mp >120 °C dec (5.14 g, 90%); ^{1}H NMR (C_6D_6) δ 7.34–7.13 (br s, 2 H), 6.60–6.37 (m, 2 H), 1.40 (s, 6 H), 1.33 (br s, 6 H), 1.23 (s, 6 H); ^{13}C NMR δ 212.6 (t, J = 3.2 Hz, CO), 147.4 (t, J = 30.2 Hz), 129.0 (t, J = 8.4 Hz), 125.1 (t, J = 1.4 Hz), 37.0 (t, J = 8.5 Hz), 29.0 (s); IR (THF) ν_{CO} 2040 (s), 2003 (s), 1963 (b-s), 1924 (w) cm^{-1}; MS, *m/e* 532 (M$^+$).

Anal. Calcd for $C_{20}H_{22}Fe_2O_2P_2$: C, 45.15; H, 4.17. Found: C, 45.37; H, 4.33.

[μ-*P*-Phenyl-*P′*-*tert*-butyl-1,2-phenylenebis(phosphido)-μ-*P*,*P′*]hexacarbonyldiiron (13). Nonacarbonyldiiron (14.10 g, 38.8 mmol) was added as a solid to a solution of 1-(phenylphosphino)-2-(*tert*-butylphosphino)benzene (4.08 g, 14.9 mmol) in benzene (200 mL) under nitrogen, and the mixture was heated at reflux for 43 h. The dark blackish orange solution was concentrated and passed through alumina using hexane, to afford an orange powder, which was crystallized from hexane to give **13** (4.27 g, 52%) as orange crystals: mp >120 °C dec; ^{1}H NMR (C_6D_6) δ 7.83–7.47 (m, 2 H), 7.33–6.95 (5 H), 6.53–6.20 (m, 2 H), 1.33 (d, J_{P-H} = 17 Hz, 9 H); ^{13}C NMR (partial, C_6D_6) δ 205.05 (dd, J_{P1-C} = 4.2 Hz, J_{P2-C} = 2.9 Hz, CO), 30.48 (dd, J_{P1-C} = 7.1 Hz, J_{P2-C} = 9.0 Hz, $C(CH_3)_3$) 21.70 (d, J_{P-C} = 3.1 Hz, $C(CH_3)_3$); IR (THF) ν_{CO} 2048 (s), 2012 (s), 1979 (s), 1958 (s), 1929 (m) cm^{-1}; MS, *m/e* 552 (M$^+$).

Anal. Calcd for $C_{22}H_{18}Fe_2O_2P_2$: C, 47.87; H, 3.29. Found: C, 47.71; H, 3.40.

[μ-1,2-Phenylenebis[(2,4,6-trimethylphenyl)phosphido]-μ-*P*,*P′*]hexacarbonyldiiron (14). Nonacarbonyldiiron (6.10 g, 16.7 mmol) was added as a solid to a solution of 1,2-bis[(2,4,6-trimethylphenyl)phosphino]benzene (2.53 g, 6.69 mmol) in benzene (200 mL) under nitrogen and the mixture heated at reflux for 5 h. The dark blackish orange solution was concentrated and passed through alumina (hexane) to afford an orange powder which was crystallized from dichloromethane to give **14** (2.37 g, 54%) as an orange microcrystalline solid: mp >120 °C dec; ^{1}H NMR (C_6D_6) 7.20 (br s, 6 H), 6.76 (m, 2 H), 2.73 (s, 12 H), 1.98 (s, 6 H); ^{13}C NMR (partial, C_6D_6) δ 203.62 (s, CO), 21.82 (s, CH_3), 12.84 (s, CH_3); IR (THF) ν_{CO} 2068 (s), 2010 (s), 1982 (s), 1966 (s), 1952 (m) cm^{-1}; MS, *m/e* 656 (M$^+$).

Anal. Calcd for $C_{30}H_{26}Fe_2O_2P_2$: C, 54.91; H, 3.99. Found: C, 54.87; H, 4.19.

Acknowledgment. Financial support from the National Science Foundation (Grant CHE81-13090 and CHE 84-19282) and the Robert A. Welch Foundation (Grant No. F573) is gratefully acknowledged.

Registry No. **2**, 80510-04-9; **4**, 82495-67-8; **5a**·$MgCl_2$, 101653-36-5; **5b**, 101653-20-7; **5c**, 101653-32-1; **6a**, 101653-21-8; **6b**, 101653-22-9; **6d**, 38023-29-9; *meso*-**6e**, 72091-02-2; *al*-**6e**, 72091-01-1; **6f**, 13991-08-7; **6g**, 101653-23-0; **8a**, 101653-31-0; **8b**, 101653-35-4; *meso*-**10a**, 101653-24-1; *al*-**10a**, 101653-25-2; *meso*-**10b**, 101653-26-3; *al*-**10b**, 101653-27-4; *meso*-**10b** (bis(sulfide)), 101653-29-6; *al*-**10b** (bis(sulfide)), 101653-30-9; **11a**, 101653-33-2; **11b**, 101653-34-3; **12**, 101653-37-6; **13**, 101653-38-7; **14**, 101653-39-8; $Fe_2(CO)_9$, 15321-51-4; phosgene, 75-44-5; *tert*-butylmagnesium chloride, 677-22-5; methylmagnesium chloride, 676-58-4; phenylmagnesium bromide, 100-58-3; mesitylmagnesium bromide, 2633-66-1.

A ^{125}Te Mössbauer Study of Complexes Containing Metal–Tellurium Multiple Bonds

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The ^{125}Te Mössbauer isomer shifts, δ, and quadrupole splittings, Δ, have been measured at 4.2 K for the following compounds: (μ-Te)[V(CO)$_3$diphos]$_2$, where diphos = ethylenebis(diphenylphosphane) (δ = 0.17, Δ < 3.8 mm s^{-1}), (μ_3-Te)[Mn(CO)$_2$(η^5-C_5H_5)]$_3$ (δ = 0.18, Δ = 5.6 mm s^{-1}), (μ-Te)[Mn(CO)$_2$(η^5-C_5Me_5)]$_2$ (δ = 0.15, Δ = 6.5 mm s^{-1}), (μ-η^2-TeCH$_2$)[Mn(CO)$_2$(η^5-C_5Me_5)]$_2$ (δ = 0.20, Δ = 6.3 mm s^{-1}), and (μ-Te)-[Cr(CO)$_3$(η^5-C_5H_5)]$_2$ (δ = 0.38, Δ = 8.4 mm s^{-1}). The isomer shifts are essentially the same regardless of whether the tellurium is acting as a six-, four-, or two-electron donor. The very small quadrupole splittings of the first three listed compounds are evidence of multiple-bond character in the tellurium–metal bonds.

Introduction

Recently there has been considerable interest in transition metal complexes containing a ligand-free chalcogen as a bridging element.[1] Examples have been found[2-4] where, on the basis of X-ray structural determination of the metal–chalcogen bond length, the presence of a multiple bond, M=E or M≡E, has been invoked. It was of interest to explore the nature of the bonding in the tellurium analogues of these complexes using ^{125}Te Mössbauer spectroscopy.

The molecules that have been investigated are illustrated in Figure 1, where only the geometry about the tellurium is shown.

In (μ-Te)[V(CO)$_3$diphos]$_2$, where diphos = ethylenebis(diphenylphosphane), the V–Te–V linkage is presumably linear in analogy with the sulfur compound where the crystal structure has been determined.[2] In the latter the V–S bond length was found to be 217.2 pm in comparison with a V–S single bond length of 230 pm. This suggests the presence of V–E multiple-bond character, with the chalcogen acting as a six-electron donor.

$$\text{diphos(CO)}_3\text{V}\equiv\text{E}\equiv\text{V(CO)}_3\text{diphos}$$

$$\text{diphos(CO)}_3\text{V}\leftrightharpoons\text{E}\rightleftharpoons\text{V(CO)}_3\text{diphos}$$

In (μ_3-Te)[Mn(CO)$_2$(η^5-C_5H_5)]$_3$ the X-ray crystal structure shows the coordination about the tellurium to be trigonal planar,[3] the tellurium atom lying 3.4 (1) pm out of the Mn_3 plane. The Mn–Te bond lengths of 247 and 251 pm compare with an anticipated single bond length of 270 pm.[4] The bonding may be described in terms of three double bonds between tellurium and manganese, although some contribution from Te→Mn bonds cannot be ruled out. The tellurium is again serving as a six-electron donor.

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(1) Herrmann, W. A.; Rohrmann, J.; Zeigler, M. L.; Zarn, T. *J. Organomet. Chem.* **1984**, *273*, 221–232.

(2) Schiemann, J.; Hübener, P.; Weiss, E. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 980–981.

(3) Herberhold, M.; Reinar, D.; Neugebauer, D. *Angew. Chem.*, int. ed. Engl. **1983**, *22*, 59–60.

(4) Herrmann, W. A.; Hecht, C.; Ziegler, M. L.; Balbach, B. *J. Chem. Soc., Chem. Commun.* **1984**, 686–687.

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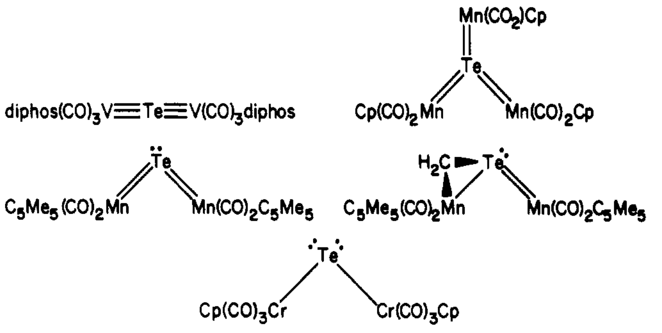

Figure 1.

Table I. ^{125}Mössbauer Parameters (mm s^{-1})

	δ[a]	Δ[b]	Γ_{av}
(μ-Te)[V(CO)$_3$diphos]$_2$[c]	0.17	3.8	6.2
(μ-Te)[V(CO)$_3$diphos]$_2$[c]	0.17	3.8	6.2
	(0.16	0	10.0)
(μ_3-Te)[Mn(CO)$_2$(η^5-C$_5$H$_5$)]$_3$	0.18	5.6	5.6
(μ_3-Te)[Mn(CO)$_2$(η^5-MeC$_5$H$_4$)]$_3$	0.06	5.4	5.9
(μ-Te)[Mn(CO)$_2$(η^5-C$_5$Me$_5$)]$_2$	0.15	6.5	6.5
(μ,η^2-TeCH$_2$)[Mn(CO)$_2$(η^5-C$_5$Me$_5$)]$_2$	0.20	6.3	5.5
(μ-Te)[Cr(CO)$_3$(η^5-C$_5$H$_5$)]$_2$	0.38	8.4	5.2

[a] δ with respect to I/Cu, the source and absorber at 4.2 K. Error in $\delta \pm 0.08$ mm s^{-1}. [b] Error in $\Delta \pm 0.1$ mm s^{-1}. [c] The spectrum of this compound could be fitted to a broad single line, $\Gamma = 10.0$ mm s^{-1}. However, this very broad line width suggests the presence of a doublet.

The X-ray crystal structure of (μ-Te)[Mn(CO)$_2$(η^5-C$_5$Me$_5$)]$_2$ shows this molecule[4] to contain a bent Mn–Te–Mn framework with a bond angle of 123.8° and a Mn–Te bond length of 245.9 pm, somewhat shorter than that observed in (μ_3-Te)[Mn(CO)$_2$(η^5-C$_5$H$_5$)]$_3$. The tellurium is now acting as a four-electron donor, and presumably there is a lone pair occupying the site of the third ligand in the η^5-C$_5$H$_5$ derivative.

On reacting (μ-Te)[Mn(CO)$_2$(η^5-C$_5$Me$_5$)]$_2$ with CH$_2$N$_2$ the addition of CH$_2$ across one Mn–Te bond occurs.[4] In the product the coordination about tellurium will be trigonal, the second Mn–Te bond lying out of the plane of the Mn–Te–CH$_2$ ring in analogy with the coordination about the chalcogen in the related selenium compound (μ-η^2-SeCH$_2$)[Cr(CO)$_3$(η^5-C$_5$H$_5$)]$_2$.

Finally, the (μ-Te)[Cr(CO)$_3$(η^5-C$_5$H$_5$)]$_2$ complex contains[1] a bent Cr–Te–Cr framework with a bond angle of 117.2° and Cr–Te bond lengths of 281.4 and 279.9 pm, indicating the presence of single bonds. Here, tellurium will possess two lone pairs and is acting as a two-electron donor.

Results and Discussion

The tellurium-125 Mössbauer data for these complexes are given in Table I.

The Mössbauer isomer shifts are determined by the s-electron density at the nucleus $|\Psi_s(0)|^2$. For ^{125}Te more positive isomer shifts correspond to a large s-electron density at the nucleus and more negative isomer shifts a small s-electron density.[5] The removal of tellurium 5p electrons in bonding is taken to increase $|\Psi_s(0)|^2$ by deshielding the 5s electrons from the nucleus, while removal of 5s electrons will clearly decrease $|\Psi_s(0)|^2$; the latter has a more pronounced effect than the former. The isomer shifts for tellurium range from −1.0 mm s^{-1} for Te(VI) species such as H$_6$TeO$_6$ to +1.6 mm s^{-1} for TeCl$_6^{2-}$. In the former $|\Psi_s(0)|^2$ is small, the removal of 5s electrons having the dominant effect, while in the latter the bonding appears to occur through 3c–2e bonds involving only the tellurium p orbitals and $|\Psi_s(0)|^2$ is large.

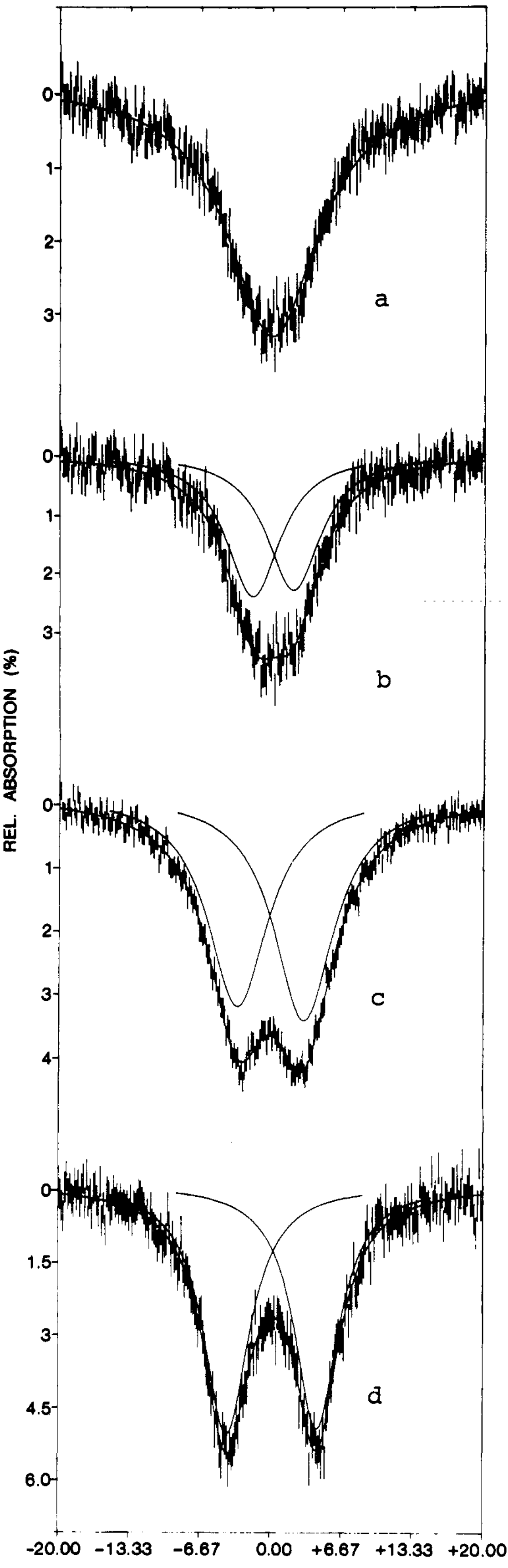

Figure 2. The ^{125}Te Mössbauer spectrum at 4.2 K of (μ-Te)[V(CO)$_3$diphos]$_2$ computed (a) as a single line and (b) as a doublet and the spectra of (c) (μ-Te)[Mn(CO)$_2$(η^5-C$_5$H$_5$)]$_3$ and (d) (μ-Te)[Cr(CO)$_3$(η^5-C$_5$H$_5$)]$_2$.

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(5) Ruby, S. L.; Shenoy, G. K. In *Mössbauer Isomer Shifts*; Shenoy, G. K., Wagner, F. E., Eds.; North Holland: New York, 1978; pp 617–659.

The isomer shifts for tellurium in the complexes studied (Table I) are all surprisingly very similar and are small and positive with respect to the reference standard. The shifts are similar to those previously observed for organotellurides.[6] It is apparent that there is no clear delineation on the basis of isomer shift between tellurium as a six-, four-, or two-electron donor in these systems. The s-electron density at the nucleus is comparable in all cases, and this must reflect the fact that the removal of 5s- and 5p-electron densities have opposite effects on the sign of δ. These must offset one another leading to a net nuclear s-electron density that remains roughly constant.

The isomer shift of $(\mu\text{-Te})[Cr(CO)_3(\eta^5\text{-}C_5H_5)]_2$ is somewhat more positive than that of the other complexes, and this is consistent with greater p character in the bonding to tellurium in this case. Alternatively the presence of two lone pairs with significant s character could explain the somewhat greater s-electron density at the tellurium nucleus.

The tellurium-125 quadrupole splittings are determined by the imbalance in the 5p-orbital populations.[6] It has been estimated that an imbalance of one 5p electron gives rise to a unit quadrupole splitting of ca. 12 mm s^{-1}.[7] Since the quadrupole coupling constants are proportional to $\langle r^{-3}\rangle$, the inverse cube of the expectation value of the radius for the orbital concerned, it is generally assumed that 5d orbitals do not contribute significantly to Δ since $\langle r^{-3}(5d)\rangle$ will be much smaller than $\langle r^{-3}(5p)\rangle$.

Quadrupole splittings in tellurium compounds and ions[6] range from 0 in octahedral species such as $Te(OH)_6$ and $TeCl_6^{2-}$ through 6–7 mm s^{-1} in the trigonal telluronium cations R_3Te^+ to 15–17 mm s^{-1} in the square-planar TeL_4^{2+} cations, where L, for example, is thiourea. Thus, if the three tellurium 5p orbitals have the same populations, as in octahedral molecules or ions, then Δ is zero. In square-planar Te(II) complexes, where there is a very considerable imbalance between the population of the $5p_z$ orbital directed out of the bonding plane and the $5p_x$ and $5p_y$ orbitals in the bonding plane, Δ is very large.

In contrast with the isomer shifts, the Mössbauer quadrupole splittings vary significantly in magnitude for the different complexes of Table I. In $(\mu\text{-Te})[Cr(CO)_3(\eta^5\text{-}C_5H_5)]_2$ the quadrupole splitting is 8.4 mm s^{-1}. Here an electron count confirms that tellurium will have two lone pairs, the tellurium acting as a two-electron donor, and the environment about tellurium may be viewed as distorted tetrahedral. The relatively large quadrupole splitting must then result from the considerable imbalance in p-electron density in the orbitals corresponding to the two lone pairs and the two Te–Cr bonds.

At the other extreme, $(\mu\text{-Te})[V(CO)_3\text{diphos}]_2$ has a splitting no greater than 3.8 mm s^{-1}. Assuming that the geometry about tellurium is indeed linear, this value of Δ is remarkably small and can only be explained by the presence of considerable V–Te multiple-bond character. The *z* axis in this molecule would be viewed as lying along the V–Te–V linkage. The similar populations of the tellurium $5p_z$, $5p_y$, and $5p_x$ orbitals, as evidenced by the very small Δ, are consistent with extensive $p\pi \rightarrow d\pi$ bonding from tellurium to vanadium involving the tellurium $5p_x$ and $5p_y$ orbitals. An attempt is underway to determine the X-ray crystal structure of this compound and to confirm that the V–Te–V linkage is indeed linear.

Similarly, in $(\mu_3\text{-Te})[Mn(CO)_2(\eta^5\text{-}C_5H_5)]_3$ and the methyl derivative the essentially planar $TeMn_3$ framework again yields a surprisingly small quadrupole splitting of ca. 5.5 mm s^{-1}, consistent with the presence of only a small imbalance in orbital populations between the $5p_z$ orbital, which here will be directed out of the bonding plane, and the in-plane $5p_x$ and $5p_y$ orbitals. This again points to the presence of significant Mn–Te multiple-bond character. The fact that the p-orbital imbalance here is somewhat greater than that in $(\mu\text{-Te})[V(CO)_3\text{diphos}]_2$ is consistent with less multiple-bond character in the Te—Mn_3 framework than that in V$\equiv$Te$\equiv$V.

For $(\mu\text{-Te})[Mn(CO)_2(\eta^5\text{-}C_5Me_5)]_2$ only two metal atoms are coordinated to the tellurium in a bent (123.8°) arrangement, and, as noted above, there is presumably a lone pair on tellurium in the $TeMn_2$ plane. The greater p-electron density in the $TeMn_2$ plane leads to a greater p-orbital imbalance and a somewhat larger quadrupole splitting, 6.5 mm s^{-1}, than that observed in the cyclopentadienyl derivatives.

On reacting $(\mu\text{-Te})[Mn(CO)_2(\eta^5\text{-}C_5Me_5)]_2$ with CH_2N_2, the resulting compound gave a chemical analysis and IR spectrum consistent with the expected product $(\mu\text{-}\eta^2\text{-}TeCH_2)[Mn(CO)_2(\eta^5\text{-}C_5Me_5)]_2$. However, the Mössbauer parameters did not change significantly. The environment about the tellurium is now very different, with two Te–Mn bonds and a Te–CH_2 bond disposed trigonally about the tellurium and a lone pair occupying a fourth coordination site. The net effect on the p-orbital imbalance about tellurium appears to be that it remains roughly constant, since the quadrupole splitting does not change significantly. The magnitude of Δ observed here is similar to that found in other tellurium compounds where the environment about tellurium is trigonal.

In summary, the Mössbauer isomer shifts provide relatively little information about the bonding to tellurium in these compounds, the net nuclear s-electron density being very similar in all cases regardless of whether tellurium is acting as a two-, four-, or six-electron electron donor. The quadrupole splittings, however, show significant differences, and the relatively small Δ values observed for linear $(\mu\text{-Te})[V(CO)_3\text{diphos}]_2$ and planar $(\mu_3\text{-Te})(Mn(CO)_2(\eta^5\text{-}C_5H_5)]_3$ point to the presence of multiple bonds to tellurium with greater multiple-bond character in the former than the latter.

Experimental Section

Syntheses. All operations were carried out under a purified argon atmosphere. The solvents were freshly distilled and purged with argon.

Synthesis of $(\mu\text{-Te})[V(CO)_3\text{diphos}]_2$ was carried out by using the method described by Schiemann.[2] On reacting Na_2TeO_3 (1:1) with $Na^+[V(CO)_4\text{diphos}]^-$ in aqueous solution under argon, a dark violet solution formed which, on addition of phosphoric acid (1 M), yielded a purple precipitate. The purple solid was filtered, dried under vacuum, and then repeatedly recrystallized from toluene/pentane (1:1) mixtures at −20 °C. Anal. Calcd for $C_{58}H_{48}O_6P_4V_2Te$: C, 58.29; H, 4.02. Found: C, 58.40; H, 4.00. IR spectrum in ether: 1972 m, 1925 s, 1878 vs cm^{-1}.

$(\mu_3\text{-Te})[Mn(CO)_2(\eta^5\text{-}C_5H_5)]_3$ was prepared by the method of Herberhold,[3] where $(\eta^5\text{-}C_5H_5)Mn(CO)_2\cdot THF$, obtained by the photolysis of $(\eta^5\text{-}C_5H_5)Mn(CO)_3$, was treated with H_2Te generated in situ from Al_2Te_3 and dilute HCl. The solution was brought to dryness after being filtered over a pad of anhydrous Na_2SO_4 and then purified by column chromatography at −20 °C on silica gel (Merck 9385) under argon. Final purification was performed by recrystallization from CH_2Cl_2/pentane at −40 °C to give a black microcrystalline compound. Anal. Calcd for $C_{21}H_{15}Mn_3O_6Te$: C, 38.46; H, 2.31. Found: C, 38.67; H, 1.99. IR spectrum in ether: 1995 m, 1939 s, 1906 m, 1925 vs cm^{-1}. The same method was used to prepare $(\mu_3\text{-Te})[Mn(CO)_2(\eta^5\text{-}MeC_5H_4)]_3$. Anal. Calcd for

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(6) Jones, C. H. W.; McWhinnie, W. R.; Berry, F. J. *Mössbauer Effect Methodology*; Gruverman, I. D., Seidel, C. H., Eds.; Plenum: New York, 1976; Vol. 10, pp 227–244.

(7) Jones, C. H. W. *Can. J. Chem.* **1977**, *55*, 3076–3080.

(8) Dance, N. S.; Jones, C. H. W. *Can. J. Chem.* **1978**, *56*, 1746–1751.

$C_{24}H_{21}Mn_3O_6Te$: C, 41.14; H, 300. Found: C, 41.18; H, 3.22. IR spectrum in ether: 1994 s, 1939 s, 1901 s cm^{-1}.

Synthesis of $(\mu\text{-Te})[Mn(CO)_2(\eta^5\text{-}C_5Me_5)]_2$ was carried out by following the method of Herrmann[4] which is very similar to the preparation of Herberhold.[3] Purification by column chromatography and recrystallization yielded a black crystalline compound. Anal. Calcd for $C_{24}H_{30}Mn_2O_4Te$: C, 46.5; H, 4.88. Found: C, 44.27; H, 4.81. IR spectrum in THF: 1982 s, 1926 vs cm^{-1}.

The reaction of the above compound with excess diazomethane in ether at −78 °C quantitatively produced a blue compound of composition $(\mu\text{-}\eta^2\text{-TeCH}_2)$ $[Mn(CO)_2(\eta^5\text{-}C_5Me_5)]_2$. Anal. Calcd for $C_{25}H_{32}Mn_2O_4Te$: C, 47.31; H, 5.04. Found: C, 47.24; H, 4.99. IR spectrum in THF: 1978 vs, 1923 s, 1907 vs, 1862 cm^{-1}.

$(\mu\text{-Te})[Cr(CO)_3(\eta^5\text{-}C_5H_5)]_2$ was obtained by stirring an excess of elemental tellurium in a THF solution of $[(\eta^5\text{-}C_5H_5)Cr(CO)_3]_2$ at room temperature for 1 h.[1] Excess tellurium was removed by filtration and the solvent then removed under vacuum to give the analytically pure compound. Anal. Calcd for $C_{16}H_{10}Cr_2O_6Te$: C, 36.22; H, 1.95. Found C, 35.80; H, 1.92, IR spectrum in THF: 2008 s, 1976 m, 1938 vs cm^{-1}.

Spectroscopic Characterization. IR spectra were recorded on a Perkin-Elmer 983 spectrometer.

Mössbauer spectra were recorded by using a Harwell Instruments constant acceleration drive, based on a Harwell 200 series wave form generator and amplifier. A 2 mCi $^{125}Sb/Cu$ source (New England Nuclear) was used. The source and absorbers were immersed in liquid helium in a Harwell Instruments Dewar. The 35.5 keV Mössbauer γ-ray was monitored through the 6-keV escape peak in a Xe/CO_2 proportional counter. The spectra were accumulated in a Nuclear Date 66 analyzer as 256-channel spectra and were subsequently computer fitted to Lorentzians[9] using the N.D. 66 as a computer terminal for transmitting data to, and for computation on, the University IBM 4341 mainframe computer. The spectrometer was routinely calibrated by using a $^{57}Co/Rh$ source and an iron foil absorber at room temperature. The ^{125}Te isomer shifts are reported with respect to $^{125}I/Cu$ as a reference standard, and this entailed adding 0.15 mm s^{-1} to the shifts measured against $^{125}Sb/Cu$ as the source.[6] In computer fitting the spectra, the line widths were left unconstrained except in the case of $(\mu\text{-Te})[V(CO)_3\text{diphos}]_2$. Here the spectrum could be fitted to a very broad single line ($\chi^2 = 280$ for 250 degrees of freedom) or to a doublet with narrower equal line widths ($\chi^2 = 247$ for 248 degrees of freedom); the latter yields an upper limit for Δ in this compound of 3.8 mm s^{-1}.

Acknowledgment. C.H.W.J. wishes to acknowledge a grant in support of this research from the Natural Sciences and Engineering Research Council of Canada.

Registry No. $(\mu\text{-Te})[V(CO)_3\text{diphos}]_2$, 88000-23-1; $(\mu_3\text{-Te})(Mn(CO)_2(\eta\text{-}C_5H_5)]_3$, 84074-22-6; $(\mu_3\text{-Te})[Mn(CO)_2(\eta^5\text{-}MeC_5H_4)]_3$, 84074-24-8; $(\mu\text{-Te})[Mn(CO)_2(\eta^5\text{-}C_5Me_5)]_2$, 92840-52-3; $(\mu,\eta^2\text{-TeCH}_2)[Mn(CO)_2(\eta^5\text{-}C_5Me_5)]_2$, 88056-69-3; $(\mu\text{-Te})[Cr(CO)_3(\eta^5\text{-}C_5H_5)]_2$, 94607-28-0.

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[9] (9) Bancroft, G. M.; Maddock, A. G.; Ong, W. K.; Prince, R. H.; Stone, A. J. *J. Chem. Soc. A* **1967**, 1966–1971.

Reaction of Bis(trimethylsilyl)acetonitrile, (Trimethylgermyl)(trimethylsilyl)acetonitrile, and Bis(trimethylgermyl)acetonitrile Anions with Aldehydes

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For a comparison of the chemical behavior of organosilicon and organogermanium compounds, bis(trimethylsilyl)acetonitrile (**3**), (trimethylgermyl)(trimethylsilyl)acetonitrile (**4**), and bis(trimethylgermyl)acetonitrile (**5**) were synthesized, and a Peterson type reaction was performed with them and a variety of aldehydes (**12**). High yields of 2-(trimethylsilyl)-2-alkenenitriles (**15**) from **3** and 2-(trimethylgermyl)-2-alkenenitriles (**20**) from **4** and **5** were obtained. High stereoselectivity giving *E* isomers was observed in the reaction of **3** and **5**. The key intermediate in the reaction is also discussed.

Organosilicon and organotin chemistry have now become important in the methodology of organic synthesis.[1] Organogermanium compounds, the middle element compounds of periodic group IVA (14^{20}), are assumed to have chemical properties that are also intermediate between those of the silicon and tin analogues. Only a few reports have compared the chemical behavior of the tetraorganocompounds of silicon, germanium, and tin.[2]

The Peterson reaction[3] has been applied for the synthesis of silylated olefins from α,α-disilylated carbanions with carbonyl compounds: e.g., 1-(trimethylsilyl)-1-alkenes from [bis(trimethylsilyl)methyl]lithium,[4] 2-(trimethylsilyl) 2,3-unsaturated carboxylic acid esters from *tert*-butyl lithiobis(trimethylsilyl)acetate.[5] Previously, we reported a synthesis of (*Z*)-alk-2-enenitriles from aldehydes with tris(trimethylsilyl)ketene imine (**2**).[6]

It appeared that disubstituted acetonitriles or trisubstituted ketene imines which have both the trimethylsilyl and trimethylgermyl groups, as in compounds **3**–**7** of eq 2, are good model compounds to directly compare the chemical reactivity between organoelement groups (Scheme I). This paper reports that the Peterson reaction of disubstituted acetonitrile anions having trimethylsilyl

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[1] (1) (a) Magnus, P. D.; Sarkar, T.; Djuric, S. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 7, Chapter 48 and references therein. (b) Colvin, E. *Silicon in Organic Synthesis*; Butterworths: London, 1981.

[2] (2) (a) Kauffmann, T. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 410. (b) Oda, H.; Morizawa, Y.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1984**, *25*, 3221. (c) Oda, H.; Oshima, K.; Nozaki, H. *Chem. Lett.* **1985**, 53.

[3] (3) For reviews of the Peterson reaction, see: Colvin, E. *Silicon in Organic Synthesis*; Butterworths: London, 1981; p 141. Ager, D. J. *Chem. Soc. Rev.* **1982**, *11*, 493; *Synthesis* **1984**, 384.

[4] (4) (a) Sakurai, H.; Nishiwaki, K.; Kira, M. *Tetrahedron Lett.* **1973**, 4193. (b) Grobel, B.-T.; Seebach, D. *Chem. Ber.* **1977**, *110*, 852.

[5] (5) (a) Hartzell, S. L.; Rathke, M. W. *Tetrahedron Lett.* **1976**, 2737. (b) Sato, Y.; Takeuchi, S. *Synthesis* **1983**, 734.

[6] (6) (a) Sato, Y.; Niinomi, Y. *J. Chem. Soc., Chem. Commun.* **1982**, 56. (b) Matsuda, I.; Okada, H.; Izumi, Y. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 528.

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