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Ylide-Metal Complexes. XIV.[1] An X-Ray Photoelectron Spectroscopic Study on Tellurium Complexes of Methylenetriphenylphosphorane

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Synopsis. A series of new tellurium complexes of methylenetriphenylphosphorane, $(C_6H_5)_3P=CH_2$ (**L**), namely, dichlorobis(methylenetriphenylphosphorane)tellurium dichloride, $[L_2TeCl_2]Cl_2$, chlorotris(methylenetriphenylphosphorane)tellurium trichloride, $[L_3TeCl]Cl_3$, and tetrakis(methylenetriphenylphosphorane)tellurium tetrachloride, $[L_4Te]Cl_4$, were examined by XPS. Binding energies of Te 3d electrons for the complexes are considerably lower than those for common Te(IV) compounds such as $(C_6H_5)_2TeCl_2$, $TeCl_4$ (correctly Te_4Cl_{16}) and others, and they diminished with increasing number of **L**'s and decreasing number of bonded chlorine atoms, indicating that **L** is an electron donor. Bonded chlorine atoms and free chloride ions were clearly distinguished from the binding energy of Cl $2p_{3/2}$ electrons.

The preparation and properties of ylide metal complexes have been widely investigated in recent years. However, the electronic states of ylide metal complexes have not been reported except for the Cu and Au complexes.[1,2] In a previous paper,[3] we reported a series of new tellurium complexes of methylenetriphenylphosphorane, $(C_6H_5)_3P=CH_2$ (**L**), namely, dichlorobis(methylenetriphenylphosphorane)tellurium dichloride, $[L_2TeCl_2]Cl_2$, chlorotris(methylenetriphenylphosphorane)tellurium trichloride, $[L_3TeCl]Cl_3$, and tetrakis(methylenetriphenylphosphorane)tellurium tetrachloride, $[L_4Te]Cl_4$. The present paper deals with the electronic states of the above tellurium complexes by means of X-ray photoelectron spectroscopy (XPS).

Experimental

Preparation of dichlorobis(methylenetriphenylphosphorane)tellurium(IV) dichloride, $[\{(C_6H_5)_3P=CH_2\}_2TeCl_2]Cl_2$ (**1**), chlorotris(methylenetriphenylphosphorane)tellurium(IV) trichloride, $[\{(C_6H_5)_3P=CH_2\}_3TeCl]Cl_3$ (**2**), and tetrakis(methylenetriphenylphosphorane)tellurium(IV) tetrachloride, $[\{(C_6H_5)_3P=CH_2\}_4Te]Cl_4$ (**3**), were carried out as reported previously.[3]

For XPS measurements, samples were placed on a gold mesh holder and introduced into a spectrometer in a 99.9995% pure nitrogen atmosphere. After evacuating to a vacuum better than 2.7×10^{-5} Pa, the sample was cooled to 180—200 K. The instrument was a VG ESCA 3 electron spectrometer and Mg$K\alpha$ X-ray (50 W) was used. Peak separation was made by a nonlinear least squares method using a mixed Gaussian-Lorentzian curve shape. The background level was determined by a method proposed by Shirley,[4] in which the level was assumed to increase in proportion to the spectral intensity, and contributions by X-ray satellites were excluded. The electron-binding energies, E_B, were calibrated by assigning 285.0 eV to the C 1s peak of the phenyl carbons in methylenetriphenylphosphorane.[1,2]

Results and Discussion

Results of XPS Measurements: Binding energy, E_B, data for three complexes are summarized in Table 1. Apparently, no indication of decomposition of the complexes was observed in regard to the ligand ylide, since E_B values and relative peak widths for phosphorus were in a range comparable to those for the ylide or the ylide-gold complexes.[2] After peak separation, however, a second peak appeared in Te 3d spectra (peak (b) in Table 1) for complexes **1**—**3** and a third peak appeared in Cl 2p spectra (peak (c) in Table 1) for complexes **1** and **2**. This indicates that, in spite of

Table 1. Binding Energies for Ylide Tellurium Compounds in eV

	Complex	Te		5/2-3/2	Cl	P		C
		$3d_{5/2}$	$3d_{3/2}$	Split	$2p_{3/2}$	2p	2s	1s
1	$[L_2TeCl_2]Cl_2$	(a) 574.7(±0.4)	585.1(±0.3)	10.4	(a) 196.9(±0.5)	132.8(±0.2)	190.5(±0.2)	285.0
		(b) 576.7(±0.2)	586.5(±0.4)	10.4	(b) 198.3(±0.1)			
					(c) 200.4[a)]			
		[1.03]	[0.98]		[0.95]	[1.08]	[1.30]	[1.00]
2	$[L_3TeCl]Cl_3$	(a) 574.5(±0.3)	584.9(±0.1)	10.4	(a) 196.8(±0.3)	132.9(±0.2)	190.3(±0.2)	285.0
		(b) 576.1(±0.1)	586.5(±0.1)	10.4	(b) 197.8(±0.5)			
					(c) 199.9[a)]			
		[1.06]	[1.03]		[0.87]	[1.08]	[1.33]	[1.00]
3	$[L_4Te]Cl_4$	(a) 574.3(±0.3)	584.7(±0.3)	10.4	(a) 196.8(±0.3)	132.8(±0.2)	190.3(±0.4)	285.0
		(b) 576.0(±0.1)	586.5(±0.4)	10.5				
		[1.12]	[1.08]		[0.95]	[1.07]	[1.28]	[1.00]

L: $(C_6H_5)_3P=CH_2$.
Uncertainties shown in parentheses are 90% confidence limits in eV. Values in brackets are a mean FWHM ratio to C 1s peak. Scattering of the ratio was always less than ±0.15.
a) An average of two data.

careful sample handling and measuring procedures, partial decomposition of the complexes could not be avoided. As expected from its instability,[3] decomposition was considerable for **1** judging from the intensity of the second peak of Te 3d. It is probable that the decomposition was caused by a trace amount of oxygen or water vapor during handling. Damage by X-ray irradiation can be disregarded, because no appreciable change in Te 3d spectra was observed after irradiating with 440 W-h of Mg*Kα* X-ray, which is about four times the irradiation for taking all the spectra. Since the samples were contaminated by decomposition products, we shall only consider the binding energy data of the complexes and avoided quantitative discussion. It was unfortunate that the validity of the peak separation could not be supported by relative peak intensities. However it is unlikely that the accuracy of peak separation is less than the case of gold complexes previously reported,[1] where the results were examined quantitatively.

Electronic States of Ylide and Tellurium Atom: The E_B[P 2p] and E_B[P 2s] for ligand ylide in complexes **1**—**3** are practically identical as shown in Table 1. Further, E_B[P 2p] agrees with the values for ylide (**L**) (132.6 eV), triphenylmethylphosphonium bromide, $[(C_6H_5)_3PCH_3]Br$ (**4**), (132.6±0.4 eV), and chlorobis(methylenetriphenylphosphorane)gold(I), $[(C_6H_5)_3P{=}CH_2]_2AuCl$ (**5**), (132.4±0.4 eV), reported previously.[1,2] The E_B[P 2s] for **1**—**3** is also in agreement with that[2] (190.1 eV) for **L**, but is slightly higher than that[2] (189.6—8 eV) for **5**. The lower E_B[P 2s] for **5** was found to be due to the interference by X-ray satellite peaks of Cl 2p orbitals. After correction for the interference, E_B[P 2s] for **5** agreed with that for **1**—**3**; with the previous calculation program,[2] contributions by X-ray satellites could not be excluded. These results indicate that the electronic state of phosphorus in complexes **1**—**3** is identical to that in **L** and complex **5**.

It was not possible to separate the ylide methylene carbon peak from the phenyl carbon peak in **1**—**3**, precisely.[2] According to the ^{1}H NMR spectra,[3] however, the electronic state of the ylide methylene group in **1**—**3** is considered to be similar to that of the methyl group in **4**, that is, the chemical shift[3] (δ=3.15—3.30) of CH_2P in **1**—**3** agrees with that[5] (δ=3.17) of PCH_3 in **4**, but differs from the values of CH_2P in **L**[6] (δ=0.13) and **5**[7] (δ=1.7). This suggests that the carbanion of the ylides in **1**—**3** is donating electrons to the tellurium atom and the density of the electrons on the tellurium atom may be higher than that in common Te(IV) compounds.

An example of a Te 3d spectrum for **3** is shown in Fig. 1. The E_B[Te 3d] of peak (a) for each complex is assigned to the Te(IV) in each complex, and peak (b) to decomposition products. Since, as mentioned above, a methylene carbon in a ligand ylide is anionic[1,2,8] and a donor of electrons, it is able to raise the density of electrons on the central tellurium atom and lower the E_B. The E_B[Te 3d] values for **1**—**3** are lower than those[9—11] for common Te(IV) compounds: usually, E_B[Te 3d$_{5/2}$]=575.3 eV and E_B[Te 3d$_{3/2}$]=585.7 eV and two examples, diphenyltellurium(IV) dichloride, $(C_6H_5)_2TeCl_2$ (**6**), and $TeCl_4$ (**7**) (correctly, Te_4Cl_{16})[12] are shown in Table 2. In addition, E_B[Te 3d] values for **1**—**3** decrease slightly with increasing number of bonded ylides. The fall of E_B[Te 3d] can be caused both by increasing the number of bonded ylides and decreasing the number of bonded chlorine atoms. Further, it is considered that the donation of electrons from the ylides to the tellurium atom in **1**—**3** may be larger than in the case in gold complex **5**.[2] The conjecture is parallel to the results of ^{1}H NMR for CH_2P in tellurium[3] and gold[7] complexes. As a first approximation, the chemical shifts, ΔE_B, can be explained by a ligand chemical shift,[9,13] in which ΔE_B is a sum of each ligand chemical shift of bonded ligands, $\Delta E(j)$, that is, $\Delta E_B=\sum\Delta E(j)$. The ligand chemical shift by

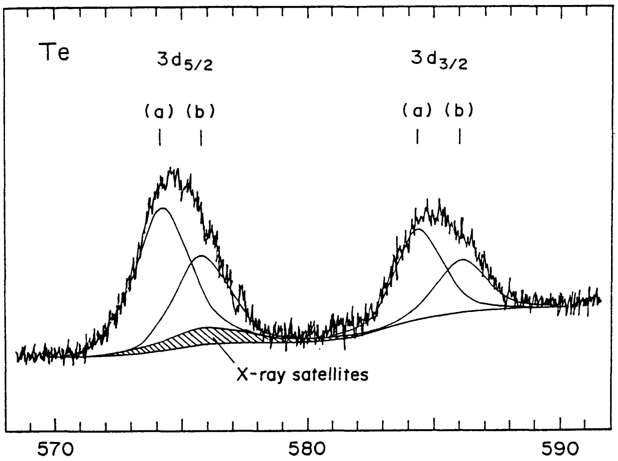

Fig. 1. The Te 3d spectrum of $[\{(C_6H_5)_3P{=}CH_2\}_4Te]Cl_4$. (See Table 1 for (a) and (b).)

Table 2. Ligand Chemical Shifts, ΔE(j), Calculated by Using Binding Energy Data in Ref. 5

	Te 3d$_{5/2}$			Te 3d$_{3/2}$		
	E_B/eV	ΔE(Ph)/eV	ΔE(Cl)/eV	E_B/eV	ΔE(Ph)/eV	ΔE(Cl)/eV
Te metal	573.1			583.5		
Ph_2Te_2	573.9[a]	0.8		584.3[a]	0.8	
Ph_2TeCl_2	576.2[a]		0.75	586.6[a]		0.75
$TeCl_4$	576.9		0.63[b]	587.3		0.63[b]
$(NH_4)_2TeCl_6$	576.9[a]		0.63	587.4[a]		0.63

Ph: C_6H_5.

a) Cited from Ref. 7 where original data[5] were converted by using E_B[C 1s]=284.8 eV for adventitious hydrocarbon. b) An average of six coordinated chlorine atoms.

the ylide, $\Delta E(\mathbf{L})$, can be calculated from E_B[Te $3d_{5/2}$] for **3** as follows by using E_B[Te $3d_{5/2}$] for metal Te, the mean value of which is calculated at 573.0±0.2 eV from compiled data:[11]

$$\Delta E(\mathbf{L}) = (574.3 - 573.0)/4 = 0.33 \text{ eV}.$$

As described above, the electronic states of bonded ylides in **1**—**3** are equivalent. Then, the ligand chemical shift by chlorine atom can be calculated as follows:

from complex **1**,
$\Delta E(\mathrm{Cl}) = (574.7 - 573.0 - 0.33 \times 2)/2 = 0.52$ eV, and
from complex **2**,
$\Delta E(\mathrm{Cl}) = 574.5 - 573.0 - 0.33 \times 3 = 0.51$ eV.

This agreement implies that the chlorine atoms in **1** and **2** are also equivalent in bonding. The ΔE(Cl) values in **1** and **2** are a little smaller than that in $(NH_4)_2TeCl_6$ (**8**) as shown in Table 2. In the case of $TeCl_4$ (**7**), which is a tetramer and should be expressed as Te_4Cl_{16},[12] each tellurium forms three short bonds to chlorine atoms (bond length 0.2312—0.2317 nm[12] and bond order 1.18[9]) and three long bonds to bridging chlorine atoms (bond length 0.2898—0.2959 nm[12] and bond order 0.11[9]), so that the contribution from the former chlorine atoms may be larger than 0.63 eV in Table 2 and that from the bridging atoms may be smaller. The structures of complexes **1** and **6** are essentially the same as for diphenyltellurium(IV) dibromide, $(C_6H_5)_2TeBr_2$ (**9**), whose structure is a distorted tetrahedron having nearly linear Br-Te-Br bonds.[14] In consideration of a smaller ΔE(Cl) in complex **1**, the Te-Cl bond length in **1** may be longer than that in **6**. The bond in complex **2** will be similar to that in **1**, as ΔE(Cl) is nearly the same.

Electronic States of the Bonded Chlorine Atom and the Free Chloride Ion: Only one chlorine species was identified in complex **3** (Table 1) and E_B[Cl $2p_{3/2}$] was close to those for $[(CH_3)_4]N^+Cl^-$[1] and similar type chloride ions in others.[15] Therefore, it is clear that peak (a) of Cl $2p_{3/2}$ for each complex is assigned to the free chloride ion. The reproducibility of E_B[Cl $2p_{3/2}$] of peak (b) for **1** and **2** is poorer compared with that of peak (a), but this peak can be assigned to bonded chlorine atom, since E_B[Cl $2p_{3/2}$] values are in a similar range with that for bonded chlorine atom in **5**.[1,2] Then, peak (c) is attributed to decomposition products. The E_B[Cl $2p_{3/2}$] of peak (c) is close to that[16] (199.9 eV) for a type of bridging chlorine atom, e.g., $Mo_6Cl_{12}(phen)_2$, phen: 1,10-phenanthroline, but it will be imprudent to conclude this at present. Due to partial decomposition of the complexes, the intensity ratios between peak (a) and (b) for **1** and **2** do not correspond to the atomic ratios of 2:2 and 3:1.

As a conclusion, all the XPS data obtained in the present work support the structures of the complexes which were constructed from the NMR data and the elemental analysis.[3]

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