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

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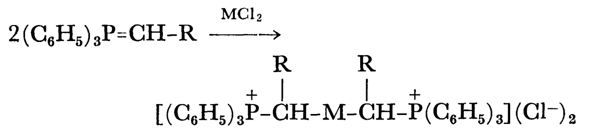
Ylide-IIb-group metal (Zn, Cd, Hg) complexes, bis(triphenylphosphonium alkylide)metal dichloride, $[(C_6H_5)_3\overset{+}{P}\text{-}\overset{R}{C}H\text{-}M\text{-}\overset{R}{C}H\text{-}\overset{+}{P}(C_6H_5)_3](Cl^-)_2$ (M: Zn, Cd, Hg), and chloro(triphenylphosphonium isobutylide)metal dichloride, $[(C_6H_5)_3\overset{+}{P}\text{-}\overset{CH(CH_3)_2}{C}H\text{-}M\text{-}Cl]Cl^-$ (M: Zn, Cd), have been obtained from alkylidenetriphenylphosphoranes, $(C_6H_5)_3P{=}CH\text{-}R$ (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 Schmidbaur[1-4] and some other researchers.[5-7] The complexes of alkylidenetriphenylphosphorane $(C_6H_5)_3$-$P{=}CH\text{-}R$ (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 alkylidenetriphenylphosphoranes[8] and arsoranes.[9] The present paper will deal with the preparation and ^1H- and ^{13}C-NMR measurements of bis(triphenylphosphoniumalkylide)metal dichloride, $[(C_6H_5)_3\overset{+}{P}\text{-}\overset{R}{C}H\text{-}M\text{-}\overset{R}{C}H\text{-}\overset{+}{P}(C_6H_5)_3](Cl^-)_2$ (M: Zn, Cd, Hg) and chloro(triphenylphosphonium isobutylide)metal chloride, $[(C_6H_5)_3\overset{+}{P}\text{-}\overset{CH(CH_3)_2}{C}H\text{-}M\text{-}Cl]Cl^-$ (M: Zn, Cd).

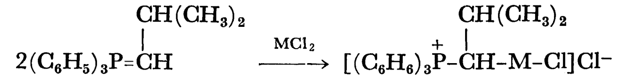
Results and Discussion

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 ($(C_6H_5)_3P{=}CH\text{-}R$, **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



$$2(C_6H_5)_3P{=}CH\text{-}R \xrightarrow{MCl_2} [(C_6H_5)_3\overset{+}{P}\text{-}\overset{R}{C}H\text{-}M\text{-}\overset{R}{C}H\text{-}\overset{+}{P}(C_6H_5)_3](Cl^-)_2$$

M	R		
	H	CH_3	$CH(CH_3)_2$
Zn	**1a**	**1b**	—
Cd	**2a**	**2b**	—
Hg	**3a**	**3b**	**3c**



$$2(C_6H_5)_3P{=}\overset{CH(CH_3)_2}{C}H \xrightarrow{MCl_2} [(C_6H_6)_3\overset{+}{P}\text{-}\overset{CH(CH_3)_2}{C}H\text{-}M\text{-}Cl]Cl^-$$

Zn	**1d**
Cd	**2d**

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 °C. All the complexes are thermally stable in the solid state. The stability of these complexes and bis(triphenylphosphonium methylide)metal chloride, $[(C_6H_5)_3\overset{+}{P}\text{-}CH_2\text{-}\overset{-}{M}\text{-}CH_2\text{-}\overset{+}{P}(C_6H_5)_3]Cl^-$ (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 $^{111/113}Cd$ 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 °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-

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Table 1. ^{1}H- and ^{13}C-NMR data of complexes and ylide

^{1}H	CH$_2$P δ/ppm	CH$_2$P $^2J_{\mathrm{HCP}}$/Hz	CH$_2$P $^2J_{\mathrm{HCM}}$/Hz	C$_6$H$_5$ δ/ppm
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$_2$P δ/ppm	CH$_2$P J_{PC}/Hz	C$_6$H$_5$ δ/ppm (J_{PC}/Hz) c-1	*o*	*m*	*p*	Temp
1a	−1.17 d	48.8	124.3	132.5	128.5	134.8	−60 °C
			(85.0)	(8.8)	(12.7)	(—)	
2a	−2.01 d	44.9	118.6	132.3	128.7	134.6	−60 °C
			(87.9)	(9.8)	(12.7)	(—)	
6	9.5 d	39.1					
La	−4.3 d	98.6					

Standard: ^{1}H-NMR; int-TMS (δ=0), ^{13}C-NMR; CD$_2$Cl$_2$ (δ=53.6 ppm). Solvent: CD$_2$Cl$_2$. M: $^{111/113}$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 Hz[14]) of the ylide-complexes with a tetrahedral-configurational cadmium atom, and it is close to those (49.4 Hz for $J_{\mathrm{HC}^{111}\mathrm{Cd}}$, 51.2 Hz for $J_{\mathrm{HC}^{113}\mathrm{Cd}}$) of diethylcadmium,[15] while the equivalent conductance of **2a** is 15 S cm^2 in dichloromethane at −50 °C. The chemical shifts (CH$_2$P) 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 that[8] of **La**. This finding is also similar to those[8,10,11] in the cases of **4**—**6**. The chemical shifts (CH$_2$P) of these complexes are at a higher field than those of **4**—**6**. The ^{1}H- 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 ^{1}H-NMR. The equivalent conductance was measured with a CM-30 (Schimadzu) conductometer.

Starting Materials. The methylene-,[16] ethylidene-,[10,17] isobutylidenetriphenylphosphoranes[10] 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 cm^3) 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 cm^3) 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 vaccum.

*Chloro(triphenylphosphonium isobutylide)cadmium Chloride (**2d**):* A dry THF (20 cm^3) 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.

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References

1) H. Schmidbaur and K. H. Räthlein, *Chem. Ber.*, **107**, 102 (1974).

2) H. Schmidbaur and J. Eberlein, *Z. Anorg. Allg. Chem.*, **434**, 145 (1977).

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

No.	**M**	MCl_2 g (mmol dm^{-3})	**R**	$(C_6H_5)_3PCHR$ g (mmol dm^{-3})	Solvent	Reaction time d	Yield g (%)	Dt/°C	Formula (Molecular weight)	Found (%)		Calcd (%)	
										C	H	C	H
1a	Zn	0.068 (0.499)	H	0.276 (1.00)	THF	1	0.32 (93.1)	190	$C_{38}H_{34}P_2ZnCl_2$ (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	$C_{40}H_{38}P_2ZnCl_2$ (716.97)	66.63	5.09	67.01	5.34
1d	Zn	0.14 (1.03)	i-C_3H_7	0.70 (2.2)	Ether	8	0.44 (94.0)	180	$C_{22}H_{23}PZnCl_2$ (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	$C_{38}H_{34}P_2CdCl_2$ (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	$C_{40}H_{38}P_2CdCl_2$ (763.99)	62.64	5.24	62.88	5.01
2d	Cd	0.09 (0.491)	i-C_3H_7	0.37 (1.16)	THF	4	0.20 (81.2)	115	$C_{22}H_{23}PCdCl_2$ (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	$C_{38}H_{34}P_2HgCl_2$ (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	$C_{40}H_{38}P_2HgCl_2$ (852.18)	56.68	4.69	56.38	4.49
3c	Hg	0.136 (0.501)	i-C_3H_7	0.40 (1.26)	THF	a)	0.40 (87.9)	199	$C_{44}H_{46}P_2HgCl_2$ (908.29)	58.22	5.26	58.18	5.10

a) 7 h.

3) H. Schmidbaur and W. Wolf, *Chem. Ber.*, **108**, 2851 (1975).

4) H. Schmidbaur and W. Richter, *Z. Anorg. Allg. Chem.*, **429**, 222 (1977).

5) E. T. Weleski, J. L. Silver, M. D. Jansson, and J. L. Burmeister, *J. Organomet. Chem.*, **102**, 365 (1975).

6) N. A. Nesmeyanov, V. M. Novikov, and O. A. Reutov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **1964**, 772 [*Chem. Abstr.*, **61**, 3143 (1964)].

7) H. Daniel and J. Paetsch, *Chem. Ber.*, **98**, 1915 (1965).

8) Y. Yamamoto and Z. Kanda, *Bull. Chem. Soc. Jpn.*, **52**, 2560 (1979).

9) a) Y. Yamamoto and H. Schmidbaur, *J. Chem. Soc., Chem. Commun.*, **1975**, 669; b) W. Richter, Y. Yamamoto, and H. Schmidbaur, *Chem. Ber.*, **110**, 1312 (1977).

10) Y. Yamamoto and H. Schmidbaur, *J. Organomet. Chem.*, **96**, 133 (1975).

11) Y. Yamamoto and H. Schmidbaur, *J. Organomet. Chem.*, **97**, 479 (1975).

12) D. Seyferth and S. O. Grim, *J. Am. Chem. Soc.*, **83**, 1610 (1961).

13) H. Schmidbaur, O. Gasser, C. Kruger, and J. C. Sekutowski, *Chem. Ber.*, **110**, 3517 (1977).

14) H. Schmidbaur, H. J. Fuller, V. Bejenke, A. Franck, and G. Huttner, *Chem. Ber.*, **110**, 3536 (1977).

15) "Advances in Organometallic Chemistry," ed by F. G. A. Stone and R. West, Academic Press, New York and London (1965), Vol. 3, p. 19.

16) a) H. Schmidbaur, H. Stuhler, and W. Vornberger, *Chem. Ber.*, **105**, 1084 (1972); b) R. Koster, D. Simic, and M. A. Grassberger, *Justus Liebigs Ann. Chem.*, **739**, 211 (1970).

17) H. Bock and H. Tom Dieck, *Z. Naturforsch., Teil B.*, **21**, 739 (1966).