Ylide-Metal Complexes. XI.[1] The Preparation and Properties of VIA Group Metal (Te) Complexes of Alkylidenetriphenylphosphoranes and the Corresponding Selenium Compounds

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Reactions of $(C_6H_5)_3P{=}CH_2$ (**L**) with $TeCl_4$ of mole ratios 2 : 1 and 3 : 1 yield new compounds: dichlorobis(methylenetriphenylphosphorane)tellurium dichloride, $[L_2TeCl_2]Cl_2$ (**1**), and chlorotris(methylenetriphenylphosphorane)tellurium trichloride, $[L_3TeCl]Cl_3$ (**2**), respectively. The reaction of ylide **L** with compound **1** yields a new compound: tetrakis(methylenetriphenylphosphorane)tellurium tetrachloride, $[L_4Te]Cl_4$ (**3**). The structure of compounds **1**—**3** is a distorted tetrahedron. The color of **1**—**3** is yellow. The electronic absorption spectra of compounds **2** and **3** show six absorption bands in the region 200—500 nm in dry dichloromethane. The reactions of ylide **L** with $(C_6H_5)_2SeCl_2$ of mole ratios 1 : 1 and 2 : 1 yield new compounds: chloro(methylenetriphenylphosphorane)diphenylselenium chloride, $[LSe(Cl)(C_6H_5)_2]Cl$ (**9**), and bis(methylenetriphenylphosphorane)diphenylselenium dichloride, $[L_2Se(C_6H_5)_2]Cl_2$ (**11**), respectively. The color of the selenium compounds is white. The tellurium and selenium compounds are thermally stable in the solid state.

A previous paper[2] of this series was concerned with a study of methylenetriphenylphosphorane, bis(methylenetriphenylphosphorane)gold(I) chloride and the corresponding copper(I) chloride by X-ray photoelectron spectroscopy. Also, we have been concerned with the preparation, properties and structures of ylide-metal complexes for I—IV group metals with unstable phosphoranes.[3-6] In the VIA group, the preparation of several selenium compounds with phosphoranes, $(C_6H_5)_3P{=}CHR$ (R: H, CH_3, SC_6H_5), has been reported.[7-10] However, the preparation of a tellurium compound with phosphorane has not been reported except for a tellurium compound with stable (ethoxycarbonylmethylene)triphenylphosphorane,[11,12] $(C_6H_5)_3P{=}CHCOOC_2H_5$. Very little is known of the preparation, properties and structures of selenium and tellurium compounds with phosphoranes[3,13-15] and arsoranes.[16,17] Thus, the present paper deals with the preparation and properties of dichlorobis(methylenetriphenylphosphorane)tellurium dichloride, $[\{(C_6H_5)_3PCH_2\}_2TeCl_2]Cl_2$, chlorotris(methylenetriphenylphosphorane)tellurium trichloride, $[\{(C_6H_5)_3PCH_2\}_3TeCl]Cl_3$, and tetrakis(methylenetriphenylphosphorane)tellurium tetrachloride, $[\{(C_6H_5)_3PCH_2\}_4Te]Cl_4$, and deals with the preparation of chloro(methylenetriphenylphosphorane)diphenylselenium chloride, $[(C_6H_5)_3PCH_2Se(Cl)(C_6H_5)_2]Cl$, and bis(methylenetriphenylphosphorane)diphenylselenium dichloride, $[\{(C_6H_5)_3PCH_2\}_2Se(C_6H_5)_2]Cl_2$.

Experimental

Measurements. The NMR spectra were measured with an R-40 (Hitachi) spectrometer, XL-200 (Varian) spectrometer for ^1H NMR, and with an FX-60 spectrometer (JEOL) for ^{13}C NMR. The electric conductivities of the solutions were determined by the use of a conductometric meter, CM-30 (Shimadzu) in dry methanol and dry dichloromethane. The electronic absorption spectra were recorded with a Shimadzu UV-210 recording spectrophotometer.

Starting Material. The methylene-[18] and ethylidene[19] triphenylphosphorane were prepared from the corresponding phosphonium bromide by the sodium amide method.

Preparation of Ylide-Metal Complexes. Dichlorobis(methylenetriphenylphosphorane)tellurium Dichloride (1): The methylene ylide (0.43 g, 1.56 mmol) was dissolved in dry THF (20 cm^3) at 0 °C under nitrogen. The THF solution was added to powder $TeCl_4$ (0.2 g, 0.74 mmol) at 0 °C. The mixture was stirred for 10 min at 0 °C. The precipitated light yellow complex was filtered and dried under vacuum. Yield: 0.50 g (82%). Decomp: 124 °C. Found: C, 56.00; H, 4.35%. Calcd for $C_{38}H_{34}P_2TeCl_4$ (MW 822.04) C, 55.52; H, 4.17%.

Chlorotris(methylenetriphenylphosphorane)tellurium Trichloride (2): The dry THF (20 cm^3) solution of methylene ylide (0.47 g, 1.70 mmol) was added to powder $TeCl_4$ (0.15 g, 0.56 mmol) under nitrogen. The mixture was stirred at room temperature for 1 d. The precipitated yellow complex was filtered, washed with pentane and dried under vacuum. Yield: 0.52 g (85%). Decomp: 106 °C. Found: C, 62.24; H, 5.01%. Calcd for $C_{57}H_{51}P_3TeCl_4$ (MW 1098.36) C, 62.33; H, 4.68%. Electronic absorption spectrum: 240 nm (ε=13100), 260 (9200), 267 (10100), 274 (8530), 350 (730), and 435 (1630) in dry dichloromethane. Λ=193 S cm^2 mol^{-1} in dry methanol solution at 19 °C; a 29.4 mg sample was dissolved 27-cm^3 of dry methanol. Complex **2** was also prepared from the reaction mixture of ylide and $TeCl_4$ in a mole ratio of 4:1 in THF.

Tetrakis(methylenetriphenylphosphorane)tellurium Tetrachloride (3): The dry THF (20 cm^3) solution of methylene ylide (0.31 g, 1.12 mmol) was added to powder $TeCl_4$ (0.15 g, 0.56 mmol) at 0 °C. The mixture was stirred for 10 min at 0 °C. Then, the THF solution (10 cm^3) of methylene ylide (0.34 g, 1.23 mmol) was added to the reaction mixture at 0 °C under nitrogen. The mixture was stirred for 150 min at room temperature. A deep-yellow complex was filtered, washed with pentane and dried. Yield: 0.63 g (82%). Decomp: 116 °C. Found: C, 66.15; H, 5.20%. Calcd for $C_{76}H_{68}P_4TeCl_4$ (MW 1374.67) C, 66.40; H, 4.99%. Electronic absorption spectrum: 238 nm (ε=18300), 262 (13000), 267 (14200), 275 (11700), 360 (900), and 447 (2030) in dry dichloromethane. Λ=328 S cm^2 mol^{-1} in dry methanol solution at 19 °C; a 34.9 mg sample was dissolved 25-cm^3 of dry methanol. Λ=75 S cm^2 mol^{-1} in dry dichloromethane solution at 21 °C; a 49.6 mg sample was dissolved in dry dichloromethane 36 cm^3.

Chloro(methylenetriphenylphosphorane)diphenylselenium Chloride (9): Diphenylselenium dichloride (0.19 g, 0.62

Table 1. ^1H and ^{13}C NMR Data of Complexes and Ylide

^1H	CH_2P		C_6H_5	Solvents
	δ/ppm	$^2J_{HCP}$/Hz	δ/ppm	
1	3.15 d (2H)	13.7	7.4—8.1 m (15H)	CD_2Cl_2
2	3.20 d (2H)	13.7	7.4—7.9 m (15H)	CD_2Cl_2
	2.94 d (2H)	14.0	7.5—8.0 m (15H)	CD_3OD
3	3.30 d (2H)	13.7	7.3—8.0 m (15H)	CD_2Cl_2
	2.93 d (2H)	14.0	7.5—8.0 m (15H)	CD_3OD
L[a]	−0.13 d (2H)	7.5	6.2—7.2 m (15H)	C_6D_6[b]

^{13}C	CH_2P		C_6H_5 δ/ppm (J_{CP}/Hz)			
	δ/ppm	J_{CP}/Hz	c-1	*o*	*m*	*p*
1	10.56 d	55.7	119.4 (87.9)	133.5 (10.7)	130.5 (13.7)	135.2 (2.9)
2	10.36 d	57.6	119.6 (87.9)	133.6 (10.7)	130.4 (12.7)	135.2 (3.9)
3	10.30 d	55.7	119.6 (87.9)	133.5 (9.8)	130.4 (11.8)	135.1 (2.9)
L[c]	−4.3 d	98.6				

Standard: ^1H NMR; internal TMS (δ=0), ^{13}C NMR; CD_2Cl_2 (δ=53.6 ppm). Solvent: CD_2Cl_2. a): Ref. 27; b): external TMS (δ=0); c): Ref. 6.

mmol) was added to a dry THF solution (8 cm^3) of methylene ylide (0.17 g, 0.62 mmol) under nitrogen. The mixture was stirred for 20 h. Then, the precipitated compound was filtered, washed with ether and dried. Yield: 0.19 g (52%). Decomp: 162 °C. Found: C, 64.48; H, 4.93%. Calcd for $C_{31}H_{27}PSeCl_2$ (MW 580.39) C, 64.15; H, 4.69%.

Chloro(ethylidenetriphenylphosphorane)diphenylselenium Chloride (10): Diphenylselenium dichloride (0.23 g, 0.76 mmol) was added to a dry THF solution (8 cm^3) of ethylidene ylide (0.25 g, 0.86 mmol) under nitrogen. The mixture was stirred for 18 h at room temperature. The precipitated white compound was filtered, washed with ether and dried. Yield: 0.28 g (62%). Decomp: 160 °C. Found: C, 64.35; H, 4.79%. Calcd for $C_{32}H_{29}PSeCl_2$ (MW 594.42) C, 64.66; H, 4.92%.

Bis(methylenetriphenylphosphorane)diphenylselenium Dichloride (11): Diphenylselenium dichloride (0.19 g, 0.62 mmol) was added to a dry THF solution (8 cm^3) of methylene ylide (0.37 g, 1.34 mmol) under nitrogen. The mixture was stirred for 1 d. The precipitated compound was filtered, washed with ether and dried. Yield: 0.28 g (52%). Decomp: 203 °C. Found: C, 70.35; H, 5.34%. Calcd for $C_{50}H_{44}P_2SeCl_2$ (MW 856.71) C, 70.10; H, 5.18%.

Bis(ethylidenetriphenylphosphorane)diphenylselenium Dichloride (12): Diphenylselenium dichloride (0.19 g, 0.62 mmol) was added to a dry THF solution (10 cm^3) of ethylidene ylide (0.40 g, 1.38 mmol) under nitrogen. The mixture was stirred for 20 h. The precipitated compound was filtered, washed with ether and dried. Yield: 0.30 g (54%). Decomp: 193 °C. Found: C, 70.43; H, 5.54%. Calcd for $C_{52}H_{48}P_2SeCl_2$ (MW 884.76) C, 70.59; H, 5.47%.

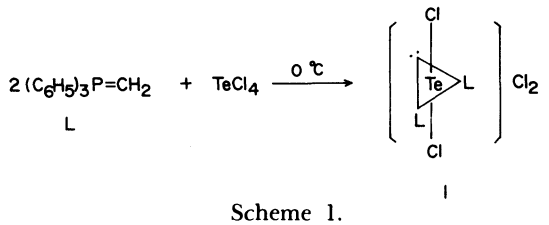
Results and Discussion

Dichlorobis(methylenetriphenylphosphorane)tellurium dichloride, $[\{(C_6H_5)_3PCH_2\}_2TeCl_2]Cl_2$ (**1**), and chlorotris(methylenetriphenylphosphorane)tellurium trichloride, $[\{(C_6H_5)_3PCH_2\}_3TeCl]Cl_3$ (**2**), were isolated from the reaction mixtures of methylenetriphenylphosphorane, $(C_6H_5)_3P{=}CH_2$ (**L**), and $TeCl_4$ in mole ratios of 2:1 and 3:1, respectively. Tetrakis(methylenetriphenylphosphorane)tellurium tetrachloride, $[\{(C_6H_5)_3PCH_2\}_4Te]Cl_4$ (**3**), was isolated from a reaction mixture of **L** and complex **1** in a mole ratio of 2:1. Complexes **1**—**3** are soluble in chloroform, dichloromethane, DMF, DMSO and water, but are insoluble in benzene, tetrahydrofuran (THF), pentane and ether. Complexes **1**—**3** in water give phosphonium chloride, $[(C_6H_5)_3PCH_3]Cl$ (**4**). Complexes **2** and **3** are stable in alcohols, though complex **1** is unstable. Their color is yellow, and they are thermally stable in the solid state.

The ^1H NMR spectra of **1**—**3** showed a doublet signal for methylene group at 2.9—3.3 ppm and a multiplet signal for phenyl groups at 7.4—8.1 ppm in a ratio of 2:15 at room temperature in dichloromethane-d_2. The coupling constant ($^2J_{HCP}$) of the methylene group is larger than that of **L**, and the chemical shift is at a lower field than that of **L** as is shown in Table 1. In the ^{13}C NMR spectra in dichloromethane-d_2, the chemical shift for methylene group is at a lower field than that of **L**, and the coupling constant (J_{CP}) for methylene group is smaller than that of **L** as is shown in Table 1. These spectral properties were similar to those of bis(methylenetriphenylphosphorane)-metal chloride, $[(C_6H_5)_3PCH_2\text{-}M\text{-}CH_2P(C_6H_5)_3]Cl_2$ (**5**) (M: IIB group metals),[5] and the corresponding ylide-metal complexes such as $[(C_6H_5)_3PCH_2\text{-}M\langle^{Cl}_{Cl}\rangle M\text{-}CH_2P(C_6H_5)_3]Cl_2$ (**6**) (M: IIA group metals)[3] and $[(C_6H_5)_3PCH_2\text{-}M(C_6H_5)_3]Cl$ (**7**) (M: IVA group metals).[4] Thus, the ylide in complexes **1**—**3** is bonded to the metal atom through the carbanionic donor atom.[19]

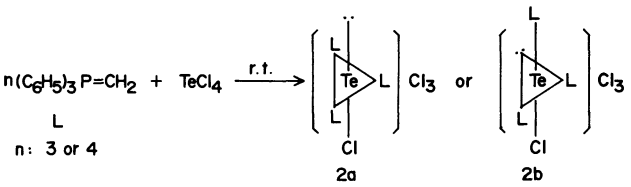
Complex **1** is not polymeric[20] since it is soluble in dichloromethane. The elemental analysis of **1** agreed with that of L_2TeCl_4. The structures of $TeCl_4$[21,22] and $(C_6H_5)_2TeBr_2$[23,24] (**8**) were found to be monomeric

distorted tetrahedrons by X-ray diffraction, i.e., the observed bond angles were 178.0±0.2° for Br–Te–Br and 96.3±1.2° for C–Te–C. Two bromine atoms in **8** are bonded to the axial positions and are at a position cis for the lone pair. Thus, we suggest that the structure of **1** is a distorted tetrahedron as is shown in Scheme 1.



Scheme 1.

Complex **2** is not polymeric[20] since it is soluble in dichloromethane and alcohols. The elemental analysis of **2** agreed with that of L_3TeCl_4. Complex **2** has free anion, judging from the molar conductance (cf. Experimental section). Thus, the structure of **2** is either **2a** or **2b** (distorted tetrahedron) as is shown in Scheme 2. We believe that the structure of **2** is **2a**:



Scheme 2.

The chlorine atoms in complex **1** are substituted with ylides, and complex **1** changes to complex **3** (described below) which is not obtained from the reaction mixture of ylide and $TeCl_4$ in the mole ratio 4:1. This difference is due to the configuration (cis or trans) between the chlorine atom and lone pair in the complex. Thus, the chlorine atom in the position cis for the lone pair can be substituted with ylide. This was confirmed in the preparation of complexes **9**—**11** (described below), which were obtained from the mixture of ylide and diphenylselenium dichloride since the chlorine atoms in diphenylselenium dichloride are in a position cis for the lone pair according to X-ray diffraction.[24,25] Thus, the chlorine atom in **2** might be in a position trans to a lone pair such as **2a**.

Complex **3** is not polymeric[20] since it is soluble in dichloromethane and alcohols. The elemental analysis of **3** agreed with that of L_4TeCl_4. Complex **3** has free anion, judging from the molar conductance. Complex **3** has been isolated only from a reaction mixture of **L** and complex **1** in the mole ratio 2:1. Thus, we suggest that the structure of **3** is a distorted tetrahedron as is shown in Scheme 3.

The electronic absorption spectra of the ylide metal complexes were observed. The spectra of **2** and **3** showed six absorption bands in dry dichloromethane as

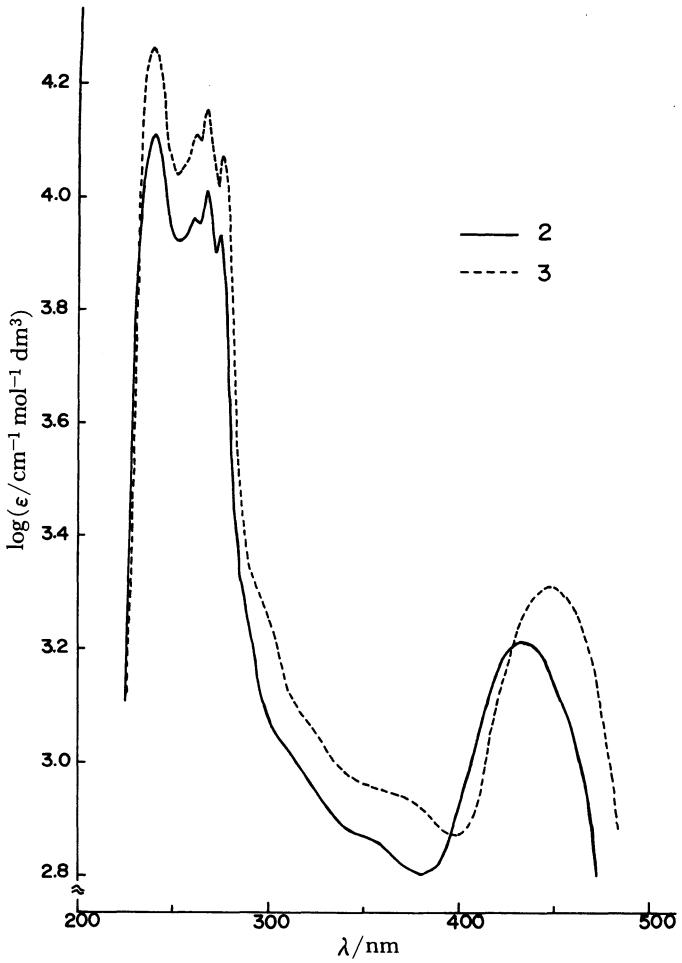
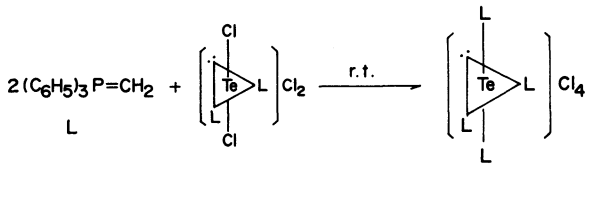


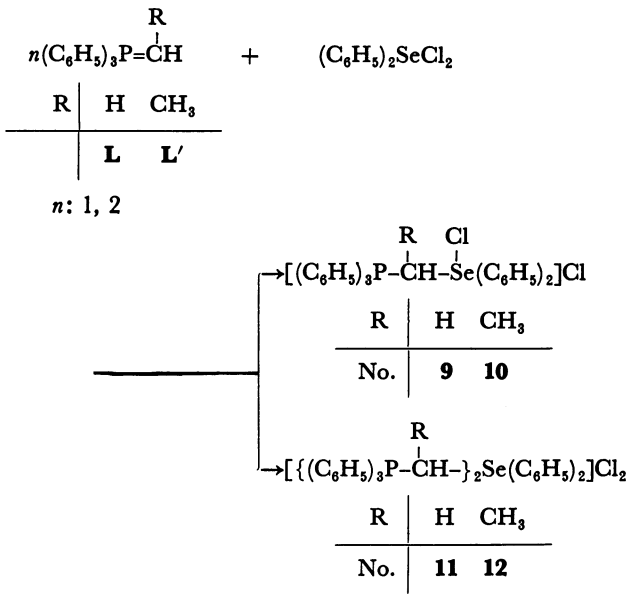
Fig. 1. The electronic absorption spectra of **2** and **3** complexes in dichloromethane.
2: $[\{(C_6H_5)_3PCH_2\}_3TeCl]Cl_3$. **3**: $[\{(C_6H_5)_3PCH_2\}_4Te]Cl_4$.



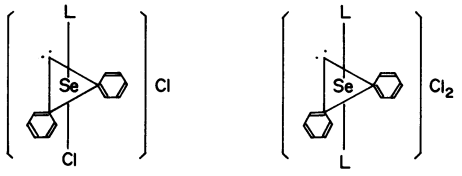
Scheme 3.

is shown in Fig. 1 and Experimental section. The absorption band at 435 nm or 447 nm can be assigned to the charge-transfer band. The absorption spectra[26] for phosphoranes did not show in the 400—500 nm region.

Chloro(methylene(or ethylidene-)triphenylphosphorane)diphenylselenium chloride (**9**, **10**) and bis(methylene(or ethylidene-)triphenylphosphorane)diphenylselenium dichloride (**11**, **12**) have been isolated from the reaction mixtures of diphenylselenium dichloride and methylene ylide (**L**) or ethylidenetriphenylphosphorane, $(C_6H_5)_3P=CH(CH_3)$ (**L'**), in the mole ratio 1:1 or 1:2.



They are soluble in alcohols, dichloromethane, chloroform, water, DMSO and DMF, but insoluble in benzene and acetone. The ^{1}H NMR spectra of **9—12** could not be observed since compounds **9—12** are unstable in alcohols, dichloromethane and chloroform at −80 °C and give the corresponding phosphonium salt (**4**). However, their decomposition temperatures differ from the melting points of the ylides **L** and **L'** and salt **4**. Their color is white, and they are thermally stable in the solid state. The elemental analyses of **9—10** and **11—12** agreed with those of [(**L** or **L'**)Se(Cl)(C_6H_5)$_2$]Cl, and [(**L** or **L'**)$_2$Se(C_6H_5)$_2$]Cl_2, respectively. Thus, the ylides are bonded to the Se atom in the solid state such as complexes **6** and **7**.[3,4] The structures of diphenylselenium dibromide, (C_6H_5)$_2$$SeBr_2$[24] (**13**), and di(*p*-tolyl)selenium dibromide, (*p*-$CH_3C_6H_4$)$_2$-$SeBr_2$[24,25] (**14**), and the corresponding dichloride[24,25] have been found to be monomeric distorted tetrahedron by X-ray diffraction. The observed C-Se-C bond angles were ca. 110° and the observed X-Se-X bond angles were ca. 180°; therefore two halogen atoms are in the position *cis* for the lone pair. Thus, the chlorine atoms in diphenylselenium dichloride are substituted with ylides, and complexes **9—12** are formed. From the above, we suggest that the structure of **9—12** is a distorted tetrahedron as is shown in Scheme 4.



9 11

Scheme 4.

The different characteristics between tellurium complexes **1—3** and selenium compounds **9—12** are their colors and stabilities in solution. The color of tellurium complexes is yellow, but that of the selenium compounds is white. The tellurium complexes are stable in methanol and dichloromethane at room temperature, but the selenium compounds are unstable in alcohols and dichloromethane at −80 °C.

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