

Ylide-Metal Complexes. IV. The Preparation and Properties of IIB-group Metal (Zn, Cd, Hg) Complexes of Alkylidenetriphenylphosphoranes

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(Received December 3, 1979)

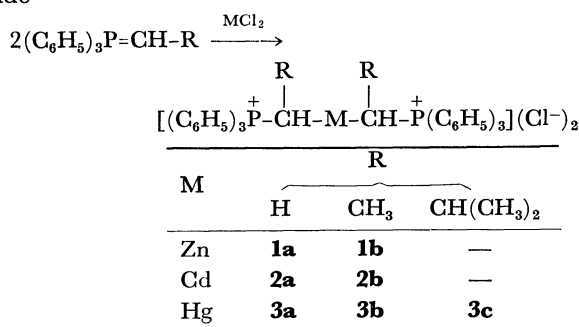
Ylide-IIB-group metal (Zn, Cd, Hg) complexes, bis(triphenylphosphonium alkylide)metal dichloride, $[(C_6H_5)_3\overset{+}{P}-\overset{R}{\underset{|}{CH}}-M-\overset{R}{\underset{|}{CH}}-\overset{+}{P}(C_6H_5)_3](Cl^-)_2$ (M: Zn, Cd, Hg), and chloro(triphenylphosphonium isobutylide)metal dichloride, $[(C_6H_5)_3\overset{+}{P}-\overset{CH(CH_3)_2}{\underset{|}{CH}}-M-Cl]Cl^-$ (M: Zn, Cd), have been obtained from alkylidenetriphenylphosphoranes, $(C_6H_5)_3P=CH-R$ (R: H, CH_3 , $CH(CH_3)_2$), and $ZnCl_2$, $CdCl_2$, or $HgCl_2$. In these organometallic complexes, the alkylidenetriphenylphosphoranes are attached to the IIB-group metals atom through the carbanionic donor atom. They are thermally stable.

The complexes of alkylidenetriphenylphosphorane and IIB-group metals have been investigated by Schmidbaur¹⁻⁴) and some other researchers.⁵⁻⁷) The complexes of alkylidenetriphenylphosphorane $(C_6H_5)_3P=CH-R$ (R: H, CH_3 , $CH(CH_3)_2$), and $ZnCl_2$, $CdCl_2$, or $HgCl_2$ have, however, been the subject of little research.

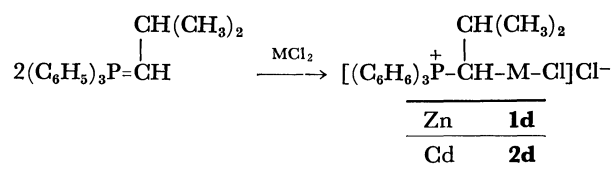
Previous papers have been concerned with the preparation and physical properties of stable 2/1- and 1/1-gold(I), silver(I) and copper(I) complexes of alkylidenetriphenylphosphoranes⁸) and arsoranones.⁹) The present paper will deal with the preparation and ¹H- and ¹³C-NMR measurements of bis(triphenylphosphonium alkylide)metal dichloride, $[(C_6H_5)_3\overset{+}{P}-\overset{R}{\underset{|}{CH}}-M-\overset{R}{\underset{|}{CH}}-\overset{+}{P}(C_6H_5)_3](Cl^-)_2$ (M: Zn, Cd, Hg) and chloro(triphenylphosphonium isobutylide)metal chloride, $[(C_6H_5)_3\overset{+}{P}-\overset{CH(CH_3)_2}{\underset{|}{CH}}-M-Cl]Cl^-$ (M: Zn, Cd).

Results and Discussion

Synthesis and Properties. 2/1 complexes of bis(triphenylphosphonium alkylide)metal dichloride (**1a**—**1b**, **2a**—**2b**, and **3a**—**3c**) and 1/1 complexes of chloro(triphenylphosphonium isobutylide)metal dichloride (**1d** and **2d**) have been isolated from a reaction mixture of alkylidene triphenylphosphorane $((C_6H_5)_3P=CH-R$, **La**; R=H, **Lb**; R= CH_3 and **Lc**; R= $CH(CH_3)_2$) and $ZnCl_2$, $CdCl_2$, or $HgCl_2$. Attempts to obtain the bis(triphenylphosphonium isobutylide)metal dichloride



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from **Lc** and $ZnCl_2$ or $CdCl_2$ invariably resulted in the isolation of a 1/1 complex of **1d** or **2d** respectively.

All the complexes except **1a** and **2a** are insoluble in most organic solvents and change to the corresponding phosphonium salts, *i.e.*, $[(C_6H_5)_3PCH_2R]Cl$, in chloroform and dichloromethane at room temperature or at a low temperature. **1a** and **2a** change slowly to the corresponding phosphonium salt in dichloromethane, but they are stable at $-40^\circ C$. All the complexes are thermally stable in the solid state. The stability of these complexes and bis(triphenylphosphonium methylide)metal chloride, $[(C_6H_5)_3\overset{+}{P}-CH_2-M-CH_2-\overset{+}{P}(C_6H_5)_3]Cl^-$ (M: Cu; **4**,¹⁰) Ag; **5**¹¹) and Au; **6**⁸), in dichloromethane is $6 \gg 1a \approx 2a > 4 \approx 5 \gg 3a$. **5** is sensitive to light, but **2a** is stable.

Also, **3a'** was prepared from **La** and $HgBr_2$ by Seyferth and Grim.¹²) Although they reported that the **3a'** was somewhat soluble in hot methanol, **3a** can be decomposed in that solvent (*cf.* the ¹H-NMR section).

NMR Spectra. The ¹H-NMR spectrum of **1a** showed a doublet signal for the CH_2P at 0.76 ppm and a multiplet signal for the phenyl groups at 7.5 ppm in a ratio of 2:15 at room temperature. The ¹H-NMR spectrum of **2a** showed satellites caused by the spin-spin coupling of the ¹¹¹/¹¹³Cd nuclei with CH_2 protons in the complex, in addition to a doublet signal for the CH_2P at 0.70 ppm and a multiplet signal for the phenyl groups at 7.5 ppm. The ¹H-NMR spectrum of **3a** could not be measured at $-45^\circ C$ because it was not soluble in dichloromethane-*d*₂. The ¹H-NMR spectrum of **3a** showed a doublet signal (J_{HCP} : 13.5 Hz) at 3.3 ppm in dichloromethane-*d*₂ at room temperature or at 3.0 ppm in hot methanol-*d*₄ for the methyl group and a multiplet signal for the phenyl groups at 7.5 ppm in dichloromethane-*d*₂ or at 7.7 ppm in methanol-*d*₄ in a ratio of 3:15. The chemical shift (δ) and the coupling constant (J_{HCP}) of methyltriphenylphosphonium bromide in methanol-

TABLE 1. ^1H - AND ^{13}C -NMR DATA OF COMPLEXES AND YLIDE

^1H	CH_2P			C_6H_5 δ/ppm
	δ/ppm	$^2J_{\text{HCP}}/\text{Hz}$	$^2J_{\text{HCM}}/\text{Hz}$	
1a	0.76 d (2H)	16	—	7.3—8.0 m (15H)
2a	0.70 d (2H)	14	54.2	7.2—7.9 m (15H)
6	1.70 d	13.0		7.5—7.9 m
La	0.13 d	7.5		

^{13}C	CH_2P		C_6H_5 δ/ppm (J_{PC}/Hz)				Temp
	δ/ppm	J_{PC}/Hz	c-1	o	m	p	
1a	-1.17 d	48.8	124.3 (85.0)	132.5 (8.8)	128.5 (12.7)	134.8 (—)	-60 °C
2a	-2.01 d	44.9	118.6 (87.9)	132.3 (9.8)	128.7 (12.7)	134.6 (—)	-60 °C
6	9.5 d	39.1					
La	-4.3 d	98.6					

Standard: ^1H -NMR; int-TMS ($\delta=0$), ^{13}C -NMR; CD_2Cl_2 ($\delta=53.6$ ppm). Solvent: CD_2Cl_2 . M: $^{111/113}\text{Cd}$.

d_4 are 3.0 ppm and 13.5 Hz for the methyl group and a multiplet signal for the phenyl groups at 7.7 ppm.

The coupling constants (J_{HCP}) of **1a** and **2a** were larger than that (7.5 Hz) of **La**, and their proton signals shifted to a lower field than that (0.13 ppm) of **La**. These spectra are similar to those^{8,10,11}) of **4**—**6**. It seems that the alkylidenetriphenylphosphoranes are attached to the metal atom through the carbanionic donor atom.^{8,11,12}) The cadmium atom in **2a** is considered to have the *SP* configuration from the following facts: the coupling constant (J_{HCM}) of **2a** is larger than those (35.4,¹³) 34.9 Hz¹⁴) of the ylide-complexes with a tetrahedral-configurational cadmium atom, and it is close to those (49.4 Hz for J_{HCMCd} , 51.2 Hz for J_{HCMCd}) of diethylcadmium,¹⁵) while the equivalent conductance of **2a** is 15 S cm² in dichloromethane at -50 °C. The chemical shifts (CH_2P) of **1a** and **2a** are at a higher field than those^{8,10,11}) of **4**—**6**. The change in the chemical shifts of these complexes is similar to that of the chemical shifts of other ylide-Ib-group and -IIb-group metal complexes.^{13,14})

The ^{13}C -NMR spectra of **1a** and **2a** were measured in dichloromethane- d_2 at -60 °C. The coupling constants (J_{PC}) of these complexes were much smaller than that⁸) of **La**. This finding is also similar to those^{8,10,11}) in the cases of **4**—**6**. The chemical shifts (CH_2P) of these complexes are at a higher field than those of **4**—**6**. The ^1H - and ^{13}C -NMR data of **1a** and **2a** are summarized in Table 1.

Experimental

Measurements. The NMR spectra were measured with an FX-60 spectrometer (JEOL) for ^{13}C -NMR, and with a JNMOMX-60 (JEOL) spectrometer and an R-40 (Hitachi) spectrometer for ^1H -NMR. The equivalent conductance was measured with a CM-30 (Schimadzu) conductometer.

Starting Materials. The methylene-,¹⁶) ethylidene-,^{10,17}) isobutylidenetriphenylphosphoranes¹⁰) were prepared from the corresponding phosphonium bromides by the sodium-

amide method.^{8,9})

The reaction mole ratio, the yield, the decomposition temperature, and the analytical data of complexes are collected in Table 2.

Preparation of 1/2 Complexes. *Bis*(triphenylphosphonium methylide)zinc Dichloride (**1a**), *Bis*(triphenylphosphonium methylide)cadmium Dichloride (**2a**), and *Bis*(triphenylphosphonium methylide)mercury Dichloride (**3a**): ZnCl_2 , CdCl_2 , or HgCl_2 was added to a dry THF (20 cm³) solution of methylenetriphenylphosphorane at room temperature under nitrogen. The color of the methylenetriphenylphosphorane changed from yellow to colorless. The white complex thus precipitated was filtered under nitrogen, washed with THF, and pentane, and dried under a vacuum.

Bis(triphenylphosphonium ethylide)zinc Dichloride (**1b**), *Bis*(triphenylphosphonium ethylide)cadmium Dichloride (**2b**), *Bis*(triphenylphosphonium ethylide)mercury Dichloride (**3b**), and *Bis*(triphenylphosphonium isobutylide)mercury Dichloride (**3c**): These complexes were prepared according to the procedure for complexes **1a**, **2a**, and **3a**.

Chloro(triphenylphosphonium isobutylide)zinc Chloride (**1d**): A dry ether (30 cm³) solution of isobutylidenetriphenylphosphorane was added to ZnCl_2 at room temperature under nitrogen. The white complex precipitated after 8 d was filtered under nitrogen, washed with ether, and then pentane, and dried under a vacuum.

Chloro(triphenylphosphonium isobutylide)cadmium Chloride (**2d**): A dry THF (20 cm³) solution of isobutylidenetriphenylphosphoranes was added to CdCl_2 at room temperature under nitrogen. After 4 d, the precipitated white complex was filtered under nitrogen, washed with THF and then pentane and dried under a vacuum.

The present work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture.

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TABLE 2. REACTION MOLE RATIO, SOLVENT, REACTION TIME, YIELDS, DECOMPOSING TEMPERATURES, AND ANALYTICAL DATA OF COMPLEXES

No.	M	$\frac{\text{MCl}_2}{\text{g}} \text{ (mmol dm}^{-3}\text{)}$	R	$\frac{(\text{C}_6\text{H}_5)_3\text{PCHR}}{\text{g}} \text{ (mmol dm}^{-3}\text{)}$	Solvent	Reaction time d	Yield g (%)	Dt/°C	Formula (Molecular weight)	Found (%) C H	Calcd (%) C H
1a	Zn	0.068 (0.499)	H	0.276 (1.00)	THF	1	0.32 (93.1)	190	$\text{C}_{38}\text{H}_{34}\text{P}_2\text{ZnCl}_2$ (688.92)	66.56 5.27	66.25 4.97
1b	Zn	0.080 (0.59)	CH_3	0.39 (1.34)	THF	1	0.34 (80.4)	163	$\text{C}_{40}\text{H}_{38}\text{P}_2\text{ZnCl}_2$ (716.97)	66.63 5.09	67.01 5.34
1d	Zn	0.14 (1.03)	<i>i</i> -C ₃ H ₇	0.70 (2.2)	Ether	8	0.44 (94.0)	180	$\text{C}_{22}\text{H}_{23}\text{PZnCl}_2$ (454.68)	57.69 5.51	58.11 5.10
2a	Cd	0.09 (0.491)	H	0.316 (1.14)	THF	3	0.34 (94.1)	114	$\text{C}_{38}\text{H}_{34}\text{P}_2\text{CdCl}_2$ (735.94)	61.84 5.06	62.02 4.66
2b	Cd	0.09 (0.491)	CH_3	0.410 (1.41)	THF	8	0.32 (85.3)	114	$\text{C}_{40}\text{H}_{38}\text{P}_2\text{CdCl}_2$ (763.99)	62.64 5.24	62.88 5.01
2d	Cd	0.09 (0.491)	<i>i</i> -C ₃ H ₇	0.37 (1.16)	THF	4	0.20 (81.2)	115	$\text{C}_{22}\text{H}_{23}\text{PCdCl}_2$ (501.70)	53.00 4.87	52.67 4.62
3a	Hg	0.135 (0.497)	H	0.276 (1.00)	THF	1	0.36 (87.9)	182	$\text{C}_{33}\text{H}_{34}\text{P}_2\text{HgCl}_2$ (824.13)	54.99 4.47	55.38 4.14
3b	Hg	0.136 (0.501)	CH_3	0.290 (1.00)	THF	3	0.36 (84.3)	185	$\text{C}_{40}\text{H}_{38}\text{P}_2\text{HgCl}_2$ (852.18)	56.68 4.69	56.38 4.49
3c	Hg	0.136 (0.501)	<i>i</i> -C ₃ H ₇	0.40 (1.26)	THF	a)	0.40 (87.9)	199	$\text{C}_{44}\text{H}_{46}\text{P}_2\text{HgCl}_2$ (908.29)	58.22 5.26	58.18 5.10

a) 7 h.

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