole splitting in the former again points to the absence of any π-bonding in the Te–CN bond of the organotellurocyanate. It is also apparent that the Te–CN bond in the parent organotellurocyanate and the X–Te–CN linkage in the halide ions lead to similar p-orbital imbalances about tellurium as reflected in the very similar values for the quadrupole splittings. Again, it would be difficult to reconcile Te–CN π-bonding in *p*-$O_2NC_6H_4CH_2TeCN$ with this observation.

The Mössbauer isomer shifts again reflect the competing effects of the p- and s-orbital vacancies on tellurium, the former tending to make δ more positive and the latter δ more negative. The small positive isomer shift for the $TeCN^-$ ion suggests that the p character in the Te–CN bond is offset to some extent by the s character of the bond, leading to a small net deshielding of the 5s electrons from the nucleus. The presence of extensive π-bonding would have been expected to lead to a substantially more positive isomer shift, and the small value of δ can be taken as further evidence, albeit indirect, for the absence of π-bonding.

In RTeCN the ^{125}Te isomer shifts are more positive than in $TeCN^-$, reflecting a net increase in the s-electron density at the tellurium nucleus and that the p character of the bonding predominates over the s character. The fact that *p*-$O_2NC_6H_4CH_2TeCN$ and the halide derivatives (PNP) *p*-$O_2NC_6H_4CH_2Te(X)CN$ all have very similar isomer shifts suggests a similarity between the Te–CN bond and the X–Te–CN linkage in terms of the s- and p-orbital populations and again points to the absence of π-bonding in *p*-$O_2NC_6H_4CH_2TeCN$.

The question remains as to the origin of the very short bond length reported for $TeCN^-$ (2.02 Å) and *p*-$O_2NC_6H_4CH_2TeCN$ (2.06 Å). Maartmaan-Moe and Songstad[10] have commented on the difficulty of accurately determining bond lengths in a linear framework such as TeCN or X–Te–CN because of thermal vibrations and have suggested that low-temperature crystallographic data will be required to clarify this question.

Experimental Section

Syntheses. All compounds were synthesized by using methods previously described in the literature. Bis(triphenylphosphine) telluride was prepared by treating tetraphenylarsonium tellurocyanate with a large excess of triphenylphosphine in acetone in the presence of a small amount of lithium perchlorate.[5] All the other R_3PTe tellurides were obtained by reacting the tertiary phosphine with the stoichiometric quality of tellurium in toluene[20] and subsequent filtration, removal of the solvent, and recrystallization from toluene/hexane. Bis(di-*tert*-butylphosphine)telluride, $(t\text{-}Bu_2P)_2Te$, was prepared by reacting Li_2Te in THF with di-*tert*-butylphosphine chloride.[21]

Solutions of KTeCN were prepared by heating tellurium metal and KCN in 1:1 ratio in Me_2SO until all the tellurium dissolved, yielding a yellow solution.[22] Because of the known instability of KTeCN no attempt was made to isolate the solid. Instead, the (PNP)TeCN and $(C_6H_5)_4AsTeCN$ salts were prepared by reacting the corresponding cyanides with tellurium in acetone. The crystalline compounds separated out on concentrating the solution. Phenyl tellurocyanate was prepared by the reduction of diphenyl ditelluride with $NaBH_4$ followed by treatment with BrCN.[22,23] The benzyl and nitrobenzyl tellurocyanates were obtained by reacting the appropriate organic chloride stoichiometrically with KTeCN in Me_2SO solution.[24] The corresponding (PNP)RTe(X)CN and $((C_6H_5)_4As)RTe(X)CN$ salts were synthesized by reacting the aryl or nitrobenzyl tellurocyanate with the (PNP)X and $((C_6H_5)_4As)X$ salts.[9] These compounds were also synthesized from (PNP)TeCN and $((C_6H_5)_4As)TeCN$ and the appropriate aryl or benzyl halide.

All isolated solid compounds gave satisfactory C and H analyses.

Spectroscopic Characterization. The ^{125}Te NMR spectra were obtained on a Bruker WM-400 spectrometer at 126.24 MHz, operating at ambient temperature using methods previously described. The line widths for the R_3PTe complexes in the absence of excess phosphine and of the tellurocyanates were 8–14 Hz. The ^{125}Te chemical shifts are reported relative to neat Me_2Te.

The ^{125}Te Mössbauer spectra were recorded by using a constant acceleration Harwell Instruments spectrometer, with the ^{125}Sb/Cu source and absorbers immersed in liquid helium as previously described.[25] Spectra were computer-fitted to Lorentzians, and the isomer shifts are quoted relative to an ^{125}I/Cu source.

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Registry No. Ph_3PTe, 51241-84-0; *n*-Bu_3PTe, 2935-46-8; *t*-Bu_3PTe, 60483-74-1; (morpholine)$_3$PTe, 75404-54-5; $(Me_2N)_3PTe$, 21992-94-9; $(t\text{-}Bu_2P)_2Te$, 74098-08-1; KTeCN, 75437-09-1; $((C_6H_5)_4As)TeCN$, 32592-42-0; (PNP)TeCn, 65300-09-6; C_6H_5TeCN, 72726-17-1; *p*-$O_2NC_6H_4TeCN$, 108345-01-3; *p*-$O_2NC_6H_4CH_2TeCN$, 78622-25-0; $((C_6H_5)_4As)C_6H_5Te(Cl)CN$, 108345-03-5; $((C_6H_5)_4As)$*p*-$O_2NC_6H_4CH_2Te(Cl)CN$, 108345-04-6; $((C_6H_5)_4As)$*p*-$O_2NC_6H_4CH_2Te(Br)CN$, 108345-05-7; (PNP)*p*-$O_2NC_6H_4CH_2Te(Cl)CN$, 83293-42-9; (PNP)*p*-$O_2NC_6H_4CH_2Te(Br)CN$, 84686-11-3; (PNP)*p*-$O_2NC_6H_4CH_2Te(I)CN$, 84686-13-5; ^{125}Te, 14390-73-9.

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