Organometallics 1991, 10, 286-291

Syntheses and Mechanistic Studies of Symmetric Tetraorganyltellurium(IV) (R_4Te) and Diorganyltellurium(II) (R'_2Te) Compounds (R = R' = Me, *n*-Bu, Me_3SiCH_2, and $CH_2{=}CH$; R' = *t*-Bu and Allyl)

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Received April 20, 1990

Tetraorganyltellurium(IV) compounds (R_4Te, R = Me, *n*-Bu, Me_3SiCH_2, and $CH_2{=}CH$) have been prepared by the reaction of $TeCl_4$ with 4 equiv of LiR or RMgX. Decomposition of the R_4Te compounds led to the formation of the symmetric diorganyltellurium(II) compounds (R_2Te). Me_4Te and $(Me_3SiCH_2)_4Te$ thermally and photolytically decomposed by a free-radical pathway. $(CH_2{=}CH)_4Te$ decomposed by noncoupling reductive elimination. While $(t\text{-Bu})_2Te$ and $(allyl)_2Te$ have also been prepared by the reaction of $TeCl_4$ with 4 equiv of (*t*-Bu)Li or (allyl)MgCl, respectively, their corresponding R_4Te intermediates could not be isolated. $(t\text{-Bu})_2Te$ was also isolated as a minor product from the reaction of (*t*-Bu)TeLi with (*t*-Bu)I in THF. $(Allyl)_2Te$ was prepared by the reaction of Li_2Te with 2 equiv of (allyl)I in THF. These compounds have been characterized by ^1H, ^{13}C, and ^{125}Te NMR spectroscopies.

Introduction

Organotellurium compounds are of interest in organic chemistry,[1] in biochemistry,[2] and as source compounds for the metal-organic chemical vapor deposition (MOCVD) of the semiconductor mercury cadmium telluride ($Hg_{1-x}Cd_xTe$).[3] Our work on source compounds has emphasized the synthesis, characterization, and decomposition pathways of organotellurium precursors for the pyrolytic and photoassisted MOCVD of $Hg_{1-x}Cd_xTe$.[4]

$Hg_{1-x}Cd_xTe$ can be grown by MOCVD between 390 and 450 °C by using Et_2Te, Me_2Cd, and elemental Hg.[3a] However, Hg evaporation and diffusion at these high temperatures is deleterious to the growth of superlattices and heterostructures with sharp interfaces. Lower film-growth temperatures can be achieved by using alternative diorganyltellurium source compounds such as $(i\text{-Pr})_2Te$,[3b] $(t\text{-Bu})_2Te$,[3c] (allyl)(Me)Te,[3d] and $(allyl)_2Te$.[4c] Although $(t\text{-Bu})_2Te$ has been used as a source compound to grow CdTe and HgTe at approximately 250 °C, the availability of $(t\text{-Bu})_2Te$ was limited due to the absence of an efficient synthetic methodology.

While many primary and secondary dialkyl tellurides have been prepared in high yields from reaction of Na_2Te with 2 equiv of an alkyl halide,[5] yields diminish to 0% when (*t*-Bu)Cl is used.[6] R_2Te compounds have been obtained by reducing $TeCl_4$ or diorganyltellurium dihalides (R_2TeX_2) with Grignard[1a,7] or organolithium reagents.[1a] We now report the high yield synthesis of $(t\text{-Bu})_2Te$ from the reaction of $TeCl_4$ and 4 equiv of (*t*-Bu)Li or (*t*-Bu)MgBr.

Scheme I

$$TeCl_4 + 4(CH_3)_3CLi \longrightarrow [((CH_3)_3C)_4Te] \longrightarrow \underset{84\%\ \text{yield}}{((CH_3)_3C)_4Te} + (CH_3)_2{=}CH_2 + (CH_3)_3CH$$

Although tetraalkyltellurium(IV) compounds were presumed unstable, we recently reported the isolation and characterization of Me_4Te.[4h] We now report the isolation and characterization of the less stable $(CH_2{=}CH)_4Te$, $(n\text{-Bu})_4Te$, and $(Me_3SiCH_2)_4Te$ compounds, as well as their decomposition pathways to give R_2Te compounds.

Results and Discussion

Synthesis of R_4Te Compounds. The reaction of at least 4 equiv of Grignard or organolithium reagents with $TeCl_4$ under Ar atmosphere in the absence of light produces very reactive tetraorganyltellurium(IV) (R_4Te) compounds (eq 1). While Me_4Te is stable up to 100 °C

$$TeCl_4 + 4RM \rightarrow R_4Te + MCl \qquad (1)$$

$$M = Li \text{ or } MgX\ (X = \text{halide})$$

$$R = Me,\ n\text{-Bu},\ Me_3SiCH_2,\ CH_2{=}CH$$

in solution, $(n\text{-Bu})_4Te$, $(Me_3SiCH_2)_4Te$, and $(CH_2{=}CH)_4Te$ slowly decompose at room temperature. These malodorous compounds are extremely air- and light-sensitive, with Me_4Te being pyrophoric and explosive when exposed to air or oxygen.

Synthesis of R_2Te Compounds. Symmetric R_2Te compounds can be prepared by either pyrolytic or pho-

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tolytic decomposition of R_4Te compounds (eq 2). Although $(allyl)_2Te$ was isolated from the reaction of $TeCl_4$ with 4 equiv of (allyl)MgCl in THF, $(allyl)_4Te$ could not be isolated.

$$R_4Te \xrightarrow{\Delta/h\nu} R_2Te + \text{organics} \qquad (2)$$

While $(CH_2{=}CH)_2Te$ has been prepared by hydrometalation of acetylene in basic solutions,[8] R_2Te compounds are typically prepared from reaction of alkyl halides and Na_2Te in liquid ammonia, alcoholic, or aqueous media.[1a,4f,5,6] The lower solubility of Na_2Te in less polar solvents precludes the use of diethyl ether and THF. We find that Li_2Te, a more covalent compound, is sufficiently soluble in THF to give $(allyl)_2Te$ in 63% yield when treated with 2 equiv of (allyl)I. This yield is lower than from the reaction of Na_2Te in ethanol with (allyl)I (75%),[4f] but no effort was made to optimize the reaction conditions. Analogous to the reaction of Na_2Te in ethanol with 2 equiv of (*t*-Bu)Cl,[6] reaction of Li_2Te in THF with 2 equiv of (*t*-Bu)I did not afford $(t\text{-Bu})_2Te$.

Synthesis and Mechanism for $(t\text{-Bu})_2Te$ Formation. $(t\text{-Bu})_2Te$ can be isolated in 84% yield from the reaction of $TeCl_4$ in THF at −78 °C with 4 equiv of (*t*-Bu)Li. $(CH_3)_2C{=}CH_2$ and $(CH_3)_3CH$ were detected by NMR in approximately a 1:1 ratio from this reaction (Scheme I). The proposed $(t\text{-Bu})_4Te$ intermediate could not be isolated. An experiment to observe spectroscopically the $(t\text{-Bu})_4Te$ intermediate by ^{125}Te NMR spectroscopy from reaction of 4 equiv of (*t*-Bu)Li with $TeCl_4$ in THF-d_8 at −90 °C revealed that $(t\text{-Bu})_2Te$ was the only tellurium species in solution at this temperature. The instability of $(t\text{-Bu})_4Te$ may be attributed to steric interactions, to free-radical formation, or to the ability of the *tert*-butyl group to undergo β-hydrogen elimination.[4i] The absence of $(CH_3)_3CC(CH_3)_3$ as an organic byproduct from the reaction in Scheme I suggests that $(t\text{-Bu})_2Te$ formation does not occur by reductive coupling of two *tert*-butyl groups.

Although $(t\text{-Bu})_4Te$ is a possible intermediate to $(t\text{-Bu})_2Te$ formation, we cannot rule out alternative pathways involving other Te(IV) intermediates such as $(t\text{-Bu})_{4-n}TeCl_n$ (for n = 1–3) or an alkyltellurenyl halide ((*t*-Bu)TeCl). While tellurenyl compounds with aromatic groups are known,[9] the first stable alkyltellurenyl halides ($(Me_3Si)_3CTeX$) were recently reported.[10] (*t*-Bu)TeCl was a proposed unstable product observed by ^{125}Te NMR spectroscopy from reaction of $TeCl_4$ with (*t*-Bu)MgCl.[7]

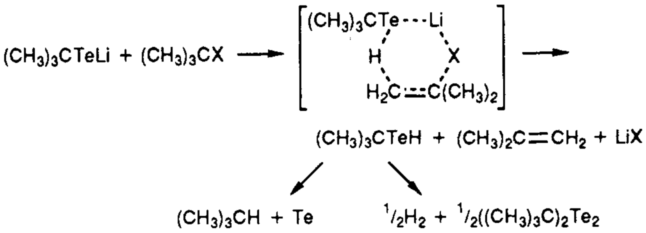
Even though the synthesis of $(t\text{-Bu})_2Te$ was first reported from the reaction of $TeCl_4$ with 3 equiv of (*t*-Bu)MgCl, no detailed experimental procedure or percent yield data were reported.[7] Furthermore, this reaction was reported to result in the formation of a mixture of $(t\text{-Bu})_2Te$ and $(t\text{-Bu})_2Te_2$. In our work, the reaction of $TeCl_4$ in THF at −78 °C with 3 equiv of (*t*-Bu)Li resulted in $(t\text{-Bu})_2Te_2$ as the major Te-containing product. While no H_2 was detected, $(CH_3)_2C{=}CH_2$ and $(CH_3)_3CH$ were detected by NMR and gas chromatography in approximately a 1:1 ratio from this reaction.

The reaction of (*t*-Bu)TeLi in THF at −78 °C with (*t*-Bu)I in a 1:1 ratio results in a mixture of $(t\text{-Bu})_2Te_2$ and $(t\text{-Bu})_2Te$ in 46% and 39% yield with respect to Te, respectively (eq 3). $(CH_3)_2C{=}CH_2$, $(CH_3)_3CH$, and H_2 were

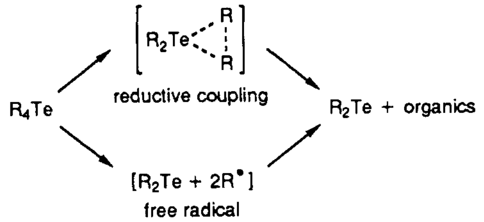
$$(t\text{-Bu})TeLi + (t\text{-Bu})I \rightarrow (t\text{-Bu})_2Te_2 + (t\text{-Bu})_2Te \qquad (3)$$

the gaseous byproducts detected by gas chromatography from this reaction. The yield of $(t\text{-Bu})_2Te$ may be reduced due to a bimolecular β-hydrogen elimination process to form the hypothetical (*t*-Bu)TeH intermediate (Scheme II). Alkyltellurols (RTeH) are extremely unstable,[1a,11] and subsequently, (*t*-Bu)TeH may decompose to H_2 and $(t\text{-Bu})_2Te_2$ or $(CH_3)_3CH$ and Te metal. Similarly, M_2Te (M = Li or Na) may also abstract protons from *tert*-butyl halides to produce either (*t*-Bu)TeH or H_2Te as an unstable intermediate. Proton abstraction from *tert*-butyl halides by basic reagents (PhLi[12] or $(Me_3Si)_2AsLi(THF)_2$[13]) results in the formation of $(CH_3)_2C{=}CH_2$. In contrast, Me_3SiCl, which is less prone to proton abstraction, forms $(t\text{-Bu})(Me_3Si)Te$ in 90% yield when treated with (*t*-Bu)TeLi.[14]

Scheme II



Scheme III



Decomposition of R_4Te Compounds. Tetraaryltellurium(IV) compounds such as $(C_6H_5)_4Te$,[15] $(C_6F_5)_4Te$,[16] and bis(2,2′-biphenylylene)tellurium(IV)[17] have been isolated from the reaction of $TeCl_4$ with the corresponding organolithium reagent. Although tetraalkyltellurium(IV) compounds are less stable than tetraaryl- or dialkyldiaryltellurium(IV) compounds, we have isolated and characterized Me_4Te,[4h] $(n\text{-Bu})_4Te$,[18] $(Me_3SiCH_2)_4Te$, and $(CH_2{=}CH)_4Te$. R_4Te compounds may decompose by reductive coupling or by free-radical formation to yield the diorganyl tellurides (R_2Te) and organic byproducts (Scheme III).[19] Studies by Barton[19] and co-workers in-

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Table I. Product Distribution in the Decomposition of Me_4Te[a]

conditions	mol % $H_2C{=}CH_2$	mol % CH_4	mol % C_2H_6
neat Me_4Te at 116 °C in the dark	1.7	10.9	87.4
50 mol % Me_4Te in 1,4-C_6H_8 at 116 °C in the dark	0.4	96.3	3.3
5 mol % Me_4Te in 1,4-C_6H_8 at 46 °C in sunlight	0.0	91.1	8.9

[a] Determined by GC analysis.

dicated tetraaryltellurium(IV) compounds exchange ligands by a fast nonradical process prior to thermal decomposition by a reductive coupling pathway to afford diaryl tellurides and biaryls as the major products. Their decomposition studies revealed that 4,4′-dimethylbiphenyl was the major organic product with neat tetrakis(4-methylphenyl)tellurium(IV) or as a 50 mol % mixture with 1,4-cyclohexadiene as a source of hydrogen atoms.[20] The ratio of 4,4′-dimethylbiphenyl to toluene produced was similiar under both reaction conditions (eq 4). This result suggests that there is little aryl free-radical trapping and the the primary mode of thermal decomposition of tetraaryltellurium(IV) compounds is reductive coupling.

$$R_4Te \xrightarrow[(2)\ \Delta/1,4\text{-}C_6H_8]{(1)\ \Delta/\text{neat}} R_2Te + \underset{\text{major}}{R_2} + \underset{\text{minor}}{RH} \qquad (4)$$

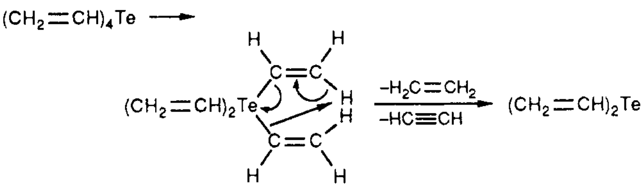
$$R = 4\text{-}MeC_6H_4$$

Thermal and photolytic decomposition of Me_4Te in the presence of 1,4-cyclohexadiene results in substantially higher CH_4:C_2H_6 ratios than the decomposition of neat Me_4Te (Table I), which indicates that Me_4Te decomposes by a free-radical pathway. Further evidence for a free-radical decomposition pathway was obtained when the thermal and photolytic decomposition of Me_4Te in the presence of methyl methacrylate resulted in the formation of poly(methyl methacrylate). This result contrasts with the reductive coupling pathway observed in the decomposition of tetraaryltellurium(IV) compounds.[19]

Crude $(n\text{-}Bu)_4Te$ was prepared from the reaction of $TeCl_4$ with 4 equiv of $(n\text{-}Bu)Li$. $(n\text{-}Bu)_4Te$ is a thermally and photolytically unstable compound that readily converts to $(n\text{-}Bu)_2Te$[18] at room temperature. An NMR sample of $(n\text{-}Bu)_4Te$ in C_6D_6 completely converted to $(n\text{-}Bu)_2Te$ after 15 min of exposure to sunlight at room temperature.

The (trimethylsilyl)methyl group imparts greater thermal and chemical stability to transition-metal alkyls by increasing the M–C bond strength and by suppressing the β-hydrogen elimination pathway.[21] For this reason, $(Me_3SiCH_2)_4Te$ was prepared from the reaction of $TeCl_4$ with 4 equiv of $(Me_3SiCH_2)MgCl$ and was isolated as an extremely air- and light-sensitive yellow solid in 75% yield. As expected, $(Me_3SiCH_2)_4Te$ is thermally stable and can be stored at 0 °C in the absence of light for months with only slight decomposition. A dilute (3% by weight) $(Me_3SiCH_2)_4Te$ solution in C_6D_6 showed 8% conversion to $(Me_3SiCH_2)_2Te$ when kept at room temperature in the dark for 18 h. However, heating a dilute solution (5% by weight) of $(Me_3SiCH_2)_4Te$ in C_7D_8 for 1 h in the dark at 55 °C and then 67 °C for an additional hour resulted in a 25% and 76% conversion to $(Me_3SiCH_2)_2Te$, respectively. Analogous to $(n\text{-}Bu)_4Te$, an NMR sample of $(Me_3SiCH_2)_4Te$ completely converted to $(Me_3SiCH_2)_2Te$ after exposure to sunlight for 15 min at room temperature with $Me_3SiCH_2CH_2SiMe_3$ as the primary byproduct. Photolytic decomposition of $(Me_3SiCH_2)_4Te$ in sunlight at room temperature in the presence of 1,4-cyclohexadiene (5 mol % $(Me_3SiCH_2)_4Te$) affords $(Me_3SiCH_2)_2Te$ and Me_4Si as the primary products by NMR spectroscopy. The formation of Me_4Si as the primary organosilicon byproduct from decomposition of $(Me_3SiCH_2)_4Te$ in the presence of a free-radical trapping reagent suggests that the primary mode of decomposition is free-radical in nature. As in the case of Me_4Te, additional evidence for a free-radical decomposition pathway was obtained when the thermal and photolytic decomposition of $(Me_3SiCH_2)_4Te$ in the presence of methyl methacrylate resulted in the formation of poly(methyl methacrylate).

Scheme IV



$(Allyl)_4Te$ could not be isolated from the reaction of $TeCl_4$ and (allyl)MgCl in a 1:4 molar ratio. This reaction produced $(allyl)_2Te$ in 51% yield. 1,5-Hexadiene was identified by gas chromatography as one of the organic byproducts in the solvent.

$(CH_2{=}CH)_4Te$ was isolated in 38% yield from the reaction of $TeCl_4$ and 4 equiv of $(CH_2{=}CH)MgBr$ in THF. A dilute C_6D_6 solution (12% by weight) of $(CH_2{=}CH)_4Te$ exhibited a 34% conversion to $(CH_2{=}CH)_2Te$ when the sample was kept at room temperature for 18 h in the dark. Ethylene and acetylene were identified as the major organic byproducts by ^1H NMR spectroscopy in approximately a 1:1 ratio, suggesting that the primary decomposition pathway of $(CH_2{=}CH)_4Te$ was not reductive coupling.

A sample of $(CH_2{=}CH)_4Te$ (0.032 g, 0.14 mmol) was heated at 75 °C for 2 h in the dark in an NMR tube with excess 1,4-cyclohexadiene (0.22 g, 2.7 mmol) as a free-radical trapping reagent. C_6D_6 was then condensed into the sample, and the ^1H NMR spectrum was recorded. The $(CH_2{=}CH)_4Te$ sample was completely converted to $(CH_2{=}CH)_2Te$. Ethylene and acetylene were again detected in a 1:1 ratio as the major organic byproducts. The invariable ethylene-to-acetylene ratio in the presence of a source of hydrogen atoms suggests that $(CH_2{=}CH)_4Te$ does not decompose to $(CH_2{=}CH)_2Te$ by a free-radical pathway. It is proposed that $(CH_2{=}CH)_4Te$ decomposes by noncoupling reductive elimination (Scheme IV).

NMR Spectra. The NMR data for R_4Te are reported in Table II. The ^{125}Te NMR spectra of R_4Te exhibited upfield resonances in comparison to the corresponding R_2Te spectra with the exception of $(Me_3SiCH_2)_4Te$. The downfield ^{125}Te chemical shift of $(Me_3SiCH_2)_4Te$ (97 ppm) with respect to $(Me_3SiCH_2)_2Te$ (42 ppm) may be attributed to steric influences. The ^1H-coupled ^{125}Te spectra for $(Me_3SiCH_2)_4Te$ and $(Me_3SiCH_2)_2Te$ are shown in Figure 1. In the case of $(Me_3SiCH_2)_4Te$, a symmetrical multiplet of seven of the nine theoretical resonances was observed due to coupling to eight protons. It appears that the $^2J_{TeH}$ coupling in the tetraalkyltellurium(IV) compounds is larger

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Table II. NMR Chemical Shifts and Coupling Constants[a]

compound	NMR spectra		
	^{1}H	^{13}C	^{125}Te[b]
$(Me)_4Te$[c]	0.99 (s)	20.6 (q, $^1J_{CH}$ = 133.4, $^1J_{TeC}$ = 127.8)	−67 (m of 11, $^2J_{TeH}$ = 34.0)[d]
$(Me)_2Te$	1.83 (s)[e]	−21.5 (q, $^1J_{CH}$ = 140.7, $^1J_{TeC}$ = 158)[f]	0 (m of 7, $^2J_{TeH}$ = 21.0)
$(CH_2{=}CH)_4Te$	6.92 (d of d, CH, $^3J_{H,H\text{-}trans}$ = 18.2, $^3J_{H,H\text{-}cis}$ = 10.8), 6.02 (d of d, CH_2 cis, $^3J_{H,H\text{-}cis}$ = 10.9, $^2J_{H,H\text{-}gem}$ = 0.8), 5.79 (d of d, CH_2 trans, $^3J_{H,H\text{-}trans}$ = 18.2, $^2J_{H,H\text{-}gem}$ = 0.9)	149.2 (C_α), 126.4 (C_β)	412 (m of 5, $^2J_{TeH}$ = 14)[g]
$(CH_2{=}CH)_2Te$	6.89 (d of d, CH, $^3J_{H,H\text{-}trans}$ = 17.7, $^3J_{H,H\text{-}cis}$ = 10.2), 6.04 (d of d, CH_2 cis, $^3J_{H,H\text{-}cis}$ = 10.2, $^2J_{H,H\text{-}gem}$ = 0.8), 5.68 (d of d, CH_2 trans, $^3J_{H,H\text{-}trans}$ = 17.7, $^2J_{H,H\text{-}gem}$ = 0.9)	128.6 (C_β), 108.6 (C_α)	534 (t, $^2J_{TeH}$ = 15)[g]
$(n\text{-}Bu)_4Te$	1.6 (br m), 1.4 (br m), 0.9 (br m)	30.2 (C_α), 33.8 (C_β), 26.6 (C_γ), 14.1 (C_δ)	215 (complex m)
$(n\text{-}Bu)_2Te$[h]	2.51 ($^3J_{HH}$ = 7), 1.6 (m), 1.3 (m), 0.84 ($^3J_{HH}$ = 7)	34.7 (C_β), 25.2 (C_γ), 13.4 (C_δ), 1.8 (C_α)	254 (m of 13, $^2J_{TeH}$ = 24, $^3J_{TeH}$ = 12)
$(Me_3SiCH_2)_4Te$	1.12 (s, CH_2), 0.20 (s, Me_3Si)	24.5 (t, CH_2, $^1J_{CH}$ = 124.0, $^1J_{SiC}$ = 48.8 $^1J_{TeC}$ = 113.4), 1.4 (q, Me_3Si, $^1J_{CH}$ = 118.3, $^1J_{SiC}$ = 50.6)	97 (m of 7, $^2J_{TeH}$ = 32)
$(Me_3SiCH_2)_2Te$	1.63 (s, CH_2), 0.09 (s, Me_3Si)	−0.3 (q of m of 7, Me_3Si, $^1J_{CH}$ = 118.9, $^3J_{CH}$ = 2.0, $^1J_{SiC}$ = 52.0, −13.2 (t of m of 6, CH_2, $^1J_{CH}$ = 129.3, $^3J_{CH}$ = 2.2, $^1J_{SiC}$ = 49.6, $^1J_{TeC}$ = 175.4)	42 (m of 5, $^2J_{TeH}$ = 12)

[a] Chemical shifts in ppm and coupling constants in Hz. Abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad). [b] All ^{125}Te chemical shifts were referenced to neat $(Me)_2Te$ and recorded at room temperature from 1 M C_6D_6 solutions. [c] Reference 4h. [d] Neat. [e] Pfister, G.; Dreskamp, H. *Ber. Bunsenges. Phys. Chem.* **1969**, *73*, 654. [f] Hope, E. G.; Kemmitt, T.; Levason, W. *Organometallics* **1988**, *7*, 78. [g] Selective decoupling of the methylene protons. [h] Reference 4b.

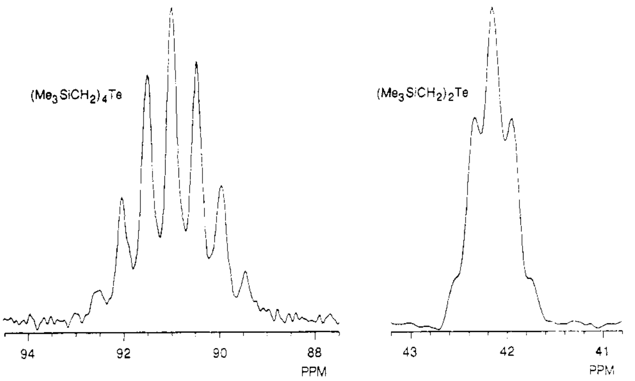

Figure 1. 63-MHz ^{1}H-coupled ^{125}Te NMR spectra (with Gaussian resolution enhancement) of $(Me_3SiCH_2)_4Te$ at −20 °C and $(Me_3SiCH_2)_2Te$ at 25 °C in C_7D_8.

than that of the analogous dialkyltellurium(II) compounds. The samples of $(CH_2{=}CH)_4Te$ and $(n\text{-}Bu)_4Te$ decomposed in the NMR spectrometers after several hours at −20 to 0 °C.

Experimental Section

General Procedures. Organic solvents were distilled under Ar from sodium/benzophenone. Synthesis was carried out under purified Ar by using Schlenk techniques.[23] Air- and moisture-sensitive materials were transferred inside a He-filled Vacuum Atmospheres glovebox. Reaction flasks were wrapped in aluminum foil to minimize exposure to light. $TeCl_4$ (99%) was purchased from Alfa and ground with a mortar and pestle in the glovebox prior to use. (Allyl)MgCl, $(CH_2{=}CH)MgBr$, (*t*-Bu)MgBr, $(Me_3SiCH_2)MgCl$, and (*t*-Bu)Li solutions as well as Te and Li were used as received from the Aldrich Chemical Company. Te powder was ground and Li rods were cut into small pieces in the glovebox prior to use. (Allyl)I was purified according to the literature.[24] R_4Te (R = *n*-Bu and $CH_2{=}CH$) were too unstable to obtain elemental analysis data. Organotellurium compounds should be handled cautiously since they are generally malodorous and toxic.[25]

^{1}H NMR spectra were recorded on C_6D_6 solutions with an IBM NR-80 spectrometer operating at 80 MHz. ^{13}C NMR spectra were recorded at 20 and 50 MHz with the IBM NR-80 and with a Nicolet NT-200-WB spectrometer, respectively. ^{125}Te NMR spectra were recorded on 1 M solutions in C_6D_6 with the Nicolet NT-200-WB spectrometer operating at 63.2 MHz, with a 10-μs pulse width (corresponding to a 45° flip angle), with a 5-s receiver delay, and referenced to neat $(Me)_2Te$ at 0 ppm. The presence of ethylene and acetylene was verified by a control experiment in which a C_6D_6 solution saturated with ethylene and acetylene was added to the NMR sample. This resulted in an increase in the intensity of the peaks near 5.3 and 1.6 ppm. IR spectra were obtained with a Nicolet 60-SX Fourier transform spectrometer. All spectra were obtained at 4-cm^{-1} resolution by using Happ-Genzel apodization and a liquid N_2 cooled mercury cadmium telluride detector/Ge coated KBr beam splitter for the 6500–450-cm^{-1} range. A deuterated triglycine sulfate detector with a polyethylene window/6.5-mm Mylar beam splitter combination was used for the 500–100-cm^{-1} range. Spectra below 550 cm^{-1} were measured in 0.1-mm path length polyethylene cells. Gas chromatographic analyses were performed with a Perkin-Elmer Sigma 2000 instrument using 2-m-long by 3-mm-diameter Spherocarb or Porajak-T columns and a hot wire detector. Compounds were identified by their retention times, and response factors of standard samples were used for quantitative analysis.

Li_2Te. To a slurry containing a 2:1:90 molar ratio of Li metal, Te powder, and THF was added a catalytic amount of naphthalene (5 mol %).[4f] The slurry initially turned burgundy and then became the green color typical of lithium naphthalide after stirring for 4 days at room temperature under Ar. The suspension was gravity-filtered, and the off-white precipitate was washed with THF and then hexane. The solid was dried under vacuum to give a quantitative yield of Li_2Te as a very air-sensitive off-white to brown solid.

Preparation of $(t\text{-}Bu)_2Te$ from (*t*-Bu)Li and $TeCl_4$. To a stirred suspension of $TeCl_4$ (20 g, 74 mmol) in 100 mL of THF at −78 °C was added dropwise (*t*-Bu)Li (187 mL, 1.6 M in pentane,

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0.30 mol) in the dark. After 1 h, the reaction mixture was slowly warmed to room temperature and stirred for an additional 2 h. The mixture was filtered and the precipitate washed with two 50-mL portions of THF. The solvent was removed from the combined filtrate and washings via fractional distillation. The air- and extremely light-sensitive pale-yellow product (15 g, 62 mmol, 84% yield based on $TeCl_4$) was isolated by vacuum distillation at 42–43 °C (4 Torr). A 62% yield based on $TeCl_4$ (11-mmol scale) was obtained from an analogous preparation when diethyl ether was used as a solvent. Anal. Calcd for $C_8H_{18}Te$: C, 39.73; H, 7.50; Te, 52.77. Found: C, 39.35; H, 7.27; Te, 52.81. ^1H NMR (C_6D_6): δ 1.60 (s). ^{13}C NMR (C_6D_6): δ 36.8 (q of heptets, $^1J_{CH} = 126$, $^5J_{CH} = 5$ Hz), 26.6 (m, $^2J_{CH} = 4.5$, $^1J_{TeC} = 186$ Hz). ^{125}Te NMR (C_6D_6): δ 1035 (m of 11 peaks, $^3J_{TeH} = 22.4$ Hz).

Preparation of (t-Bu)$_2$Te from (t-Bu)MgBr and $TeCl_4$. To a stirred suspension of $TeCl_4$ (3.2 g, 12 mmol) in 100 mL of THF at −78 °C was added dropwise (t-Bu)MgBr (25 mL, 2.0 M in THF, 50 mmol). The mixture was stirred for 1 h at −45 °C and then stirred for an additional 2 h at room temperature. The mixture initially turned brownish black while warming to room temperature. The pale-yellow mixture was filtered at room temperature, the white precipitate was washed with 50 mL of fresh THF, and the filtrate and washing were combined. The THF was removed by fractional distillation and (t-Bu)$_2$Te (1.44 g, 50% yield based on $TeCl_4$) was isolated at 42–43 °C (4 Torr).

Preparation of (t-Bu)$_2$Te from (t-Bu)TeLi and (t-Bu)I. To a stirred slurry of Te powder (4.79 g, 37.5 mmol) in 25 mL of THF at −78 °C was added dropwise (t-Bu)Li (26 mL, 1.6 M in pentane, 42 mmol). The mixture was warmed to room temperature and stirred for 10 min and then cooled to −78 °C. (t-Bu)I (5.2 mL, 8.0 g, 44 mmol) was added to the stirring slurry at −78 °C and stirred for 1 h. The yellow-green mixture turned dark red on warming to −23 °C. After stirring for 30 min at −23 °C, the mixture was warmed to room temperature. Pentane and THF were removed by distillation at atmospheric pressure and (t-Bu)$_2$Te (3.5 g, 15 mmol, 39% yield based on Te metal) was isolated at 42–43 °C (4 Torr) and (t-Bu)$_2$Te$_2$ (3.2 g, 8.7 mmol, 46% yield based on Te metal) was isolated by vacuum distillation at 72.5 °C (0.8 Torr).

Preparation of (Allyl)$_2$Te from (Allyl)MgCl and $TeCl_4$. Analogous to the preparation of (t-Bu)$_2$Te using (t-Bu)MgBr, (allyl)$_2$Te was prepared on a 37-mmol scale with (allyl)MgCl. After the addition of (allyl)MgCl, the reaction was refluxed for 3 h in the dark and cooled to −78 °C, and then 50 mL of hexane was added. The cold slurry was quickly filtered by using a coarse frit. The white precipitate was washed with two 40-mL portions of hexane to yield a light-yellow supernatant. THF and hexane were removed at 40 °C, and the crude product was collected in a −196 °C trap under vacuum. The product was purified by vacuum distillation in the dark (39–40 °C, 2 Torr). Pure (allyl)$_2$Te was obtained as a malodorous air-, heat-, and light-sensitive yellow liquid (4.0 g, 19 mmol, 51% yield based on $TeCl_4$). ^1H, ^{13}C, and ^{125}Te NMR spectra were consistent with those in the literature.[4f]

Preparation of (Allyl)$_2$Te from Li_2Te and (Allyl)I. To a stirred suspension of ground Li_2Te (5.0 g, 35 mmol) in 30 mL of THF at −25 °C was added dropwise (allyl)I (6.6 mL, 12 g, 72 mmol) in 10 mL of THF. The mixture was slowly warmed to room temperature and stirred overnight. The mixture was cooled to −78 °C and treated with 20 mL of hexane. The cold mixture was quickly filtered, and the white precipitate was washed with two 20-mL portions of hexane. The solvents from the combined filtrate and washings were removed by distillation, and the crude product was collected in a −196 °C trap. (Allyl)$_2$Te (4.7 g, 22 mmol, 63% yield based on Li_2Te) was purified by distillation at 35–36 °C (1 Torr).

(n-Bu)$_4$Te. To a stirring suspension of pulverized $TeCl_4$ (3.5 g, 13 mmol) in 25 mL of diethyl ether was added dropwise with stirring n-BuLi (1.6 M in hexane, 34 mL, 54 mmol) at −78 °C. The suspension turned brown initially and then orange–yellow after the addition was complete. After the slurry was stirred for 1 h at 0 °C, the mixture was cooled back to −78 °C and then quickly filtered to yield an orange–yellow supernatant. The white precipitate was washed with two 25-mL portions of hexane. The solvent of the combined solutions was removed under vacuum at 0 °C to yield an orange viscous residue. The unstable crude product (4.9 g) was extremely air- and light-sensitive and was immediately characterized by NMR.

(Me_3SiCH_2)$_4$Te. To a stirring suspension of pulverized $TeCl_4$ (3.5 g, 13 mmol) in 25 mL of ether was added dropwise with stirring (Me_3SiCH_2)MgCl (1.0 M in diethyl ether, 55 mL, 55 mmol) at −78 °C. The suspension turned brown initially and then light yellow after the addition was complete. After the yellow slurry was stirred for 2 h at 0 °C, 3 mL of 1,4-dioxane was added to precipitate the Mg salts. The mixture was stirred for 1 h at 0 °C, cooled to −78 °C, and then quickly filtered to yield a yellow supernatant. The white precipitate was washed with two 25-mL portions of pentane. The solvent of the combined solutions was removed under vacuum to yield a yellow solid. The extremely air- and light-sensitive yellow product (4.7 g, 9.9 mmol, 76% yield based on $TeCl_4$) was recrystallized at −78 °C from a concentrated pentane solution. Anal. Calcd for $C_{16}H_{44}Si_4Te$: C, 40.33; H, 9.31; Te, 26.78. Found: C, 40.48; H, 8.04; Te, 27.13. IR (Nujol, KBr plates): 2950 (s), 2926 (s), 2898 (m), 2873 (m), 2856 (m), 1458 (mw), 1438 (mw), 1411 (mw), 1384 (mw), 1364 (w), 1343 (w), 1300 (w), 1262 (m), 1250 (s), 1243 (s), 1069 (mw), 1034 (w), 999 (w), 907 (m), 837 (vs), 777 (m), 757 (m), 741 (m), 710 (m), 687 (m), 640 (mw), 581 (w) cm^{-1}. Far-IR (hexane solution, polyethylene cell): 527 (s), 402 (vs), 290 (s), 268 (m), 256 (m), 161 (s) cm^{-1}.

(Me_3SiCH_2)$_2$Te. (Me_3SiCH_2)$_2$Te was prepared on a 15-mmol scale in an analogous fashion as (Me_3SiCH_2)$_4$Te. After removal of the solvent at 35 °C, the remaining viscous yellow liquid was heated to 75 °C for about 1 h at 15 Torr. The crude product was collected in a −196 °C trap under vacuum and purified at 61–62 °C at 1 Torr to yield a pale-yellow liquid (2.4 g, 7.9 mmol, 53% yield based on $TeCl_4$). Anal. Calcd for $C_8H_{22}Si_2Te$: C, 31.81; H, 7.34; Te, 42.25. Found: C, 32.24; H, 6.85; Te, 42.55. IR (neat, KBr plates): 2953 (s), 2899 (m), 1445 (w), 1409 (m), 1384 (mw), 1365 (m), 1300 (w), 1259 (s), 1249 (vs), 1044 (m), 1019 (w), 979 (mw), 850 (vs), 836 (vs), 771 (m), 753 (m), 704 (m), 692 (m) cm^{-1}. Far-IR (neat, polyethylene cell): 527 (s), 508 (m), 267 (vs), 229 (s), 177 (w) cm^{-1}.

($CH_2{=}CH$)$_4$Te. To a stirring suspension of ground $TeCl_4$ (7.0 g, 26 mmol) in 30 mL of THF was added dropwise with stirring ($CH_2{=}CH$)MgBr (1.0 M in THF, 109 mL, 109 mmol) at −78 °C. The suspension turned brown initially and then yellow after the addition was complete. After stirring the yellow slurry for 2.5 h at room temperature, 10 mL of 1,4-dioxane was added to precipitate the Mg salts. The mixture was stirred for 45 min at room temperature, cooled to −78 °C, and then quickly filtered by using a coarse frit to yield a yellow supernatant. The white precipitate was washed with two 25-mL portions of hexane. The solvent of the combined solutions was fractionally distilled under vacuum at room temperature to yield an oily yellow residue. The product was then extracted with four 25-mL portions of pentane and filtered. The solvent was removed under vacuum, and the crude product was collected in a −196 °C trap. The product was stirred under vacuum (10 Torr) at room temperature for 1 h to remove traces of solvent. A pale-yellow fraction of ($CH_2{=}CH$)$_2$Te (0.11 g, 0.6 mmol, 2% yield based on $TeCl_4$) was collected at 3.5 Torr at 27–29 °C. ($CH_2{=}CH$)$_4$Te remained after ($CH_2{=}CH$)$_2$Te was removed. ($CH_2{=}CH$)$_4$Te is an extremely air- and moisture-sensitive yellow malodorous liquid (2.33 g, 9.9 mmol, 38% yield based on $TeCl_4$).

($CH_2{=}CH$)$_2$Te. ($CH_2{=}CH$)$_2$Te was prepared on a 26-mmol scale in an analogous fashion as ($CH_2{=}CH$)$_4$Te. The mixture was heated to 50 °C for 1 h in the dark prior to the addition of 1,4-dioxane. The slurry was cooled to −78 °C and quickly filtered by using a coarse frit. The precipitate was washed with two 50-mL portions of hexane. The solvents were removed by fractional distillation from the combined filtrate and washing. The product was collected by vacuum distillation at 34–35 °C (18 Torr) to yield an air- and light-sensitive pale-yellow liquid (1.42 g, 7.8 mmol, 30% yield based on $TeCl_4$). Anal. Calcd for C_4H_6Te: C, 26.44; H, 3.33; Te, 70.23. Found: C, 27.82; H, 3.61; Te, 69.97. ^1H, ^{13}C, and ^{125}Te NMR spectra were consistent with those in the literature.[8,26,27]

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Acknowledgment. We gratefully acknowledge financial support from the Office of Naval Research as well as the postdoctoral fellowship from the American Society for Engineering Education/Office of Naval Technology for R.W.G. We also thank J. H. Johnson and Drs. E. D. Erickson for the gas chromatography, M. P. Nadler for the FT-IR, and D. C. Harris for helpful comments and suggestions.

Metallacyclic Zirconoxycarbene Complexes from Metal Carbonyls and (η^2-Formaldehyde)zirconocene Dimer

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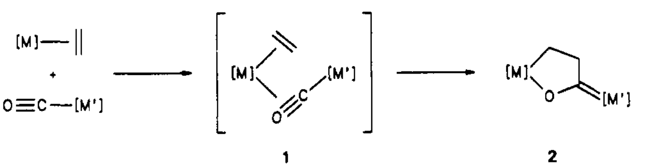
Received June 7, 1990

The metallatricyclic (η^2-formaldehyde)zirconocene dimer **10** reacts with metal carbonyl complexes $L_nM(CO)$ **4** [L_nM = $Mo(CO)_5$, $W(CO)_5$, $CpCo(CO)$, $CpRh(CO)$, $CpV(CO)_3$, $(C_6F_5)_2Pt(CO)$] to give the metallatricyclic zirconoxycarbene complexes $Cp_2Zr(\mu\text{-}OCH_2)ZrCp_2(\mu\text{-}OCH_2C[{=}ML_n]O)$ **12a–f** in good yield. In each case, only one of the two Cp_2ZrOCH_2 metallaoxirane units of **10** can be reacted with the [M]–C≡O functionality. Under equilibrium conditions, the oxygen atom in the five-membered metallacycle adjacent to the CH_2 group bridges the zirconium center of the Cp_2ZrOCH_2 structural subunit. In the photochemical-assisted $W(CO)_6$ addition to $[Cp_2Zr(\mu\text{-}OCH_2)]_2$, a mixture of regioisomeric zirconoxycarbene complexes **12b** and **16** is formed under kinetic control. In **16**, an oxonium type oxygen atom is adjacent to the carbene carbon center. The metallatricyclic zirconoxycarbene rhodium complex $Cp_2Zr(\mu\text{-}OCH_2)ZrCp_2(\mu\text{-}OCH_2C[{=}RhCp(CO)]O)$ (**12d**) was characterized by X-ray diffraction. Complex **12d** crystallizes in space group $P2_1/n$ with cell parameter a = 11.537 (2) Å, b = 26.442 (5) Å, c = 12.249 (2) Å, β = 92.00 (2)°, Z = 4, $R(F_o^2)$ = 0.051, and $R_w(F_o^2)$ = 0.083. The Rh=C(carbene) bond is rather short at 1.930 (5) Å.

Introduction

Heteroatom-stabilized transition-metal carbene complexes have found many uses as stoichiometric reagents or as catalysts for the transformation of organic substrates.[1] Many of these electrophilic carbene complexes can easily be prepared from metal carbonyls by employing E. O. Fischer's synthesis, i.e., by adding a nucleophile to the carbonyl carbon atom of the [M]—C≡O moiety followed by electrophilic O-alkylation.[2] We have introduced an essentially nonnucleophilic alternative for the [M]—C≡O to [M]—carbene interconversion that is often applicable in cases where the conventional carbene complex synthesis meets its limits. Here, very reactive metal (η^2-olefin) type complexes, especially of the early transition-metal elements or actinides, add to the [M]—C≡O unit to give an unstable CO-bridged bimetallic intermediate (**1**), which rapidly undergoes electrocyclic ring closure to directly give a metallacyclic metal oxycarbene complex (**2**).[3]



We originally employed conjugated diene group 4 metallocene complexes as reagents for this nonnucleophilic carbene complex synthesis.[4] In addition, we have shown that thermally generated (η^2-aryne)titanocene or -zirconocene species as well as (η^4-butadiene)$ThCp^*_2$ can be used.[5] Mashima et al.[6] have reacted (η^2-ethylene)$TiCp^*_2$[7] with several metal carbonyls to synthesize metal carbene complexes. Thiele et al. have employed the related (η^2-$CH_2{=}CH_2$)- and (η^2-CH≡CH)MCp_2 (M = Ti, Zr, Hf) complexes for this purpose.[8] Up to now, neither E. O.

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