

Ylide-Metal Complexes. VI.¹⁾ The Preparation and Properties of IVA-group Metal (Ge, Sn, Pb) Complexes of Alkylidenetriphenylphosphoranes

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Synopsis. (Triphenylphosphonium alkylide)triphenylmetal chloride $[(C_6H_5)_3P^+CHR-M(C_6H_5)_3]Cl^-$ (R: H, Me, *i*-pr; M: Ge, Sn, Pb) and (triphenylphosphonium alkylide)metal chloride $[(C_6H_5)_3P^+CHR]_nMCl_n^-$, (M=Ge, $n=4$; M=Pb, $n=2$) have been isolated from a reaction mixture of alkylidenetriphenylphosphoranes and IVA-group metal compounds. The ylide in $[(C_6H_5)_3P^+CH_2-Pb(C_6H_5)_3]Cl^-$ is bonded to the lead atom through the carbanionic donor atom.

In this series, previous papers have been concerned with IB-group metal (Cu, Ag, Au) complexes^{2,3)} and IIB-group metal⁴⁾ (Zn, Cd, Hg) complexes of alkylidenetriphenylphosphoranes. The complexes of alkylidenetriphenylphosphorane $(C_6H_5)_3P=CH-R$ (R: H, Me, *i*-pr) and IVA-group metal (Ge, Sn, Pb) have, however, been the subject of little research, except for the germanium and tin complexes⁵⁾ with methylenetriphenylphosphorane (R=H). The present paper deals with the preparation and properties of IVA-group metal complexes of alkylidenetriphenylphosphoranes. Their properties are compared with those of IB-group metal^{2,3)} and IIB-group metal⁴⁾ complexes of those ylides.

Results and Discussion

(Triphenylphosphonium alkylide)triphenyl IVA-group metal complexes (**1a**, **2a—c**, and **3a—c**) have been isolated from a reaction mixture of alkylidenetriphenylphosphorane (methylene, **La**; ethylidene, **Lb**; and isobutylidene, **Lc**) and triphenylmetal chloride, $(C_6H_5)_3MCl$ (M: Ge, Sn, and Pb).

No	$\begin{array}{c} R \\ \\ (C_6H_5)_3P=CH \\ + \quad (C_6H_5)_3MCl \end{array}$			$\begin{array}{c} R \\ \\ [(C_6H_5)_3P^+CH-M(C_6H_5)_3]Cl^- \end{array}$			
	La	Lb	Lc				
R	H	CH ₃	CH(CH ₃) ₂				
	Yellow	Orange	Red				
No	1a	2a	2b	2c	3a	3b	3c
M	Ge	Sn	Sn	Sn	Pb	Pb	Pb
R	H	H	Me	<i>i</i> -pr	H	Me	<i>i</i> -pr

The **3a** is stable in dichloromethane, but it is unstable in chloroform.

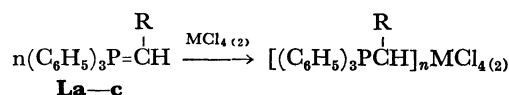
The ¹H-NMR spectrum of the **3a** showed a doublet signal for CH₂P at 2.68 ppm and a multiplet signal for phenyl groups at around 7.5 ppm in a ratio of 2:15 at -60 °C in dichloromethane-*d*₂. The coupling

constant (J_{HCP}) of the **3a** was 13.5 Hz, which was larger than that (7.5 Hz) of the **La**. The chemical shift of **3a** was at a lower field than that (δCH_2P : 0.13 ppm)⁶⁾ of **La**. These spectral properties were sim-

ilar to those of the $[(C_6H_5)_3P^+CH-M-CHP(C_6H_5)_3]Cl_n^-$ (**4**) (M: IB-group metal,^{2,3)} IIB-group metal,⁴⁾ R: H; $n=1, 2$), so the ylide is bonded to the lead atom through the carbanionic donor atom.

Other complexes **1a**, **2a—c**, and **3b—c** are unstable in dichloromethane or chloroform at -60 °C, and ¹H NMR spectra of these complexes were not obtained. In both solvents, they are changed to the alkyltriphenylphosphonium chloride, $[(C_6H_5)_3P^+CH_2-R]Cl^-$ (**5**) (R: H (**5a**), Me (**5b**), *i*-pr (**5c**)). Their melting points or decomposition temperatures are not those of ylides, triphenylmetal chloride or salts **5**. Their color is white and they are thermally stable in the solid state. These properties resemble those of **4** (R: Me, *i*-pr),²⁻⁴⁾ and the ylides seem to be bonded to the metal atom in the solid state. The lability of **3b** and **3c** compared with **3a** complex can be ascribed to the difference in the carbanionic donor character of ylides.

Other types of ylide IVA-group metal chlorides (**6a—c** and **7a—b**) have been isolated from the reaction mixture of the GeCl₄ or PbCl₂ with the ylides (**La—c**). They are unstable in dichloromethane or chloro-



No	6a	6b	6c	7a	7b
M	Ge	Ge	Ge	Pb	Pb
R	H	Me	<i>i</i> -pr	H	Me

form at -60 °C and changed to the corresponding phosphonium salts (**5a—c**); therefore, their structures are still uncertain.

The **1a**, **2a**, **6a**, and **7a** complexes are unstable compared with **4** (R=H), *i.e.*, the Cu, Ag, Au, Zn and Cd complexes of **La** are stable at -60 °C. Germanium complexes of **1a** and **6a—c** are highly hygroscopic.

Experimental

Measurements. The ¹H NMR spectra were measured with an R-40 (Hitachi) spectrometer.

The reaction mole ratio of the ylides and the metal compounds, the melting point, the reaction time and analytical data of complexes are collected in Table 1. The precipitated white complexes are stable in dry THF at r.t. They are soluble in dichloromethane or chloroform and are insoluble in other common organic solvents.

TABLE 1. REACTION MOLE RATIO, REACTION TIME, YIELDS, MELTING POINT, AND ANALYTICAL DATA OF COMPLEXES

No	M	$\frac{\text{MCl}_{4(2)}}{(\text{C}_6\text{H}_5)_3\text{MCl}}$ g (mmol)	R	$(\text{C}_6\text{H}_5)_3\text{PCHR}$ g (mmol)	Reaction temperature °C	Reaction time d	Yield g (%)	Mp θ_m /°C (Dp θ_d /°C)	Formula (Molecular weight)	Found (%)		Calcd (%)	
										C	H	C	H
1a	Ge	0.37 (1.09)	H	0.40 (1.45)	r.t.	1	0.35 (71.4)	—	$\text{C}_{37}\text{H}_{32}\text{PGeCl}$ (615.67)	71.49	5.51	72.18	5.24
2a	Sn	0.42 (1.09)	H	0.46 (1.66)	r.t.	2	0.61 (84.6)	(252)	$\text{C}_{37}\text{H}_{32}\text{PSnCl}$ (661.77)	67.18	5.20	67.15	4.87
2b	Sn	0.39 (1.01)	CH_3	0.36 (1.24)	r.t.	1	0.59 (86.3)	(310)	$\text{C}_{38}\text{H}_{34}\text{PSnCl}$ (675.80)	68.15	4.63	67.53	5.07
2c	Sn	0.35 (0.91)	<i>i</i> - C_3H_7	0.42 (1.32)	r.t.	0.5	0.52 (81.4)	(325)	$\text{C}_{40}\text{H}_{38}\text{PSnCl}$ (703.85)	68.21	5.25	68.26	5.44
3a	Pb	0.69 (1.46)	H	0.46 (1.66)	r.t.	0.5	0.80 (73.2)	162—165	$\text{C}_{37}\text{H}_{32}\text{PPbCl}$ (750.20)	58.92	4.33	59.24	4.30
3b	Pb	0.49 (1.03)	CH_3	0.34 (1.17)	r.t.	2	0.66 (83.5)	175—176	$\text{C}_{38}\text{H}_{34}\text{PPbCl}$ (764.23)	59.56	4.61	59.72	4.48
3c	Pb	0.29 (0.61)	<i>i</i> - C_3H_7	0.30 (0.94)	0	1.5	0.41 (84.6)	182—184	$\text{C}_{40}\text{H}_{38}\text{PPbCl}$ (792.28)	60.29	5.27	60.64	4.83
6a	Ge	0.066 (0.308)	H	0.34 (1.23)	r.t.	0.5	0.25 (61.5)	—	$\text{C}_{76}\text{H}_{68}\text{P}_2\text{GeCl}_4$ (1319.65)	69.51	6.03	69.17	5.20
6b	Ge	0.090 (0.42)	CH_3	0.26 (0.90)	r.t.	0.5	0.20 (77.0)	—	$\text{C}_{40}\text{H}_{38}\text{P}_2\text{GeCl}_4$ (795.07)	59.86	5.30	60.43	4.82
6c	Ge	0.136 (0.63)	<i>i</i> - C_3H_7	0.63 (1.978)	r.t.	0.5	0.45 (77.8)	—	$\text{C}_{66}\text{H}_{68}\text{P}_2\text{GeCl}_4$ (1169.58)	68.25	6.25	67.79	5.95
7a	Pb	0.11 (0.40)	H	0.28 (1.01)	r.t.	2	0.22 (66.7)	(195)	$\text{C}_{38}\text{H}_{34}\text{P}_2\text{PbCl}_2$ (830.65)	54.85	4.24	54.95	4.13
7b	Pb	0.17 (0.61)	CH_3	0.75 (2.58)	r.t.	1	0.31 (59.3)	(206)	$\text{C}_{40}\text{H}_{38}\text{P}_2\text{PbCl}_2$ (858.70)	54.26	4.59	55.95	4.46

Preparation of Complexes. (Triphenylphosphonium methylide)triphenyllead Chloride (**3a**): Triphenyllead chloride (0.69 g, 1.46 mmol) was added to a dry THF (15 cm³) solution of triphenylmethylenephosphorane (**La**) (0.46 g, 1.66 mmol) at r.t. under nitrogen. The mixture was stirred for 12 h; then the precipitated white complex was filtered under nitrogen, washed with dry ether and dried under vacuum.

(Triphenylphosphonium alkylide)triphenylgermanium (**1a**), -tin (**2a—c**), and -lead (**3b**, **3c**) Chloride: These complexes were prepared according to the procedure for **3a**.

Tetra(triphenylphosphonium methylide)germanium Tetrachloride (**6a**): Tetrachlorogermanium (0.066 g, 0.308 mmol) was added to the dry THF (15 cm³) solution of **La** (0.34 g, 1.23 mmol) at r.t. under nitrogen. The mixture was stirred, and the color of **La** changed from yellow to colorless, after 12 h, the white complex which precipitated was filtered under nitrogen, washed with dry ether, and dried under vacuum.

Di(triphenylphosphonium ethylide)germanium Tetrachloride (**6b**), Tri(triphenylphosphonium isobutylide)germanium Tetrachloride (**6c**), Di(triphenylphosphonium methylide)lead Dichloride (**7a**), and Di-

(triphenylphosphonium ethylide)lead Dichloride (**7b**): These complexes were prepared according to the procedure for **6a**.

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