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Ylide-Metal Complexes. VII.[1] The Preparation and Properties of IIA Group Metal(Be, Mg) and IIIA Group Metal(Al, Ga, In) Complexes of Alkylidenetriphenylphosphoranes

Yoshihisa Yamamoto

Faculty of Pharmaceutical Science, Higashi Nippon Gakuen University, Ishikari-Tobetsu, Hokkaido 061-02

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The reactions of $(C_6H_5)_3P{=}CH_2$ (**L**) with $BeCl_2$ or $MgCl_2$ in the mole ratio of 2 : 1 or 4 : 1 yield new dimeric compounds of di-μ-chloro-bis[(methylenetriphenylphosphorane)metal] dichloride, $[(C_6H_5)_3PCH_2\text{–}M{<}^{Cl}_{Cl}{>}M\text{–}CH_2P(C_6H_5)_3]Cl_2$ (M: Be and Mg). The configuration of these metals is trigonal. The reactions of **L** with $AlCl_3$, $GaCl_3$ or $InCl_3$ in the mole ratio of 2 : 1 yield new compounds of di-μ-chloro-bis[bis(methylenetriphenylphosphorane)metal] tetrachloride, $[\{(C_6H_5)_3PCH_2\}_2M{<}^{Cl}_{Cl}{>}M\{CH_2P(C_6H_5)_3\}_2]Cl_4$ (M: Al, Ga, and In). The reactions of **L** with $AlCl_3$ or $GaCl_3$ in the mole ratio of 3 : 1 or 5 : 1 yield new compounds of μ-chloro-bis[tris(methylenetriphenylphosphorane)metal] pentachloride, $[\{(C_6H_5)_3PCH_2\}_3M\text{–}Cl\text{–}M\{CH_2P(C_6H_5)_3\}_3]Cl_5$ (M: Al, Ga). These dimers, bridged by chloride anions, are thermally stable.

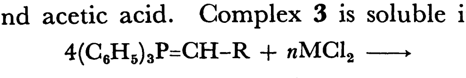
Many investigations[2] of IIA Group and IIIA Group metal complexes with methylenetri(or di)alkylphosphoranes have been reported, but there have been few investigations of metal complexes with triphenylphosphorane derivatives. A previous paper has been concerned with IVA Group metal (Ge, Sn, Pb) complexes[3] of alkylidenetriphenylphosphoranes. The present paper will deal with the preparation and properties of di-μ-chloro-bis[(methylenetriphenylphosphorane)metal] dichloride, $[(C_6H_5)_3PCH_2M{<}^{Cl}_{Cl}{>}MCH_2P(C_6H_5)_3]Cl_2$ (M: Be, Mg), di-μ-chloro-bis[bis(methylenetriphenylphosphorane)metal] tetrachloride, $[\{(C_6H_5)_3PCH_2\}_2M{<}^{Cl}_{Cl}{>}M\{CH_2P(C_6H_5)_3\}_2]Cl_4$ (M: Al, Ga, In), and μ-chloro-bis[tris(methylenetriphenylphosphorane)metal] pentachloride, $[\{(C_6H_5)_3PCH_2\}_3M\text{–}Cl\text{–}M\{CH_2P(C_6H_5)_3\}_3]Cl_5$ (M: Al, Ga).

Results and Discussion

Beryllium, Magnesium, and Calcium Complexes. Di-μ-chloro-bis[(alkylidenetriphenylphosphorane)metal (Be, Mg)] dichlorides have been isolated from a reaction mixture of alkylidenetriphenylphosphorane, $(C_6H_5)_3P{=}CHR$ (**L** (R : H) and **L′** (R: CH_3)), with $BeCl_2$ or $MgCl_2$. Complexes **1** and **2** are soluble only in acidic solvents, such as sulfuric acid, nitric acid, hydrochloric acid, and acetic acid. Complex **3** is soluble in DMF, DMSO, MeOH, and water, but insoluble in chloroform and dichloromethane. They are all highly hygroscopic. No calcium complex could be isolated from the reaction mixture of **L** and $CaCl_2$ in the mole ratio of 2 : 1 or 4 : 1.

$$4(C_6H_5)_3P{=}CH\text{-}R + n\,MCl_2 \longrightarrow$$

M	Be	Mg
n	2	1



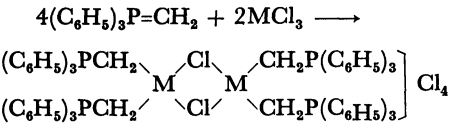
$$\left[(C_6H_5)_3P\overset{R}{C}H\text{-}M{<}^{Cl}_{Cl}{>}M\text{-}\overset{R}{C}HP(C_6H_5)_3\right]Cl_2$$

No.	**1**	**2**	**3**
M	Be	Be	Mg
R	H	Me	H

The ^1H NMR spectrum of **3** showed a doublet signal for the methylene group at 2.17 ppm and a multiplet signal for phenyl groups at 7.3—8.0 ppm (in the ratio of 2 : 15) in CD_3OD at −80 °C. The chemical shift of the methylene group is at a lower field than that[4] (0.13 ppm) of **L**. The coupling constant ($^2J_{HCP}$) of **3** is 12.3 Hz, larger than that[4] (7.5 Hz) of **L**. These features are similar to those of bis(methylenetriphenylphosphorane)metal chloride, $[(C_6H_5)_3PCHR\text{–}M\text{–}CHRP(C_6H_5)_3]Cl_n$ (**4**) (R: H, M: IB Group and IIB Group metal[5]) and (methylenetriphenylphosphorane)-triphenylmetal chloride, $[(C_6H_5)_3PCH_2\text{–}M(C_6H_5)_3]Cl$ (**5**) (M: IVA Group metal[3]). Thus, the ylide **L** is bonded to the metal atom through the carbanionic donor atom.[3,5] Complexes **1** and **2** are unstable in 3.6 mol dm^{-3} D_2SO_4 at −34 °C, giving a alkyltriphenylphosphonium chloride, $[(C_6H_5)_3PCH_2\text{–}R]Cl$ (R: H (**6a**), CH_3 (**6b**)). The decomposition temperatures did not agree with the melting points of the ylides or salts **6**. Their colors are white. These properties resemble those of **4** (R: CH_3, $CH(CH_3)_2$),[5] and the ylides seem to be bonded to the beryllium atom in the solid state.[3] Two structures for the beryllium compounds have been considered possible: either a tetrahedral (monomeric,[6] dimeric,[7] and polymeric[8]) or a trigonal (monomeric,[9] dimeric,[10] and trimeric[11]) configuration. In the cases of **1**—**3**, they are not soluble in chloroform and dichloromethane. This is different from the **4**[5] (linear configuration), and **5**[3] and IIIA Group metal complexes (tetrahedral configuration). The elemental analyses of **1**—**3** agreed with that of $[LMCl_2]_n$. Complex **3** has free anion from the equivalent conductance. Thus, we suggest that the structure of **1**—**3** can be neither a linear nor tetrahedral configuration, but a dimeric trigonal structure.

Aluminium, Gallium, Indium, and Thallium Complexes. 2 : 1 Complexes: Di-μ-chloro-bis[bis(methylenetriphenylphosphorane)metal (Al, Ga, In)] tetrachlorides have been isolated from a reaction mixture of **L** and $AlCl_3$,

$GaCl_3$ or $InCl_3$ in the mole ratio of 2 : 1. Complexes **7**—**9** are soluble in alcohols, chloroform, dichloromethane, DMF, DMSO, and water, but are unstable in these solvents at room temperature and are changed to the corresponding phosphonium chloride (**6a**). In dichloromethane, **7** and **8** are stable at −80 °C. Complex **9** was slowly changed to **6a** in dichloromethane at −80 °C, the ^1H NMR spectrum of **9** showing signals of both **9** and **6a**. No thallium complex could be isolated from the reaction mixture of **L** and TlI in the mole ratio of 2 : 1.

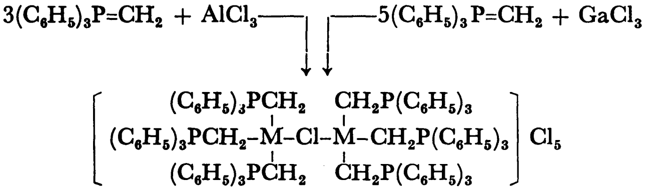


$$4(C_6H_5)_3P{=}CH_2 + 2MCl_3 \longrightarrow \left[\begin{array}{ccccc}(C_6H_5)_3PCH_2 & & Cl & & CH_2P(C_6H_5)_3\\ & M & & M & \\ (C_6H_5)_3PCH_2 & & Cl & & CH_2P(C_6H_5)_3\end{array}\right]Cl_4$$

No.	**7**	**8**	**9**
M	Al	Ga	In

The ^1H NMR spectra of **7** and **8** showed a doublet signal for CH_2P at 3.2 and 2.7 ppm respectively and a multiplet signal for phenyl groups at 7.4—7.9 ppm in a ratio of 2 : 15 at a low temperature in dichloromethane-d_2. In complexes **7**—**9**, the coupling constants ($^2J_{HCP}$) of the methylene group are larger than that of **L** and the chemical shifts are at a lower field than that of **L**, the chemical shift of **7** being the lowest, as is shown in Table 1. The configuration of these metals is assumed to be tetrahedral from the following facts: **7**—**9** are not polymeric, because they are soluble in dichloromethane and alcohols. The elemental analyses of **7**—**9** agreed with that of $[L_2MCl_3]_n$. The structures of $AlCl_3$, $GaCl_3$, $InCl_3$ and related compounds are of a dimeric, tetrahedral configuration.[12] Complexes **7** and **8** have free anion, judging from the equivalent conductance. Thus, it is suggested that **7**—**9** are dimers bridged by chloride anions and with a tetrahedral configuration.

3 : 1 Complexes: μ-Chloro-bis[tris(methylenetriphenylphosphorane)metal (Al, Ga)] pentachlorides have been isolated from a reaction mixture of **L** with $AlCl_3$ or $GaCl_3$ in the mole ratio of 3 : 1 or 5 : 1. The complexes are soluble in alcohols, chloroform, dichloromethane, DMF, DMSO, and water. The gallium complex **11** is stable in dichloromethane at −62 °C, though the aluminium complex **10** is unstable under the same conditions, giving the corresponding phosphonium salt (**6a**). The ^1H NMR spectrum of **11** showed a doublet signal for the methylene group at 2.8 ppm and a multiplet signal for the phenyl groups at 7.4—7.9 ppm, in the ratio of 2 : 15, at −62 °C. The chemical shift and the coupling constant ($^2J_{HCP}$: 16.7 Hz) of the methylene group of **11** are very similar to those of **8** as is shown in Table 1. The elemental analyses of **10** and **11** agreed with that of $[L_3MCl_3]_n$. Complex **11** has free anion, judging from the equivalent conductance. Thus, **10** and **11** can also be assumed to be dimers bridged by a chloride anion.



$$3(C_6H_5)_3P{=}CH_2 + AlCl_3 \longrightarrow \qquad 5(C_6H_5)_3P{=}CH_2 + GaCl_3 \longrightarrow$$

$$\left[\begin{array}{ccccc} & (C_6H_5)_3PCH_2 & & CH_2P(C_6H_5)_3 & \\ (C_6H_5)_3PCH_2- & M & -Cl- & M & -CH_2P(C_6H_5)_3\\ & (C_6H_5)_3PCH_2 & & CH_2P(C_6H_5)_3 & \end{array}\right]Cl_5$$

No.	**10**	**11**
M	Al	Ga

Table 1. ^1H NMR data of complexes

No.	CH_2P		C_6H_5	Temp	Solvent and standard
	δ	$^2J_{HCP}$/Hz	δ	°C	
3	2.17d(2H)	12.3	7.3—8.0m(15H)	−80	1)
7	3.2d(2H)	14.6	7.4—7.9m(15H)	−80	2)
8	2.7d(2H)	16.7	7.4—7.9m(15H)	−62	2)
9	2.2d	15.2	7.2—7.9m	−80	2)
11	2.8d(2H)	16.7	7.4—7.9m(15H)	−62	2)
L′[a)]	0.13d(2H)	7.5	6.2—7.2m(15H)	r.t.	

Solvents: 1) CD_3OD, 2) CD_2Cl_2. Standard: internal TMS (δ=0). a): Ref. 4.

The stable alkylidenetriphenylphosphorane complexes in dichloromethane are those with metals of IB Group (Cu, Ag, Au),[5b—d] IIB Group (Zn, Cd)[5a] and IIIA Group (Al, Ga) and with Pb.[3]

Experimental

Measurements. The ^1H NMR spectra were measured with R-40 (Hitachi) and SXP4-100 pulse ST (Bruker) spectrometers. The electric conductivities of solutions were determined by the use of a conductmetric meter, CM-30 (Shimadzu) in methanol for **3** or in dichloromethane for **7**, **8**, and **11** at a low temperature.

Starting Materials. The methylene-[13] and ethylidenetriphenylphosphoranes[5d] were prepared from the corresponding phosphonium bromides by the sodium-amide method.

Preparation of Complexes. *Di-μ-chloro-bis[(methylenetriphenylphosphorane)beryllium] Dichloride (1)*: Beryllium dichloride (0.07 g, 0.876 mmol) was added to a dry THF (6 cm^3) solution of **L** (0.55 g, 1.99 mmol) at room temperature under a nitrogen atmosphere. The mixture was stirred for 12 h, then the white complex thus precipitated was filtered under nitrogen, washed with dry ether, and dried under a vaccum. Yield: 0.27 g (86.5%). Decomp 224 °C. Found: C, 64.81; H, 5.19%. Calcd for $C_{38}H_{34}P_2Be_2Cl_4$ (MW 712.46) C, 64.05; H, 4.81%.

Di-μ-chloro-bis[(ethylidenetriphenylphosphorane)beryllium] Dichloride(2): This complex was prepared from a reaction mixture of beryllium dichloride (0.06 g, 0.751 mmol) and **L′** (0.436 g, 1.50 mmol) in THF (6 cm^3). After 10 h, the white complex thus precipitated was filtered, washed with dry ether, and dried. Yield: 0.10 g (36.0%). Decomp 220 °C. Found: C, 63.41; H, 5.40%. Calcd for $C_{40}H_{38}P_2Be_2Cl_4$ (MW 740.50) C, 64.88; H, 5.17%.

Di-μ-chloro-bis[(methylenetriphenylphosphorane) magnesium] Dichloride (3): Complex **3** was prepared from magnesium dichloride (0.035 g, 0.368 mmol), **L** (0.41 g, 1.48 mmol), and THF (6 cm^3) at room temperature. After 4 d, the white complex thus precipitated was filtered under nitrogen, washed with ether, and dried. Yield: 0.10 g (73.2%). Decomp 60 °C. Found: C, 61.16; H, 4.78%. Calcd for $C_{38}H_{34}P_2Mg_2Cl_4$ (MW 743.06) C, 61.42; H, 4.61%.

Di-μ-chloro-bis[bis(methylenetriphenylphosphorane)aluminium] Tetrachloride (7): Aluminium trichloride (0.12 g, 0.9 mmol) was added to a dry THF (8 cm^3) solution of **L** (0.49 g, 1.77 mmol) under nitrogen. After 22 h, the white complex thus precipitated was filtered under nitrogen, washed with dry pentane, and dried under a vacuum. Yield: 0.4 g (64.8%). Decomp 225 °C. Found: C, 66.67; H, 5.18%. Calcd for $C_{76}H_{68}$-

$P_4Al_2Cl_6$ (MW 1371.92) C, 66.54; H, 5.00%.

Di-μ-chloro-bis[bis(methylenetriphenylphosphorane)gallium] Tetrachloride (8): Gallium trichloride (0.43 g, 2.44 mmol) was added to a THF (20 cm^3) solution of **L** (1.35 g, 4.88 mmol). The color of the **L** changed from yellow to colorless. The white complex thus precipitated was filtered after 2 h, washed with dry ether and dried. Yield: 1.61 g (90.5%). Decomp 187 °C. Found: C, 63.14; H, 5.08%. Calcd for $C_{76}H_{68}P_4Ga_2Cl_6$ (MW 1457.40) C, 62.63; H, 4.70%.

Di-μ-chloro-bis[bis(methylenetriphenylphosphorane)indium] Tetrachloride (9): Indium trichloride (0.08 g, 0.36 mmol) was added to a THF (10 cm^3) solution of **L** (0.20 g, 0.72 mmol). The yellow color of **L** changed to colorless. The white complex thus precipitated was filtered after 10 h, washed with dry ether, and dried. Yield: 0.18 g (64.3%). Decomp 197 °C. Found: C, 59.11; H, 4.21%. Calcd for $C_{76}H_{68}P_4In_2Cl_6$ (MW 1547.62) C, 58.98; H, 4.43%.

μ-Chloro-bis[tris(methylenetriphenylphosphorane)aluminium] Pentachloride (10): This complex was prepared from $AlCl_3$ (0.08 g, 0.6 mmol) and **L** (0.5 g, 1.81 mmol) in THF (10 cm^3). After 22 h, the white complex was filtered. Yield: 0.38 g (65.8%). Decomp 231 °C. Found: C, 70.02; H, 6.08%. Calcd for $C_{114}H_{102}P_6Al_2Cl_6$ (MW 1924.56) C, 71.15; H, 5.34%.

μ-Chloro-bis[tris(methylenetriphenylphosphorane)gallium] Pentachloride (11): This complex was prepared from $GaCl_3$ (0.09 g, 0.511 mmol), **L** (0.77 g, 2.79 mmol), and THF (12 cm^3). After 10 h, the white complex thus precipitated was filtered, washed with ether, and dried. Yield: 0.12 g (23.4%). Decomp 204 °C. Found: C, 67.11; H, 5.47%. Calcd for $C_{114}H_{102}P_6Ga_2Cl_6$ (MW 2010.04) C, 68.12; H, 5.12%.

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