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Studies of Silyl and Germyl Group 6 Species. 5.[1] Silyl and Germyl Derivatives of Methane- and Benzenetellurols

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The silyl and germyl derivatives of methane- and benzenetellurols H_3MTeR (M = Si, Ge; R = CH_3, C_6H_5) and the methylated analogues $(CH_3)_3MTeR$ (M = Si, Ge, Sn; R = CH_3, C_6H_5) have been prepared and characterized. The synthetic routes include reactions of halides with lithium organotellurolates and trimethyl(organotelluro)silanes. The spectroscopic properties of these species are reported and discussed. Tellurophenol, C_6H_5TeH, is identified in the hydrolysis of trimethyl(phenyltelluro)silane.

We recently reported the characterization of some simple silyl and germyl organoselenium derivatives of the type H_3MSeR (M = Si, Ge; R = CH_3, C_6H_5) and $(CH_3)_3MSeR$ (M = Si, Ge, Sn; R = CH_3, C_6H_5)[3,4] analogous to the methoxy- and (methylthio)silanes[5-7] and -germanes.[5,8-10] Studies of silyl- and germyltellurium species are comparatively scant. The symmetrical hydridic tellurides $(H_3Si)_2Te$ and $(H_3Ge)_2Te$ have been reported[11,12] and appear to be far less stable than the corresponding organo-substituted species $(R_3M)_2Te$ (M = Si,[11,13-15] Ge,[15-17] Sn;[15,16,18,19] R = CH_3, C_2H_5, C_6H_5). Reports of organotellurium group 4 derivatives are limited to fully substituted R_3MTeR' (R = R' = C_2H_5) species,[15,18,20,21] In the present study the formation of the hydrides $H_3SiTeCH_3$, $H_3SiTeC_6H_5$, $H_3GeTeCH_3$, and $H_3GeTeC_6H_5$ and their methylated analogues is described by using synthetic routes derived from earlier work.

Results and Discussion

In earlier work[3,4] we showed that the synthesis of organoselenium group 4 species containing the C–Se–M (M = Si, Ge, Sn) skeleton could be achieved by forming the C–Se linkage before the Se–M linkage. In this sequence the C–Se moiety was present in either organoselenolates, LiSeR (R = CH_3, C_6H_5), or organoselenoaluminates, $LiAl(SeR)_4$, which underwent facile salt elimination with halosilanes. We find that this approach is also applicable to the synthesis of the analogous organotellurium species in only slightly lower overall yield.

As reported by other workers[22] we find that elemental tellurium readily inserts into the C–Li bond of organolithium reagents to form the organotellurolates lithium methanetellurolate, $LiTeCH_3$, and lithium benzenetellurolate, $LiTeC_6H_5$ (eq 1). The tellurolates were not isolated, and attempts to completely remove tetrahydrofuran from these species were unsuccessful, suggesting that in the crystalline state there may be coordination with this solvent. However, their subsequent reaction in situ with trimethylchlorosilane gave satisfactory yields (>60%) of the expected (methyltelluro)- and (phenyltelluro)trimethylsilanes (eq 2). Earlier attempts to form the C–Te–Si species by reaction of trimethylchlorosilane with the telluro Grignard reagent $C_6H_5TeMgBr$ gave only the symmetric disproportionation product bis(trimethylsilyl) telluride, $[(CH_3)_3Si]_2Te$, in low yield.[13]

$$\mathrm{Te + LiR \xrightarrow{THF} LiTeR} \qquad R = CH_3,\ C_6H_5 \tag{1}$$

$$\mathrm{(CH_3)_3SiCl + LiTeR \xrightarrow{25\ ^\circ C} (CH_3)_3SiTeR + LiCl} \qquad R = CH_3,\ C_6H_5 \tag{2}$$

The comparative salt elimination method using complex aluminates of the type $LiAl(TeR)_4$ was unsuitable[23] due to the instability of the required organotellurol, RTeH, precursors.[24] For this reason the protolytic cleavage of silicon and germanium carbodiimides with organotellurols was not attempted although corresponding reactions with organoselenols have proved synthetically viable.[4,25]

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Table I. ^{1}H NMR Parameters[a] of the Methyltelluro and Phenyltelluro Species

compd	$\delta(CH_3)$	$\delta(MH')$	$\delta(CH_3')$	$\delta(C_6H_5)$	*J*(CH') M	*J*(CH') Te	*J*(TeCH)	*J*[(TeMCH) (*vic*)]
$H'_3SiTeCH_3'$[b]		3.89	1.64			146.7	22.3 (2)	
$H'_2Si(TeCH_3')_2$		4.70	1.67					
$H'_3SiTeC_6H_5$		3.99		7.13 7.72				
$H'_2Si(TeC_6H_5)_2$		4.72						
$(CH_3)_3SiTeCH_3'$[c]	0.56		1.49		120.3	141.8	18.4 (8)	7.2 (3)
$(CH_3)_3SiTeC_6H_5$	0.47			7.15 7.76	121.8			7.2 (9)
$H'_3GeTeCH_3'$[d]		3.75	1.73			146.1	22.0 (0)	
$H'_3GeTeC_6H_5$[e]		3.87		7.14 7.75				
$(CH_3)_3GeTeCH_3'$[c]	0.68		1.52		127.3	142.1	19.1 (4)	5.2 (8)
$(CH_3)_3GeTeC_6H_5$	0.59			7.05 7.68	129.3			6.0 (1)
$(CH_3)_2Ge(TeCH_3')_2$	1.21		1.67		131.6	138.6	20.8 (9)	4.9 (4)
$(CH_3)_3SnTeCH_3'$[c,f]	0.53		1.55		133.2	142.9	21.9 (0)	ca. 3.1
$(CH_3)_3SnTeC_6H_5$[g]	0.46			7.10 7.81	133.9			*i*
$(CH_3)_3PbTeCH_3'$[h]	ca. 1.4		ca. 1.8					

[a] The spectra were recorded at ambient temperature in C_6H_{12} solution (ca. 5% v/v). Chemical shifts are in ppm to low field of tetramethylsilane. Coupling constants (^{13}CH, ^{29}SiH) are ±0.1 Hz. [b] *J*(SiH) = 219.9 Hz; *J*[(TeSiH)(*gem*)] = 27.5 (4) Hz. [c] CCl_4 solution. [d] *J*[(TeGeH)(*gem*)] = 19.8 Hz. [e] *J*[(TeGeH)(*gem*)] = 21.9 (3) Hz. [f] *J*[(SnH)(*gem*)] = 57.5 (3) Hz for ^{119}Sn and 54.9 (3) Hz for ^{117}Sn; *J*[(SnH)(*vic*)] = 28.47 Hz for ^{119}Sn and 27.33 for ^{117}Sn. [g] *J*[(SnH)(*gem*)] 57.6 (3) Hz for ^{119}Sn and 55.0 (8) Hz for ^{117}Sn. [h] *J*[(PbH)(*gem*)] = ca. 65 Hz. [i] Not observed.

Reactions similar to (eq 2) also occur with halogermanes and -stannanes but the well-established silyl–germyl/silyl–stannyl exchange reaction[3,4,26] provides a more convenient route to the germanium and tin derivatives. Rapid and essentially quantitative exchange occurs when organotellurosilanes and fluorogermanes (eq 3) or chlorostannanes (eq 4) are mixed at room temperature.

$$(CH_3)_3SiTeCH_3 + H_3GeF \rightarrow H_3GeTeCH_3 + (CH_3)_3SiF \qquad (3)$$

$$(CH_3)_3SiTeC_6H_5 + (CH_3)SnCl \rightarrow (CH_3)_3SnTeC_6H_5 + (CH_3)_3SiCl \qquad (4)$$

Attempts to prepare SiH_3 derivatives using bromosilane in reaction 2 with the tellurolates were unsuccessful even at low temperatures. Typically, less than 25% of the silicon was recovered (as volatile silane and disilyl telluride), the remainder being present in intractable polymeric material. Pure samples of the hydrides $H_3SiTeCH_3$ and $H_3SiTeC_6H_5$ were obtained from the unusual exchange reaction of iodo- or bromosilane with the appropriate trimethylsilyl derivative (eq 5). In the

$$H_3SiX + (CH_3)_3SiTeR \rightarrow H_3SiTeR + (CH_3)_3SiX$$
$$X = Br, I;\ R = CH_3, C_6H_5 \qquad (5)$$

absence of reliable thermochemical data for the silyl/trimethylsilyl system it appears that the $(CH_3)_3Si$ group in these reactions is acting as a "harder" acid (in the Pearson[27] sense) than the H_3Si group. More work is clearly needed to clarify the electronic effects affecting these systems.

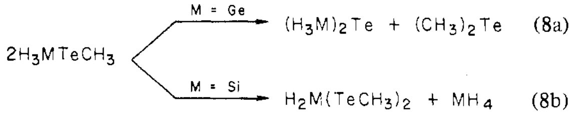
The tellurides are all sparingly volatile, pale yellow liquids with characteristic foul persistent odors. When pure, they are stable for long periods at room temperature in sealed glass tubes. Like the selenosilanes[3,4] the tellurosilanes are particularly labile to protolytic cleavage. With HBr, HI, H_2O, and CH_3OH the Si–Te bond is cleaved to give the corresponding halosilane, siloxane, and methoxysilane, respectively, and organotellurol byproduct (e.g., eq 6). This type of reaction

$$(CH_3)_3SiTeC_6H_5 + H_2O \rightarrow [(CH_3)_3Si]_2O + C_6H_5TeH \qquad (6)$$

may prove useful in the synthesis of arenetellurols which are not accessible by conventional methods.[24]

On prolonged storage or in contact with laser excitation (488 nm) the fully organo-substituted derivatives $(CH_3)_3MTeR$ show some disproportionation to the symmetric tellurides (e.g., eq 7). The parent hydrides, H_3MTeR, have alternative decomposition routes. (Methyltelluro)germane undergoes slow conversion to digermyl telluride and dimethyl telluride (eq 8a) while the competing condensation reaction seems to be more favorable for the silyl analogue (eq 8b). We have noted earlier

$$2(CH_3)_3SnTeCH_3 \rightarrow [(CH_3)_3Sn]_2Te + (CH_3)_2Te \qquad (7)$$



$$2H_3MTeCH_3 \xrightarrow{M = Ge} (H_3M)_2Te + (CH_3)_2Te \qquad (8a)$$
$$2H_3MTeCH_3 \xrightarrow{M = Si} H_2M(TeCH_3)_2 + MH_4 \qquad (8b)$$

that $(H_3Ge)_2Se$ decomposes to $H_2Ge(SeGeH_3)_2$, $HGe(SeGeH_3)_3$, and $Ge(SeGeH_3)_4$ with evolution of GeH_4[28] and that similar reactions occur with $H_3GeSeGeMe_3$ to give Me_3GeH and GeH_4 along with condensation products.[29]

^{1}H NMR Spectra. The organotellurol derivatives all give first-order spectra (Table I) consistent with free rotation about the C–M and M–Te bonds. The chemical shifts (δ) and coupling constants (*J*, Hz) correlate well with those of previously reported tellurosilanes[11] and -germanes[12] and provide the initial confirmation of the molecular species. The data obtained in the present work complete earlier studies of mixed

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Table II. Raman Spectra (cm^{-1}) of the Methyltelluro Species (Liquids)[a]

$H_3SiTeCH_3$[b]	$(CH_3)_3SiTeCH_3$[c]	$H_3GeTeCH_3$	$(CH_3)_3GeTeCH_3$	$(CH_3)_3SnTeCH_3$	tentative assignt
3014 w, dp	3018 w, dp	3015 w, dp	3013 sh, dp		$\nu(CH_3)$ asym (Te)
2935 m, p	2939 s, p	2937 m, p	2936 s, p	2938 m, p	sym (Te)
	2957 m, dp		2978 m, dp	2988 br, dp	asym (M)
	2900 vs, p		2908 vs, p	2919 m, p	sym (M)
2171 sh, dp		2081 sh			$\nu(MH_3)$ asym
2148 s, p		2070 s, p			sym
1417 vw, dp	1413 w, dp	1415 w, dp	1416 br, dp	1403 vw	$\delta(CH_3)$ asym (Te, M)
1221 w, p	1219 m, p	1222 w, p	1216 m, p	1214 m, p	sym (Te)
	1258 w, p		1240 m, p	1187 m, p	sym (M)
920 vw, dp		851 w			$\delta(MH_3)$ asym
871 vw, p		781 w			sym
	842 w	877 w	826 w	ca. 838 vw	$\rho(CH_3)$ (TeM)
	750 w		ca. 755 vw	ca. 770 vw	(M)
	697 w, dp		600 m, dp	522 m, dp	$\nu(MC)$ asym
	618 s, p		561 vs, p	507 s, p	sym
557 w		ca. 504 sh			$\rho(MH_3)$
513 s, p	514 vs, p	520 s, p	507 vs, p	[d]	$\nu(CTe)$
340 vs, p	326 vs, p	239 vs, p	226 vs, p	184 vs, p	$\nu(MTe)$
	231 m, dp		191 sh		$\delta(MC_3)$ asym
	187 vs, p		173 vs, p	138 s, p	sym
	ca. 165 sh		ca. 158 sh	109 sh	$\rho(MC_3)$
140 m		138 m	ca. 135 sh		$\delta(CTeM)$
			113 w		

[a] Key: w, weak; m, medium; s, strong; v, very; sh, shoulder; p, polarized; dp, depolarized. All spectra were recorded at room temperature. [b] Bands in the gas-phase IR spectrum were observed at $\nu(CH_3)$ 3026 w and, 2949 wm, $\nu(SiH_3)$ 2167 vs and 2155 vs, $\delta(CH_3)$ 1430 w and 1231 m, $\delta(SiH_3)$ 959 s and 885 vs, $\rho(CH_3)$ 865 w, and $\rho(SiH_3)$ 559 m. [c] Bands in the gas-phase IR spectrum were observed at $\nu(CH_3)$ 3027 w, 2967, and 2915 m, $\delta(CH_3)$ 1414 br, 1261 s, and 1231 m, $\rho(CH_3)$ 850 vs and 759 m, $\nu(SiC)$ 697 m, and 627 m, $\nu(SiTe)$ 344 m, and $\delta(SiC_3)$ 248 w. [d] Line contained in $\nu(SnC)$ envelope (see text).

group 4–group 6 systems of the types H_3MER and $(CH_3)_3MER$ {M = Si, Ge, [Sn]; E = O, S, Se, Te; R = CH_3, C_6H_5}. In the hydride series, H_3MER, the MH_3 α-proton shifts show typical trends apparently related to σ-bond induction by the group 6 element [E]: e.g., $\delta[H_3SiECH_3]$ 4.52 [O], 4.29 [S], 4.15 [Se], 3.89 [Te]; $\delta[H_3GeECH_3]$ 5.12 [O], 4.48 [S], 4.19 [Se], 3.75 [Te].[3b,9,10,30] Similar trends extend to the phenyl derivatives.[4,31] By comparison the CH_3 β-proton shifts in the $(CH_3)_3MER$ series show trends which are the reverse of those expected from the inductive effect of the chalcogen. These shifts appear to be related to the size of the substituent E and hence attributable[32] to second-order effects such as magnetic anisotropy and van der Waals or dispersion forces: e.g., $\delta[(CH_3)_3SiECH_3]$ 0.07 [O], 0.27 [S], 0.36 [Se], 0.56 [Te]; $\delta[(CH_3)_3GeECH_3]$ 0.27 [O], 0.51 [S], 0.55 [Se], 0.68 [Te].[3a,13,25,33]

Similar features are observed for the shifts of the CH_3Te protons. Thus for the series $(CH_3)_3MTeCH_3$ there is progressive deshielding of the CH_3Te protons with increasing atomic number of the group 6 element [M], viz., δ 1.49 [Si], 1.52 [Ge], 1.55 [Sn], 1.8 [Pb]. For series such as H_3MECH_3 and $(CH_3)_3MECH_3$ the effect of changing the chalcogen [E] on the CH_3E resonance is again apparently controlled by σ-bond induction by E: e.g., $\delta[H_3GeECH_3]$ 3.49 [O], 2.05 [S], 1.95 [Se], 1.73 [Te];[3b,9,10] $\delta[(CH_3)_3SiECH_3]$ 3.35 [O], 1.93 [S], 1.70 [Se], 1.73 [Te].[3a,13,32]

The aromatic resonances in the tellurophenols resemble those in the selenophenols;[4] viz., two envelopes are resolved, the low-field set (intensity 2) being attributable to meta protons and the high-field set (intensity 3) to ortho and para protons; and similar M–Te (p–d) π interactions are suggested by the similarity of the ortho/para proton shifts in the silicon, germanium, and tin species. Our studies of the selenium and tellurium derivatives now indicate that it is unlikely that the observation of a single aromatic resonance envelope in the thiophenols is an indicator of negligible aromatic ring–ligand interaction as proposed earlier.[31]

In both series satellites were observed due to proton coupling with the magnetic isotope of tellurium (^{125}Te, $I = {}^1/_2$, 6.99%), indicating that under the condiitons of study there is no rapid exchange of silyl, germyl, or stannyl groups. There is no obvious trend in the ^{29}Si–H coupling constants in the silyl species H_3SiECH_3: viz., 216.2 [O], 218.5 [S], 216.4 [Se], 219.9 [Te] Hz.

Raman Spectra. The observed frequencies for the methyltelluro and phenyltelluro species are given in Tables II and III. The assignments are made by assuming unhindered rotation about the C–Te bond and are based on earlier studies of the selenium analogues[3,4] and related tellurium-containing molecules, viz., $(H_3M)_2Te$ (M = C,[34] Si,[11] Ge[12]), $[(CH_3)_3M]_2Te$ (M = Si,[14] Ge,[16] Sn[16]), and CH_3TeH.[35]

In the (methyltelluro)silanes and -germanes (Table II) polarized lines in the low-frequency region of the spectrum are unambiguously assigned to skeletal stretching fundamentals: viz., $\nu(CTe)$ ca. 510 cm^{-1}; $\nu(CM)$ 697 and 618 [Si], 600 and 561 [Ge] cm^{-1}; $\nu(MTe)$ 326 [Si], 226 [Ge], 184 [Sn] cm^{-1}. In the tin species $(CH_3)_3SnTeCH_3$, $\nu(CTe)$ and $\nu(CSn)$ are accidentally degenerate and are both assigned to an unresolved envelope centered at 507 cm^{-1}. Other spectral lines are in typical regions expected for the functional groups present. A preliminary normal-coordinate analysis of the hydride species H_3MTeCH_3 (M = Si, Ge) indicates that there is little mixing of force constants for the skeletal modes.[36] The experimental frequencies are reproduced by using force constants of 1.533 and 1.576 mdyn Å^{-1} for Si–Te and Ge–Te stretchings, respectively.

By comparison, the phenyltelluro derivatives exhibit more complicated spectra, but following the approach used earlier

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Table III. Raman Spectra (cm^{-1}) of the Phenyltelluro Species (Liquids)[a]

$(CH_3)_3SiTeC_6H_5$	$H_3GeTeC_6H_5$	$(CH_3)_3GeTeC_6H_5$	$(CH_3)_3SnTeC_6H_5$	tentative assignt[b]
2957 m, dp		2977 m, dp	2988 w, dp	$\nu(CH_3)$ asym
2896 vs, p		2905 s, p	2915 s, p	sym
	2079 sh, dp			$\nu(GeH_3)$ asym
	2065 vs, p			sym
ca. 1410 vvw		1402 vw, dp	1434 vw	$\delta(CH_3)$ asym
1252 wm, p		1239 m, p	1188 m, p	sym
1055 w, p	1059 w, p	1060 w, p	1055 w, p	X-sens (*q*)
839 w, p		819 w	764 vw	$\rho(CH_3)$
755 w, dp		742 w	742 vw	
	856 w, dp			$\delta(GeH_3)$
	775 w			
650 m, p	656 m, p	653 m, p	647 wm, p	X-sens (*r*)
	ca. 510 w			$\rho(GeH_3)$
693 w, dp		604 m, dp	521 m, dp	$\nu(MC)$ asym
617 m, p		564 s, p	500 vs, p	sym
257 s, p[c]	257 m	258 m	248 m	X-sens (*t*)
327 vs, p	238 vs, p[d]	233 vs, p[d]	177 s, p[e]	$\nu(MTe)$
227 m, dp[d]				$\delta_{asym}(MC_3)$
	209 s, p		138 s, p	$\delta(CTeM)$
188 s, p[e]		172 vs, p[e]	156 s, p	$\delta_{sym}(MC_3)$
	177 m, dp			X-sens (*x*)
152 m, dp		137 m, dp	100 ms, dp	$\rho(MC_3)$

[a] See footnote to Table II. Lines attributable to the substituent-insensitive phenyl modes were observed at ν(CH) 3052 m, p (*z*), ν(CC) 1573 m, dp (*k*), 1475 vw (*m*), 1440 vw (*n*), and 1330 vw (*o*), β(CH) 1186 w, p (*a*), 1154 w, dp (*c*), 1017 m, p (*b*), and ring 998 vs, p (*p*), γ(CH) 901 (vw) (*i*), 840 (vw) (*g*), and 742 (vw) (*f*), α(CCC) 617 w, dp (*s*), ϕ(CC) 399 vvw (*w*), and combinations 3143 w, p (2*k*), 1611 (*s* + *p*), 1380 (2ν), and 1285 w, p (?). [b] Italic letters in parentheses denote Whiffen notation for monosubstituted benzenes.[38] [c] Envelope may contain δ(CTeSi). [d] Envelope may contain X-sens (*u*). [e] Envelope may contain X-sens (*x*).

for the selenium analogues[4] the 24 substituent-insensitive phenyl ring vibrations may be correlated with the corresponding degenerate modes in benzene.[37] The 6 substituent-sensitive modes (X-sens in Table III) may be assigned by comparison with the spectra of monosubstituted benzenes.[38] As would be expected these frequencies are close to those reported[38] for C_6H_5I. Frequencies arising from the MH_3 and $(CH_3)_3M$ groups are observed in similar regions for both methyltelluro and phenyltelluro series, the spectra being consistent with the expected local C_{3v} symmetry at the group 4 atom M. The torsional modes were not observed for either series.

Experimental Section

Apparatus. The manipulation of all volatile/air-sensitive compounds was carried out in a greaseless Pyrex-glass vacuum/inert atmosphere system of conventional design.[39] The use of Teflon-in-glass high-vacuum valves and minimum quantities of silicone-type lubricant for detachable glass joints in the apparatus reduced considerably the usual contamination problems[24] associated with volatile tellurium compounds. The allied spectroscopic techniques were as described previously.[4]

Materials. Silyl and germyl halides were prepared by standard methods[40] and their purity established spectroscopically. Other materials were reagent grade of commercial origin. The silyl and germyl groups in the tellurides were analyzed by reaction with hydrogen iodide.[31]

Preparation of Silyl Derivatives of Methane- and Benzenetellurols. (a) Reaction of Tellurium with Organolithium Reagents. In a typical experiment powdered tellurium (1.6651 g, 13.05 mmol) and methyllithium (ca. 16 mmol in diethyl ether) were allowed to react in dry tetrahydrofuran (THF) (15 mL) as described for $LiSeCH_3$.[3a] The solvents were removed in vacuo after ca. 20 h, leaving a yellow-brown crystalline residue (ca. 2.9 g) in the reaction vessel. Traces of $(CH_3)_2Te$ were identified[34] in the volatile material in some reactions. Attempts to recrystallize the crude lithium methanetellurolate, $LiTeCH_3$, led to the formation of $(CH_3Te)_2$ and other unidentified tellurium-containing species resulting from solvent cleavage. The crude $LiTeCH_3$ also contained residual THF which could not be removed by prolonged pumping in high vacuum, suggesting possible ether coordination in the solid state. Fresh solutions of $LiTeCH_3$ in THF showed ν(CTe) at ca. 505 cm^{-1} in the Raman spectrum and $\delta(CH_3)$ at 1.7 in the ^1H NMR spectrum. Treatment of a sample of $LiTeCH_3$ with HBr did not give CH_3TeH. Noncondensable gas was formed, and the NMR spectrum of the volatile products indicated the formation of $(CH_3Te)_2$ [$\delta(CH_3)$ 2.69,[41] ν(TeTe) 190 cm^{-1} [42]], with additional weak resonances attributable to THF and unidentified higher telluroorganics. A similar reaction between tellurium (2.0813 g, 16.31 mmol) and phenyllithium (ca. 20 mmol in benzene/diethyl ether) led to the formation of lithium benzenetellurolate, $LiTeC_6H_5$ (ca. 3.9 g), as reported by other workers.[22] This material was used without further purification.

(b) Reaction of Trimethylchlorosilane with Lithium Organotellurolates. Treatment of crude $LiTeCH_3$ (ca. 2.3 g) with $(CH_3)_3SiCl$ (ca. 15.7 mmol) at 25 °C produced a vigorous exothermic reaction during which the mixture turned from brown to off-white. After 1 h the volatile material was pumped from the reactor and bulk fractionated by using traps held at −45 and −196 °C. The contents of the former were recycled through further traps at −23, −45, and −196 °C. Pure samples of trimethyl(methyltelluro)silane, $(CH_3)_3SiTeCH_3$ (9.64 mmol, 64%; vapor pressure ca. 3 torr at 25 °C; *m*/*e* 210–218, $P^+ = [C_4H_{12}SiTe]^+$. Anal. Calcd for $C_4H_{12}SiTe$: Si, 13.01. Found: Si (as $(CH_3)_3SiI$), 12.7.), were recovered from the −45 °C trap, small quantities of $(CH_3)_4Si$, $[(CH_3)_3Si]_2O$, THF, and unchanged $(CH_3)_3SiCl$ in the −196 °C traps, and dimethyl ditelluride and traces of the symmetrical species $[(CH_3)_3Si]_2Te$ (^1H NMR resonances at δ 2.7 and 0.60, respectively) in the −23 °C trap, both accounting for <10% of the tellurium used in the reaction.

A similar reaction between $LiTeC_6H_5$ (ca. 3.9 g) and $(CH_3)_3SiCl$ (ca. 25 mmol) gave trimethyl(phenyltelluro)silane, $(CH_3)_3SiTeC_6H_5$ (10.7 mmol, 66%; vapor pressure < torr at 25 °C; *m*/*e* 257–265, $P^+ - 15 = [C_8H_{11}SeTe]^+$; $\delta(CH_3)$ 0.47. Anal. Calcd for $C_9H_{14}SiTe$: Si, 10.11. Found: Si (as $(CH_3)_3SiI$), 9.1.), which was volatile at 80 °C in vacuo and small amounts of $(C_6H_5Te)_2$ and $[(CH_3)_3Si]_2Te$, together accounting for ca. 14% of the tellurium used in the reaction. The presence of LiC_6H_5 in the crude $LiTeC_6H_5$ was confirmed by

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the recovery of $(CH_3)_3SiC_6H_5$ (ca. 3 mmol; $\delta(CH_3)$ 0.08).

Cleavage of the tellurosilanes with selected protic species was similar to that observed[3a,4] for the selenosilanes; viz., $(CH_3)_3SiTeCH_3$ and CH_3OH gave $(CH_3)_3SiOCH_3$ (95%), $(CH_3)_3SiTeCH_3$ and HBr gave $(CH_3)_3SiBr$ (91%), and $(CH_3)_3SiTeC_6H_5$ and H_2O gave $[(CH_3)_3Si]_2O$ (92%). The tellurol byproducts were not estimated due to their ready decomposition to the corresponding ditellurides, hydrogen, and in some cases metallic tellurium. Benzenetellurol, C_6H_5TeH, was observed qualitatively in the NMR spectrum of the hydrolysis products of $(CH_3)_3SiTeC_6H_5$ [δ(TeH) −2.4 (J(TeH) = 49.5 Hz)].

(c) Reaction of Bromosilane with Lithium Organotellurolates. Treatment of a diethyl ether slurry of crude $LiTeCH_3$ (ca. 0.4 g) with H_3SiBr (ca. 1 mmol) at −78 °C gave $(H_3Si)_2Te$ (ca. 20%) and traces of silane as the only volatile silicon species. Similarly, no (organotelluro)silane was recovered from the reaction of H_3SiBr and $LiTeC_6H_5$.

Exchange Reactions of Trimethyl(organotelluro)silanes. (a) Reactions with Fluorogermanes. In a typical experiment fluorogermane (1.60 mmol) and $(CH_3)_3SiTeCH_3$ (1.31 mmol) were allowed to react in an ampule (10 mL) at 25 °C (15 min). The products were fractionated by using baths at −23 and −196 °C. The former bath retained pure $H_3GeTeCH_3$ (1.22 mmol, 93%, *m/e* 212–224, $P^+ = [CH_6GeTe]^+$. Anal. Calcd for CH_6GeTe: Ge, 33.3. Found: Ge (as GeH_3I), 30.4.); the latter bath contained a mixture of $(CH_3)_3SiF$ (ca. 1.2 mmol) and unchanged H_3GeF (ca. 0.35 mmol), identified by ^1H NMR spectra.[43] In similar experiments $H_3GeTeC_6H_5$ (91%), $(CH_3)_3GeTeCH_3$ (87%), and $(CH_3)_3GeTeC_6H_5$ (87%) were obtained from a deficit of the (organotelluro)silane with the corresponding fluorogermane. With use of $(CH_3)_2GeCl_2$ (1.18 mmol) with excess of $(CH_3)_3SiTeCH_3$ (3.09 mmol) the disubstituted species $(CH_3)_2Ge(TeCH_3)_2$ [1.05 mmol, 89%; $\delta(CH_3)$ 1.21, 1.67] was isolated as a nonvolatile orange oil. Raman lines assigned as skeletal modes were observed as follows (cm^{-1}): 599 (w, dp) and 567 (m, p), $\nu(GeC_2)$; 514 (s, p), ν(CTe); 243 (m, dp) and 208 (vs, p), $\nu(GeTe_2)$; 192 (sh), 171 (vs, p), and 61 (vs, p), $\delta(GeTe_2)$. In a control experiment a 1:1 mixture of $(CH_3)_2GeCl_2$ and $(CH_3)_3SiTeCH_3$ gave only weak resonances at 1.21 and 1.67 ppm attributable to $(CH_3)_2Ge(TeCH_3)_2$ and strong additional lines at 1.30 and 1.74 ppm (integrated intensities 2:1) which we assign to the mixed chloro(methyltelluro) species $(CH_3)_2Ge(Cl)TeCH_3$. As found for other silicon- and germanium-group 6 compounds,[29,44] the value of $K_{25\,°C}$ of 1.6 for the equilibrium mixture is significantly less than the statistical random value of 0.25.

(b) Reactions with Chlorostannanes. Typically $(CH_3)_3SnCl$ (1.79 mmol) reacted smoothly with $(CH_3)_3SiTeCH_3$ (2.05 mmol) at 25 °C (15 min) to give $(CH_3)_3SnTeCH_3$ (1.69 mmol, 94%) as an involatile yellow oil. The volatile material contained only $(CH_3)_3SiCl$ and unchanged $(CH_3)_3SnCl$ as indicated by ^1H NMR spectra. Similarly $(CH_3)_3SnCl$ and $(CH_3)_3SiTeC_6H_5$ gave $(CH_3)_3SnTeC_6H_5$ (89%).

(c) Reactions with Halosilanes. Bromosilane (0.66 mmol) and a deficit of $(CH_3)_3SiTeCH_3$ (0.42 mmol) were sealed in a semimicro NMR tube. The NMR spectrum showed that no reaction had occurred after 5 min. After 15 min at 60 °C the NMR spectrum showed additional resonances in the ratio 1:1 at 3.8 and 1.6 ppm assigned to $H_3SiTeCH_3$ and a strong resonance at 0.57 ppm (intensity 3) assigned to $(CH_3)_3SiBr$, corresponding to ca. 10% reaction. After 10 h at 60 °C no $(CH_3)_3SiTeCH_3$ remained and the tube was reopened on the vacuum line and the products were fractionated by using traps held at −45 and −196 °C. The latter trap contained unchanged H_3SiBr and $(CH_3)_3SiBr$ (molar ratio ca. 1:2) and the former trap (methyltelluro)silane, $H_3SiTeCH_3$ (0.38 mmol, 90%; *m/e* 170–176, $P^+ = [CH_nSiTe]^+$). A similar qualitative experiment using H_3SiI and $(CH_3)_3SiTeCH_3$ showed complete exchange to $H_3SiTeCH_3$ and $(CH_3)_3SiI$ after 5 h at 60 °C. Cleavage of $H_3SiTeCH_3$ with HI gave H_3SiI (87%). The exchange reaction between $(CH_3)_3SiTeC_6H_5$ and iodosilane led to the formation of $H_3SiTeC_6H_5$ (78%).

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Registry No. $H_3SiTeCH_3$, 34117-15-2; $H_2Si(TeCH_3)_2$, 73296-28-3; $H_3SiTeC_6H_5$, 73296-29-4; $H_2Si(TeC_6H_5)_2$, 73296-30-7; $(CH_3)_3SiTeCH_3$, 34117-12-9; $(CH_3)_3SiTeC_6H_5$, 73296-31-8; $H_3GeTeCH_3$, 34117-16-3; $H_3GeTeC_6H_5$, 73296-32-9; $(CH_3)_3GeTeCH_3$, 34117-13-0; $(CH_3)_3GeTeC_6H_5$, 73296-33-0; $(CH_3)_2Ge(TeCH_3)_2$, 73296-34-1; $(CH_3)_3SnTeCH_3$, 34117-14-1; $(CH_3)_3SnTeC_6H_5$, 73296-35-2; $(CH_3)_3PbTeCH_3$, 73296-36-3; $LiTeCH_3$, 60919-62-2; $LiTeC_6H_5$, 52251-60-2; $(CH_3)_3SiCl$, 75-77-4; $(CH_3)_3SiBr$, 2857-97-8; $[(CH_3)_3Si]_2O$, 107-46-0; C_6H_5TeH, 69577-06-6; $(CH_3)_3SiOCH_3$, 1825-61-2; H_3SiBr, 13465-73-1; $(H_3Si)_2Te$, 19415-73-7; H_3GeF, 13537-30-9; $(CH_3)_3GeF$, 661-37-0; $(CH_3)_2GeCl_2$, 1529-48-2; $(CH_3)_2Ge(Cl)TeCH_3$, 73296-37-4; $(CH_3)_3SnCl$, 1066-45-1; H_3SiI, 13598-42-0.

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Binuclear Ferric Porphyrins Bridged by the Dianions of Hydroquinones

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Binuclear high-spin ferric porphyrin complexes containing hydroquinone dianion bridging moieties are formed by the reaction of Fe^{II}(TPP) (TPP is the dianion of *meso*-tetraphenylporphyrin) with several *p*-quinones including *p*-benzoquinone, tetrachloro-*p*-benzoquinone, tetrafluoro-*p*-benzoquinone, tetrabromo-*p*-benzoquinone, duroquinone, and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone. Two *o*-quinones, tetrachloro-*o*-benzoquinone and tetrabromo-*o*-benzoquinone, also react with Fe^{II}(TPP) to form binuclear ferric complexes with catechol dianion bridging moieties. In the case of the hydroquinone complexes, C–O IR stretching bands are identified in the range of 1431–1483 cm^{-1} to support the presence of a dianionic hydroquinone bridging unit. ^{57}Fe Mössbauer data indicate that the iron ions in both types of complexes are in the high-spin ferric state ($S = {}^5/_2$). The [Fe(TPP)]$_2$(hydroquinone) complexes exhibit weak antiferromagnetic exchange interactions ($\hat{H} = -2J\hat{S}_1\cdot\hat{S}_2$) with J values ranging from −3.6 to −15.5 cm^{-1}. The tetrachlorocatecholate complex [Fe(TPP)]$_2$(Cl$_4$cat) also exhibits a weak interaction with $J = -2.2$ cm^{-1}.

Introduction

While it has been established that quinones play an integral role in electron-transport chains, interacting perhaps with iron metalloproteins,[2,3] only two studies dealing with the interaction of metalloporphyrins with quinones have appeared in the literature. Hill, Williams, and co-workers reported the results

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