Journal of Organometallic Chemistry, 212 (1981) 35—42
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

SYNTHESIS AND RAMAN SPECTRA OF UNSYMMETRICAL ORGANOTELLURIDES CONTAINING A TELLURIUM/GROUP IVA ELEMENT BOND ($ArTeMPh_3$; M = Ge, Sn, Pb)

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(Received September 16th, 1980)

Summary

A series of tellurium(II) compounds containing tellurium/Group IVA element bonds of the general formula $ArTeMPh_3$ (Ar = phenyl, *p*-tolyl, *p*-anisyl, *p*-bromophenyl; M = Ge, Sn, Pb) were prepared and examined by various chemical and spectroscopic means, including Raman spectroscopy, for characterization of metal—metal bond vibrations. These materials are air-stable, light-yellow solids, soluble in a variety of organic solvents, and an excellent source of the ArTe radical in reactions with transition metals. In reactions of these compounds with complexes of copper and palladium, the tellurium/Group IVA element bond was cleaved, with formation of transition metal complexes formulated as TeAr-bridged polymers.

Introduction

Although several tellurium(II) compounds containing Group IVA element bonds are known, most of these compositions are of the general type $R_3MTeM'R_3$ (where M, M' = Ge, Sn or Pb; R = alkyl or aryl) [1—8]. Two additional papers described the preparation of several mixed tellurium-tin compounds ($ArTeSnPh_3$) [9,10] and the reactions of these derivatives with cuprous chloride or bromide to form arylteliuro compounds of copper(I) [9]. Recently we synthesized and characterized several unsymmetrical organotellurium(II) derivatives [11] containing Ge, Sn or Pb. We now report the preparation and Raman characterization of these compounds and evaluate their utility as sources of $ArTe^-$ ligands in reactions with transition metal compounds.

Experimental

The unsymmetrical organotellurides were prepared in air, but all reactions of these compounds with transition metals were run under argon in Schlenk tubes.

Triphenylgermanium chloride, triphenyllead chloride, triphenyltin chloride and sodium borohydride were obtained from Alfa. Diphenyl ditelluride [12], dichlorobis(benzonitrile)palladium(II) [13] and cuprous chloride [14] were prepared by published procedures. All other compounds and solvents were obtained from Eastman Organic Chemicals. Melting points were recorded in air and are uncorrected.

Raman spectra were recorded on a Cary model 82 Raman spectrometer in the region from 50 to 4000 cm^{-1}. Compounds were excited at 647.1 and 676.4 nm with a Spectra-Physics (S-P) model 165 krypton ion laser. An argon laser (S-P) was used for the 514.5 nm excitation. A Coherent Radiation model 590 dye laser provided tuning in the 575 to 620 nm excitation range. For these samples, the following settings were generally optimum: 5 cm^{-1} bandwidth, 5 sec pen period, 10,000 or 20,000 cps sensitivity.

Spinning pressed discs of the solid samples were measured by Raman with the Cary spinning-sample accessory. This method greatly reduces absorption and heating effects by averaging the laser spot over a large sample area. A wide range of laser excitation was also used in the model-590 jet-stream laser. Rhodamine 6G laser dye was pumped with ~3—4 W (sum of all lines) from the argon gas laser. Owing to the large amount of collimated background fluorescence emission from the dye laser, it is necessary to use a premonochromator filtering system prior to sample irradiation. Instrumental modifications were made in the laser line filtering system to readily obtain excitation from any line with λ_0 between 450 and 680 nm. Many fluorescent plasma emission lines from the laser gas must also be eliminated to prevent interference with the Raman measurement.

Organotellurides containing Ge, Sn, or Pb were synthesized by the same general route, illustrated below for $Ph_3GeTeC_6H_5$. Relevant data on the other compounds synthesized are given in Table 1.

Synthesis of phenyl(triphenylgermyl)tellurium(II)

Diphenyl ditelluride (2.56 g, 6.25 mmol) was mixed with 3 ml of benzene and 9 ml of ethanol. The mixture was heated to reflux in a water bath, and a solution of sodium borohydride (0.38 g, 10 mmol) in 9 ml of 1 *N* sodium hydroxide was added dropwise. The reduction was complete when the red color of the ditelluride had disappeared. Triphenylgermanium chloride (5.1 g, 15 mmol) was then added quickly as a solid, and the reaction mixture was stirred for 5 min. It was then poured into 50 ml of water, and the resulting mixture was extracted with ether (3 × 70 ml). The ether extract was dried over anhydrous sodium sulfate, filtered and reduced to dryness. Recrystallization of the residue from hexane yielded 3.9 g (61%) of a yellow solid, m.p. 105—107°C.

Synthesis of bis(phenyltelluro)palladium(II)

$PhTeGePh_3$ (1.27 g, 2.5 mmol) was added to a solution of dichlorobis(benzonitrile)palladium(II) (0.48 g, 1.25 mmol) in 50 ml of chloroform. The reaction was stirred at room temperature for 24 h and filtered, and the precipitate was washed well with ether and dried to yield 0.55 g (85%) of a brown solid, m.p. 140—142°C. Analysis: Found: C, 27.7; H, 1.7; Pd, 20.5; Te, 46.1. $C_{12}H_{10}PdTe_2$ calcd.: C, 27.94; H, 1.95; Pd, 20.63; Te, 46.47%.

TABLE 1

ArTeMPh$_3$ COMPOUNDS (M = Ge, Sn, Pb)

Compound	Analysis Found (calcd.) (%)			Recryst. solvent	m.p. (°C)	Yield (%)
	C	H	Te[a]			
$C_6H_5TeGePh_3$	57.0 (56.68)	4.2 (3.96)	21.5 (25.09)	hexane	105—107	61
p-$CH_3C_6H_4TeGePh_3$	57.9 (57.45)	4.5 (4.24)	22.2 (24.41)	hexane	88—90	60
p-$CH_3OC_6H_4TeGePh_3$	55.9 (55.75)	4.1 (4.12)	20.1 (23.69)	hexane	89—91	23
$C_6H_5TeSnPh_3$	52.3 (51.97)	3.7 (3.63)	22.5 (23.00)	hexane	95—97	76
p-$CH_3C_6H_4TeSnPh_3$	53.6 (52.8)	4.0 (3.90)	19.7 (22.44)	hexane	78—80	61
p-$CH_3OC_6H_4TeSnPh_3$	51.2 (51.35)	3.9 (3.79)	21.9 (21.82)	hexane	78—80	65
$C_6H_5TePbPh_5$	45.4 (44.82)	3.2 (3.13)	17.9 (19.83)	hexane	90—92	75
p-$CH_3C_6H_4TePbPh_3$	45.8 (45.69)	3.4 (3.37)	15.7 (19.41)	hexane	87—89	67
p-$CH_3OC_6H_4TeGePh_3$	45.0 (44.60)	3.3 (3.29)	16.8 (18.95)	hexane	71—73	60
p-$BrC_6H_4TePbPh_3$	39.7 (39.92)	3.0 (2.65)	14.1 (17.67)	hexane	80—82	64

[a] Tellurium analyses were consistently poor for this series of compounds. This may be due to interference by the second metal in the compound.

Synthesis of phenyltellurocopper(I)

PhTeGePh$_3$ (1.27 g, 2.5 mmol) and cuprous chloride (0.25 g, 2.5 mmol) were mixed in 75 ml of chloroform. The reaction was stirred at room temperature for 24 h and filtered, and the precipitate was washed well with ether and dried to yield 0.3 g (45%) of a red-brown solid, m.p. 115—117°C. Analysis: Found: C, 26.5; H, 1.9; Cu, 23.4; Te, 47.1. C_6H_5CuTe calcd.: C, 26.87; H, 1.88; Cu, 23.69; Te, 47.57%.

Results and discussion

Compounds of the type ArTeMPh$_3$ have been prepared by the reductive cleavage of the appropriate diaryl ditelluride followed by reaction with the Group IVA organometallic chloride:

$$TeCl_4 + HAr \text{ (or } ArHgCl) \rightarrow ArTeCl_3 + HCl \text{ (or } HgCl_2)$$

$$\left.\begin{array}{l} ArTeCl_3 \xrightarrow[K_2S_2O_5]{\text{reduction}} \\ \text{or} \\ ArLi \xrightarrow[2)HCl/O_2]{1)Te^0} \end{array}\right\} Ar_2Te_2$$

$$Ar_2Te_2 \xrightarrow[NaBH_4]{NaOH} NaTeAr \xrightarrow[M=Ge,Sn,Pb]{Ph_3MCl} ArTeMPh_3$$

The diaryl ditellurides were prepared by reduction of the aryltellurium trichloride, prepared by reaction of $TeCl_4$ with the aromatic compound (Ar = p-$CH_3OC_6H_4$) or an arylmercuric chloride (Ar = p-$CH_3C_6H_4$), and by oxidative hydrolysis of the ArTeLi derivative (Ar = p-BrC_6H_4, C_6H_5), the synthetic route being chosen on the basis of experimental convenience for a given derivative [15]. In general, the syntheses proceeded in good yield (60—80%) and gave analytically pure products after one or two recrystallizations from an organic solvent. Table 1 lists the compounds that were prepared, along with their melting points and analytical data.

Most of these compounds are new; the only other mixed organotellurium/main group element bonded compounds (where M is Ge, Sn or Pb) known are $Et_3GeTeEt$ [16,17] and $Ph_3SnTeAr$ (Ar = phenyl, p-anisyl, p-ethoxyphenyl and p-phenoxyphenyl) [10]. $Et_3GeTeEt$ was synthesized from reaction of Et_3GeH and Et_2Te at 140° C, an additional product being the symmetrical compound $(Et_3Ge)_2Te$ [16,17]. The reactivity of such hydrides towards diethyltelluride increases in the order $Si < Ge << Sn$; thus a similar reaction between Et_2Te and Et_3SnH yielded only the symmetrical compound $(Et_3Sn)_2Te$. $Ph_3SnTeAr$ has been prepared from reaction of the diaryl ditelluride and triphenyltin hydride [10].

An attempt to prepare $Ph_3SiTePh$ and Ph_3CTePh by our general method outlined above was unsuccessful.

The unsymmetrical tellurides listed in Table 1 were isolated as stable, colorless to light yellow, low-melting (70—110° C) solids, soluble in common organic solvents (chloroform, acetone, benzene, hexane).

The thermal stability of each of the compounds was evaluated (Table 2). In general, the melting point (T_m) (as determined by DSC) is low, but the temperature at which the compounds decompose is high (250—275° C; exceptions are $Ph_3PbTePh$ and $Ph_3PbTeC_6H_4p$-CH_3). Also noteworthy is the percentage residue remaining for each sample after thermal decomposition. This number increases in the order $Ge < Sn < Pb$ compounds and indicates that the tin and lead compounds deposit more metallic or binary compound residue on decomposition.

Laser-Raman spectroscopy was used to characterize the Te—M bonds by the very strong low-frequency Raman modes expected in the 50—250 cm^{-1} region

TABLE 2

THERMAL STABILITY OF $ArTeMPh_3$ COMPOUNDS (M = Ge, Sn, Pb)

Compound	T_m (°C)	$T_{gross\ dec}$ (°C)	% Residue at T (°C)
$C_6H_5TeGePh_3$	112	261	3 (452)
p-$CH_3C_6H_4GeGePh_3$	95	252	2 (374)
p-$CH_3OC_6H_4TeGePh_3$	78	261	2 (485)
$C_6H_5TeSnPh_3$	103	270	12 (485)
p-$CH_3C_6H_4TeSnPh_3$	81	274	10 (485)
p-$CH_3OC_6H_4TeSnPh_3$	80	252	10 (485)
$C_6H_5TePbPh_3$	96	157	22 (485)
p-$CH_3C_6H_4TePbPh_3$	83	154	22 (485)
p-$CH_3OC_6H_4TePbPh_3$	79	207	18 (419)
p-$BrC_6H_4TePbPh_3$	96	207	22 (485)

TABLE 3

RAMAN BANDS CHARACTERISTIC OF METAL—METAL VIBRATIONS IN $ArTeMPh_3$ COMPOUNDS (M = Ge, Sn, Pb) WITH TYPICAL UV ABSORPTION BAND MAXIMA

Compound	Raman (solid) ν(MTe) (cm^{-1})	UV (nm in $CHCl_3$)
$C_6H_5TeGePh_3$	173	322
p-$CH_3OC_6H_4TeGePh_3$	182	
$C_6H_5TeSnPh_3$	161	325
p-$CH_3C_6H_4TeSnPh_3$	164	
p-$CH_3OC_6H_4TeSnPh_3$	168	
$C_6H_5TePbPh_3$	147	377
p-$CH_3C_6H_4TePbPh_3$	154	
p-$CH_3OC_6H_4TePbPh_3$	153	
p-$BrC_6H_4TePbPh_3$	156	
$(Ph_3Ge)_2Te$ [a]	167	
$(Ph_3Sn)_2Te$ [b]	153	
$(Ph_3Pb)_2Te$ [c]	113	
$(Me_3Ge)_2Te$ [d]	236	
$(Me_3Sn)_2Te$ [d]	191	
$(Me_3Pb)_2Te$ [d]	161	

[a] Ref. 3. [b] Ref. 1. [c] Ref. 2. [d] Ref. 21.

for these metal—metal interactions [18—20]. The intense metal—metal Raman bands are listed in Table 3 along with some typical absorption maxima in the UV for these compounds. Raman spectra obtained for this study were excited far from these electronic absorptions, and a spinning-sample technique was used with a defocussed laser beam. These methods were used to avoid photolytic or thermal sample decomposition. In addition, the samples were laser excited at 514.5 nm (Ar^+), at 590 nm (Rh-6G dye), and at 676.4 nm (Kr^+) to ensure consistent Raman results over this wide wavelength range. Figure 1 shows Raman spectra of the Ph_3MTePh compounds with 514.5 nm excitation; similar results, except for some relative intensity variations, were also obtained using low-power excitation (45 mW) at 676.4 nm. The strongest low-frequency bands in Fig. 1 reveal the M—Te vibrations at 147 cm^{-1} (Pb—Te), 161 cm^{-1} (Sn—Te) and 173 cm^{-1} (Ge—Te); this trend towards higher frequency M—Te vibrations moving up Group IVA (Pb $<$ Sn $<$ Ge) is consistent with the studies of Schumann et al. [19] on M—Te bonding. Results and trends presented here are also consistent with those observed by Spiro [18] and others [20] on Ge, Sn and Pb compounds.

Further information on Raman spectra of M—Te bands was obtained using the known symmetric model compounds: $Ph_3MTeMPh_3$ (M = Ge, Pb, Sn) [1—3]. Figure 2 shows spectra of these symmetric compounds. The very intense symmetrical M—Te—M (ν_s) bond vibrations appear at 113 cm^{-1} (Pb—Te—Pb), 153 cm^{-1} (Sn—Te—Sn) and 167 cm^{-1} (Ge—Te—Ge), which is a trend similar to that of the $(Me_3M)_2Te$ series [21] noted in Table 3. In Figs. 1 and 2 the Raman pattern for the monosubstituted phenyl groups [22] appears at higher frequencies with ring bending near 650 cm^{-1}, symmetric ring stretching near 1000 cm^{-1}, and ring deformation centered near 1575 cm^{-1}. A strong phenyl C—H band was also observed near 3050 cm^{-1} in the Raman spectra of all of these compounds.

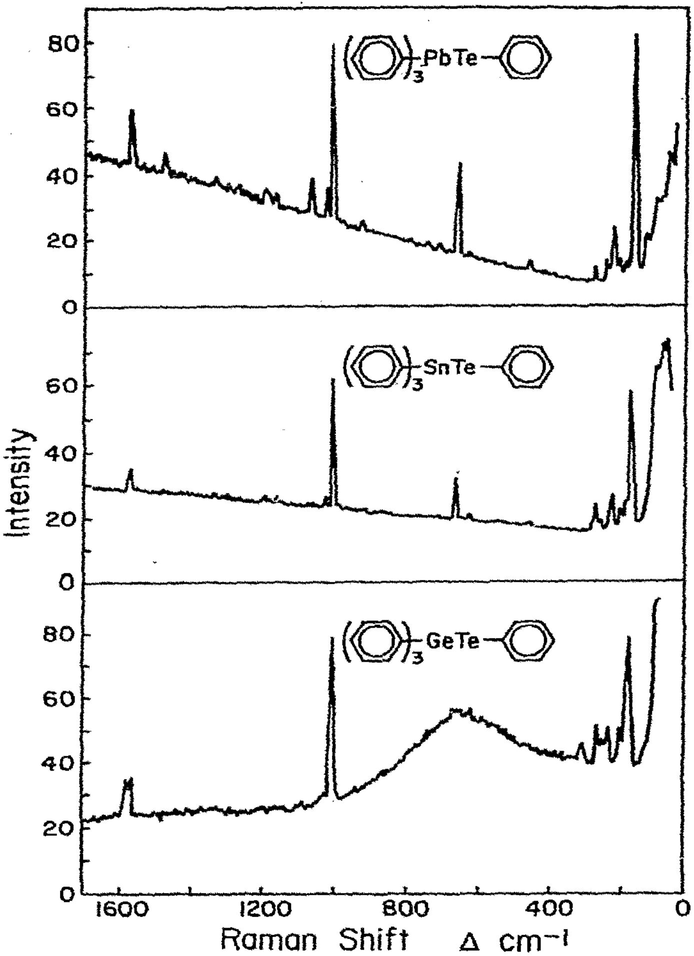

Fig. 1. Raman spectra of spinning solid samples of Ph_3MTePh (M = Pb, Sn, Ge). Resolution is 5 cm^{-1} with 514.5 nm excitation at 160 mW laser power.

The potential of these organotellurium compounds to function as ligands for various transition metals was evaluated. Unlike the diaryl [23,24] or dialkyl tellurides [23,25], which easily substitute for the labile benzonitrile ligand in dichlorobis(benzonitrile)palladium(II) to form four-coordinate complexes, these unsymmetrical metal—metal bonded tellurides react with cleavage of the Te—Ge or Te—Sn bond.

$$(PhCN)_2PdCl_2 + \begin{array}{c} ArTeGePh_3 \\ \text{or} \\ ArTeSnPh_3 \end{array} \rightarrow \begin{array}{c} Pd(ArTe)_2 + Ph_3MCl \\ (M = Ge, Sn) \end{array}$$

Reaction is immediate upon mixing of the two starting materials in chloroform, and the products, $Pd(TeAr)_2$, are isolated as dark red-brown, insoluble materials with melting points ~150°C. These materials are likely polymeric, although this cannot be verified experimentally because the insolubility of the com-

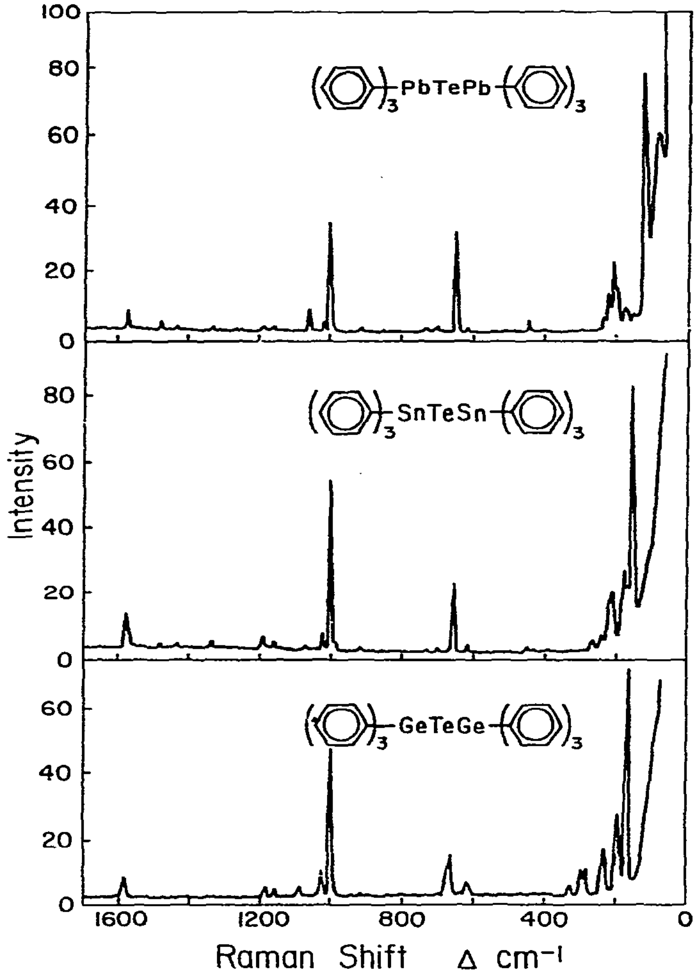

Fig. 2. Raman spectra of the $Ph_3M—Te—MPh_3$ compounds. Intense ν_S symmetric stretches of M—Te—M bonds are recorded below 200 cm^{-1}. Resolution is 5 cm^{-1} with 590 nm dye-laser excitation at 53 mW power.

pounds precluded molecular-weight measurements in solution. The formation of $Pd(TeAr)_2$ from similar reactions of dichlorobis(benzonitrile)palladium(II) and the telluroesters (ArTeCOAr') has been observed [26]. The exact mechanism of this reaction is unknown, although it is likely that an unstable intermediate $[(Ph_3MTeAr)_2PdCl_2$ or $(ArTeCOAr')_2PdCl_2]$ decomposes with formation of $Pd(TeAr)_2$ and the chloride-containing by-products. The reaction of Ph_3Pb-TePh with $(PhCN)_2PdCl_2$ was also studied, but the product(s) were unidentified.

Related dimeric complexes with both terminal and bridging $ArTe^-$ ligands have been prepared by oxidative addition reactions of $Pd(PPh_3)_4$ [24] and diaryl ditellurides ($[Pd(PPh_3)(TeAr)_2]_2$; Ar = 2-thienyl, p-EtO-C_6H_4).

Reactions of Ph_3MTePh with cuprous chloride (M = Ge, Sn, Pb) gave a red-brown insoluble solid, CuTePh, which is thought to contain bridging TeAr ligands in a polymeric structure.

$$Ph_3MTePh + CuCl \xrightarrow[\text{room temp.}]{CHCl_3} (CuTePh)_n$$

Analogous polymeric complexes with alkyl tellurol ligands [$(CuTeR)_n$; R = Et, n-Bu, n-C_5H_{11}] [27] have been prepared by reaction of NaTeR (generated in situ by borohydride cleavage of R_2Te_2) with CuCl in ethanol.

We are continuing our investigation of the utility of these organotellurium derivatives as reagents in tellurium ligand chemistry.

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