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FLUXIONAL BIS(DIPHENYLPHOSPHINO)METHANE COMPLEXES OF ALUMINIUM- AND GALLIUM-ALKYLS *

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Summary

Bis(diphenylphosphino)methane forms a 1 : 2 complex with triethylaluminium, but 1 : 1 complexes with trimethylaluminium, trimethyl- and triethyl-gallium, and chlorodimethylgallium. The trialkyl complexes have NMR-equivalent $P(C_6H_5)_2$ groups in solution in the temperature range +20 to −80 °C, probably because of a very rapid site exchange of the metal atoms. A single crystal X-ray diffraction study of the Me_2GaCl complex (**5**) showed that in the solid the metal is coordinated to only one phosphorus atom. In this case a splitting of the ^{31}P signal into an AB quartet could be observed in toluene solution below −60 °C. Crystal data: monoclinic space group $P2_1/c$, a 11.172(3), b 10.431(2), c 24.881(6) Å, β 115.26(2)°, V 2622.26 Å^3 at −40 °C, d(calc) 1.316 g cm^{-3} for $Z = 4$. $R = 0.057$ and $R_w = 0.054$ for 280 parameters and 3181 observed reflections with $I > 2.0\sigma(I)$. The Ga–P distance is 2.535(2) Å.

Introduction

Bis(diphenylphosphino)methane, first synthesized by Issleib and Müller in 1959 [1], is at present playing a key rôle as a small-bite bidentate ligand for di- and poly-nuclear metal complexes [2]. Most of the relevant studies have dealt with the compounds derived from the later transition elements, the majority of the examples involving the coinage metals [3–8], palladium and platinum [9–11], where the problems of metal–metal interaction, of oxidative addition reactions, and of neighbouring group effects have attracted considerable interest.

Far less is known about the particular features of the corresponding complexes of the main group metals, although a few aluminium-alkyl complexes were synthesized as early as 1966 [12]. Following some earlier work on structural and dynamic effects

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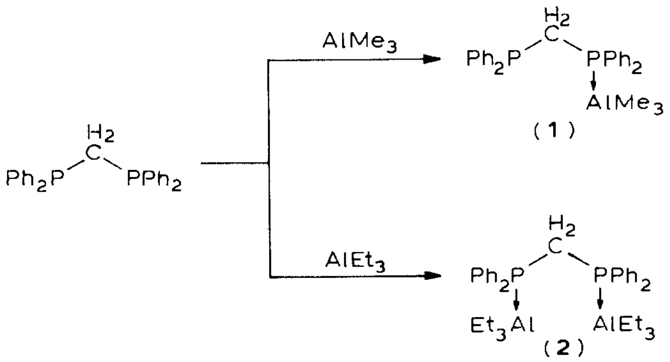
of small-bite 1,3-difunctional ligand complexes of organometallic compounds [13–18] we report now on the synthesis and properties of the title compounds, where fluxional behaviour with extremely low energy barriers for the metal shift P $\rightarrow$ P has been observed. However, contrary to the findings with organic derivatives of the alkali and alkaline earth metals [19], no deprotonation of the P–CH_2–P bridge of the ligand has been achieved using the Group III alkyls. This result is also at variance with the results for the bis(diphenylphosphino)amine analogue which is easily deprotonated at the NH moiety by $R_3Al(Ga)$ reagents [20].

Synthesis and spectral data

Surprisingly, bis(diphenylphosphino)methane was found to react in different ways with an excess of uncomplexed aluminium trimethyl and triethyl. Consistently, the reactions (in toluene solvent) at 20 to 40 °C showed no evolution of gaseous by-products (methane or ethane, respectively), but the product from Me_3Al was a 1 : 1 complex, while Et_3Al gave a 1 : 2 complex:

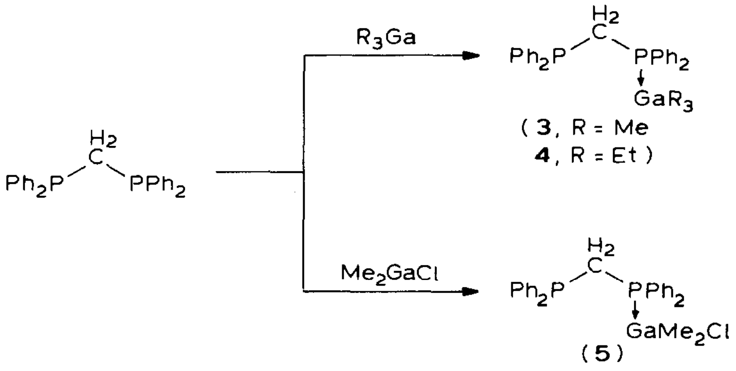


Compound **1** is precipitated from the reaction mixture as colourless crystals upon addition of pentane, but complex **2** appears as a crystalline solid only after evaporation of the solvent followed by the addition of hexane. Even after washing with hexane and drying in vacuo (4×10^{-3} torr, 40 °C) two equivalents of Et_3Al are retained in the material. Prolonged heating of the complexes above their melting points and to 190 °C for several hours causes no alkane evolution.

The two gallium trialkyl adducts **3** and **4** were obtained similarly, but purification of the products was less straightforward because of their high solubility in hydrocarbons and because of the large melting point depressions caused by traces of excess starting materials. The stoichiometries again indicate a 1 : 1 mol ratio of the components. Good product crystallinity was finally achieved when the more polar dimethylgallium chloride [21] was used; this gave the well-defined 1 : 1 complex **5**.

Complexes **3** and **4** are more susceptible to thermal decomposition than **1** and **2** and rapidly turn yellow on being heated to 160 °C. But again, no alkane is eliminated at this temperature. As expected, all of the compounds **1–5** are very sensitive to air and moisture.

The NMR data for the compounds **1–5** confirm the shown stoichiometries through the integral ratios of the proton resonances. The number of resonances and the multiplicity of the signals are also in agreement with the above formulae, but

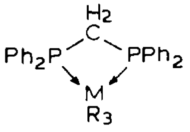


(3, R = Me
4, R = Et)

(5)

virtually symmetrical metal coordination is indicated not only for **2**, but also for **1** and **3–5**. The ^1H and ^{13}C resonances for the CH_2 group show symmetrical 1 : 2 : 1 splitting due to virtually equivalent phosphorus atoms, and the $\{^1H\}$-^{31}P spectra comprise sharp singlet signals. The C_6H_5 groups also give only one set of ^{13}C signals (C(1) to C(4)).

In explaining these facts therefore both a symmetrical structure **A**, with a pentacoordinated metal atom, and a rapid metal site exchange (as shown in **B**) have to be considered. The latter appeared to be the less likely, as for compounds **1–4** the NMR spectra are temperature-independent in the range from ambient temperature to $-80\,^\circ C$. Only if the activation barriers for the site exchange **B** were extremely low could the unsymmetrical, but fluxional structure, remain undetected at the low temperature limit of these experiments [22].



(**A**)

(**B**)

In order to determine the true ground state structure, at least for the solid state, a single crystal X-ray diffraction study was carried out with compound **5**, which because it has an electronegative substituent (Cl) and the lowest steric hindrance is the most likely to have a pentacoordinate structure. However, it was only for this compound that the ^{31}P signal was split into an AB pattern below $-60°C$, with $\delta P(A) - 8.0$ ppm, $\delta P(B) - 21.6$ ppm and $^2J(P(A)P(B))$ 100 Hz (in toluene at $-81\,°C$).

The crystal and molecular structure of compound 5

The results of the structure analysis are summarized in Fig. 1 and in the Tables 1 and 2. The unit cell contains individual molecules in which the chlorodimethylgallium moiety is attached to only one of the two phosphorus donor centers of the ligand. The most significant consequence of the mono-adduct formation is a marked difference between the bridging bonds P(1)–C(1)–P(2): P(1)–C(1), which involves tetracoordinate phosphorus, is shorter (1.809(5) Å) than P(2)–C(1) (1.867(5) Å), which involves tricoordinate phosphorus. A similar though less pronounced trend, is

TABLE 1

FRACTIONAL ATOMIC COORDINATES OF THE NON-HYDROGEN ATOMS OF COMPOUND 5 WITH e.s.d.'s, IN UNITS OF THE LAST SIGNIFICANT FIGURE, IN PARENTHESES

Atom	*x/a*	*y/b*	*z/c*	Atom	*x/a*	*y/b*	*z/c*
Ga	0.6361(1)	0.0823(1)	0.9597(1)	C(33)	1.0483(8)	0.2049(11)	0.8589(4)
Cl	0.4199(2)	0.1371(2)	0.9212(1)	C(34)	0.9645(7)	0.3059(8)	0.8350(3)
P(1)	0.6840(1)	0.2477(1)	0.8968(1)	C(35)	0.8558(6)	0.3213(7)	0.8473(3)
P(2)	0.5138(1)	0.1111(1)	0.7825(1)	C(4)	0.3436(5)	0.1442(5)	0.7281(2)
C(1)	0.5469(5)	0.2656(5)	0.8243(2)	C(41)	0.3026(5)	0.1612(5)	0.6670(2)
C(2)	0.7005(5)	0.3969(5)	0.9360(2)	C(42)	0.1702(6)	0.1821(7)	0.6301(2)
C(21)	0.5896(6)	0.4670(6)	0.9296(2)	C(43)	0.0779(6)	0.1860(8)	0.6524(3)
C(22)	0.6011(6)	0.5686(6)	0.9683(3)	C(44)	0.1153(6)	0.1664(8)	0.7120(3)
C(23)	0.7216(7)	0.6012(6)	1.0124(2)	C(45)	0.2476(6)	0.1443(7)	0.7502(2)
C(24)	0.8343(6)	0.5312(6)	1.0186(3)	C(5)	0.6107(5)	0.1279(6)	0.7394(2)
C(25)	0.8226(5)	0.4306(6)	0.9807(2)	C(51)	0.6879(6)	0.0232(7)	0.7399(2)
C(3)	0.8295(6)	0.2334(6)	0.8830(3)	C(52)	0.7598(7)	0.0266(10)	0.7056(3)
C(31)	0.9132(7)	0.1310(7)	0.9067(3)	C(53)	0.7550(7)	0.1332(12)	0.6730(3)
C(32)	1.0264(9)	0.1215(11)	0.8943(4)	C(54)	0.6830(7)	0.2386(9)	0.6735(3)
				C(55)	0.6108(6)	0.2374(6)	0.7069(2)
				C(6)	0.6593(8)	−0.0916(7)	0.9355(3)
				C(7)	0.7255(7)	0.1576(6)	1.0391(2)

observed in the Ph–P bond lenghts to P(1) and P(2). The P(1)–C(1)–P(2) angle of 110.4(3)° shows virtually no deviation from the standard tetrahedral value. The valence angles at the tetracoordinated P-atom (P(1)) are close to the tetrahedral value, while those at the tricoordinated P-atom (P(2)) are close to 100°, which is typical for most tertiary phosphines.

At the gallium center, the Cl–Ga–P(1) angle is surprisingly small (92.0(1)°) and the C(6)–Ga–C(7) angle is exceedingly large (127.1(3)°), while the remaining angles are again in the conventional tetrahedral region. Together with the long Ga–P(1) (2.535(2)) and Ga–Cl (2.260(2) Å) bonds these parameters are indicative of rather weak P–Ga bonding [23,24]. The much shorter P–Ga bond length in Me$_3$P–GaCl$_3$

TABLE 2

SELECTED BOND DISTANCES (Å) AND ANGLES (°) IN COMPOUND 5

Ga–P(1)	2.535(2)	Ga–C(6)	1.962(7)
Ga–Cl	2.260(2)	Ga–C(7)	1.959(6)
P(1)–C(1)	1.809(5)	P(2)–C(1)	1.867(5)
P(1)–C(2)	1.804(5)	P(2)–C(4)	1.837(5)
P(1)–C(3)	1.804(6)	P(2)–C(5)	1.828(6)
P(1)–C(1)–P(2)	110.4(3)	P(1)–Ga–Cl	92.0(1)
C(1)–P(1)–Ga	111.9(2)	P(1)–Ga–C(6)	110.5(2)
C(1)–P(1)–C(2)	107.3(2)	P(1)–Ga–C(7)	101.5(2)
C(1)–P(1)–C(3)	105.5(3)	Cl–Ga–C(6)	111.1(2)
C(2)–P(1)–C(3)	106.4(3)	Cl–Ga–C(7)	108.6(2)
C(2)–P(1)–Ga	104.6(2)	C(6)–Ga–C(7)	127.1(3)
C(3)–P(1)–Ga	120.4(2)		
C(1)–P(2)–C(4)	98.4(2)		
C(1)–P(2)–C(5)	102.6(2)		
C(4)–P(2)–C(5)	103.6(2)		

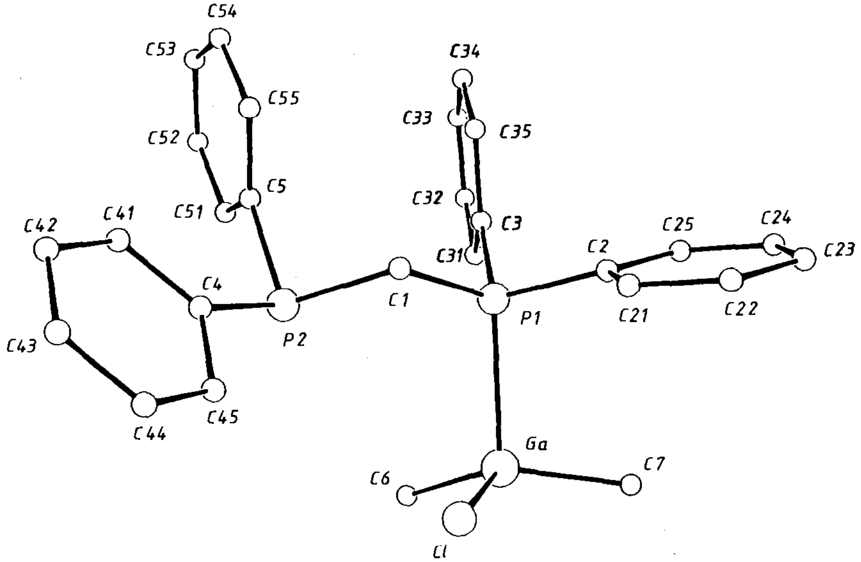
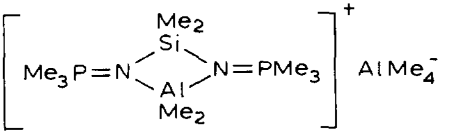


Fig. 1. Perspective view of the molecular geometry of compound 5 (ORTEP) with the numbering of atoms. Hydrogen atoms are omitted for clarity.

(2.353(2) Å) may be due, at least partly, to inductive effects [23]. From the observed bond length pattern in a variety of donor-acceptor complexes it is well known that the donor-acceptor bond is particularly sensitive to substituent effects [25]. The Ga–C bond lengths, on the other hand, are similar to those in standard four-, five- or six-coordinated Ga complexes [24].

There is no evidence in the structure of molecule **5**, however, for an imminent intramolecular approach of P(2) to Ga (P(2)–Ga 4.031(2) Å), a possibility suggested by the NMR data, and shown in formula **A**, which may represent a transition state or intermediate in the metal site exchange process in solution. Also, the intermolecular distances to Ga and P(2) show no approaches closer than 4.0 and 4.4 Å, respectively. This is in contrast to earlier findings in a variety of donor-acceptor complexes of gallium with nitrogen donor molecules, where ready five-membered ring chelate formation with or without concomitant ionization was observed [24]. The differences in those systems are certainly due to the weaker donor properties of phosphorus as compared with nitrogen, as well as to the strain in the four-membered ring generated by chelate formation in **5**.

An ionic structure $[\text{dpmAlEt}_2]^+[\text{AlEt}_4]^-$ should also be considered for molecule **2**, although there is no experimental evidence for a significant concentration of such a species in solution. In a previous example, **C**, NMR spectra gave unambiguous proof for this type of structure [26]:



(C)

Experimental

General: All experiments were carried out under an atmosphere of dry, pure nitrogen. Solvents and glassware were dried and saturated or filled with nitrogen, respectively. The metal alkyls were commercially available or obtained as gifts from Siemens AG, Erlangen (GaR_3). Me_2GaCl was prepared by a published procedure [21].

Bis(diphenylphosphino)methane-trimethylaluminium, 1

Trimethylaluminium (0.29 g, 4.06 mmol) was added to a solution of bis(diphenylphosphino)methane (0.77 g, 2.05 mmol) in 5 ml of toluene. The mixture was kept at 40 °C for 1.5 h. A colourless precipitate formed upon addition of 3 ml hexane and cooling to −30 °C. The product was washed with cold hexane and dried in vacuo. Yield 0.6 g (64%), mp. 85 °C. Anal.: Found: C, 72.50; H, 6.80; P, 13.80; mol. mass (MS), 456. $C_{28}H_{31}AlP_2$ calcd.: C, 73.67; H, 6.84; P, 14.00%; mol. mass, 456,49. NMR ^1H: (C_6D_6) δ −0.48 (s, 9 H, CH_3), 2.65 (t, ^2J(PH) 4 Hz, 2 H, CH_2), 6.35–7.10 (m, 20 H, C_6H_5); ^{13}C (C_6D_6) δ −7.8 (s, CH_3), 24.4 (t, ^1J(PC) 13 Hz, CH_2), 128.0 ("t" + s, C(3),(4) of C_6H_5), 133.1 ("t", C(2) of C_6H_5); ^{31}P (C_6D_6) δ 22.6 (s {^1H}). The spectra are largely unchanged at −80 °C (in toluene).

Bis(diphenylphosphino)methane-bis(triethylaluminium), 2

Triethylaluminium (0.510 g, 4.45 mmol) and the ligand (0.869, 2.24 mmol) were dissolved in 4 ml of toluene and heated to 60 °C for 1.5 h. The solvent was then removed in vacuo and the solid residue crystallized and washed with hexane and dried in vacuo. Yield 0.65 g (47%), mp. 54 °C. Anal.: Found: C, 72.3; H, 8.70; P, 9.61. $C_{36}H_{52}Al_2P$ calcd.: C, 70.57; H, 8.55; P, 10.11%; mol. mass, 612.71. NMR: ^1H (C_6D_6) δ −0.2 (q, 12 H, CH_2), 0.9 (t, ^3J(HH) 7 Hz, 18 H, CH_3), 2.4 (t, ^2J(PH) 4.0 Hz, 2 H, CH_2P), 6.0–6.50 (m, 20 H, C_6H_5); ^{13}C (C_6D_6) δ −9.8 (s, CH_2Al), −1.04 (s, CH_3), 13.26 (t, ^1J(PC) 13.18 Hz, CH_2P), 118.0 ("t" + s, C(3),(4) of C_6H_5), 123.2 ("t", C(2) of C_6H_5); ^{31}P (C_6D_6) δ −19.7 (s, {^1H}). The spectra are largely unchanged at −80 °C (in toluene).

Bis(diphenylphosphino)methane-triethylgallium, 4

Triethylgallium (0.62 g, 3.96 mmol) and the ligand (0.76 g, 1.97 mmol) were mixed in 5 ml of toluene and heated to 100–120 °C for 4 h. The mixture was cooled to −30 °C after careful addition of an upper layer of hexane. After 24 h the white precipitate was collected and dried in vacuo. Yield 0.6 g (56%), mp. 48 °C. Anal.: Found: C, 66.10; H, 6.90; P, 10.07. $C_{31}H_{37}GaP_2$ calcd.: C, 68.78; H, 6.89; P, 11.44%; mol. mass, 541.30. NMR: ^1H (C_6D_6) δ 0.15 (q, 6 H, CH_2), 0.95 (t, ^3J(HH) 7 Hz, 9 H, CH_3), 2.15 (t, ^2J(PH) 4.0 Hz, 2 H, CH_2P), 6.20–6.95 (m, 20 H, C_6H_5); ^{13}C (C_6D_6) δ 4.0 (s, CH_2), 12.0 (s, CH_3), 28.2 (t, ^1J(PC) 21 Hz, CH_2P), 128–136 (m, C_6H_5); ^{31}P (C_6D_6) δ −18.9 (s, {^1H}). The spectra are largely unchanged in toluene at −80 °C.

Bis(diphenylphosphino)methane-trimethylgallium, 3

This compound was not obtained pure. The ^1H NMR spectrum of the impure material had resonances at δ −0.5 (s, CH_3), 2.3 (t, CH_2, ^2J(PH) 1.5 Hz) and 6.4–6.9 (m, C_6H_5). The ^{31}P resonance was at δ −22.6 (in C_6D_6). The compound did not crystallize with a well-defined ratio of reactants.

Bis(diphenylphosphino)methane-chlorodimethylgallium, 5

To the ligand (5 g, 13.02 mmol) in toluene was added $Me_2GaCl \cdot (Et_2O)_{1/2}$ (2,24 g, 13.1 mmol). The mixture was heated to 50 °C for 10 min and then the solvent was evaporated to leave only a small volume. Colourless crystals were isolated from the toluene at −10 °C. Yield 4.5 g (66%), mp. 119 °C. Anal.: Found: C, 61.25; H, 5.40; Cl, 6.77; P, 11.68. $C_{27}H_{28}ClGaP_2$ calcd.: C, 62.41; H, 5.43; Cl, 6.82; P, 11.92%; mol. mass, 519.63. NMR: ^1H (C_6D_6) δ −0.2 (s, 6 H, CH_3), 2.7 (t, ^2J(PH) 4 Hz, 2 H, CH_2P), 6.5–7.2 (m, 20 H, C_6H_5); ^{13}C (C_6D_6) δ −2.27 (s, CH_3), 23.97 (t, ^1J(PC) 10.25 Hz, CH_2P), 128.6–133.8 (m, C_6H_5); ^{31}P (C_6D_6) δ −20.8 ppm (s, {^1H}). For the spectrum at −81 °C, see text.

Structure determination of 5

Crystal data: $C_{27}H_{28}ClGaP_2$, $M_r = 519.645$, monoclinic $P2_1/c$, a 11.172(3), b 10.431(2), c 24.881(6) Å, β 115.26(2)°, V 2622.26 Å^3, at −40 °C, d(calcd) 1.316 g cm^{-3} for $Z = 4$, $F(000)$ 1072. 4579 reflections were measured on a Syntex $P2_1$ automated four-circle diffractometer using graphite-monochromatized Mo-K_α radiation ($\lambda = 0.71069$ Å, ω-scans, $\Delta\omega = 1°$, $\dot{\omega} \geq 0.9°$/min, $1 \leq \vartheta \leq 24°$, T −40 °C). After Lorentz and polarization corrections and merging of equivalent reflections ($R_{int} = 0.037$, SHELX 76), 4101 unique structure factors remained, 920 of which were deemed "unobserved" ($F \leq 4\sigma(F_0)$) and excluded from all further calculations. An absorption correction was not applied (μ(Mo-K_α) = 12.79 cm^{-1}).

The structure was solved by direct methods (SHELX 76), which yielded the heavy atoms and parts of the phenyl rings, and completed by Fourier syntheses. After anisotropic refinement of the non-H atoms, all methyl and methylene H atoms could be located in difference maps; those of the phenyl rings were introduced at idealized geometrical positions (d(C–H) 0.98 Å). Anisotropic refinement of the non-H atoms with H atoms as fixed atom contributions ($U(CH_3) = 0.10$, $U(CH_2) = 0.05$, $U(CH) = 0.05/0.08$ Å^2) converged at $R = 0.057$, $R_w = 0.054$, $w = k/\sigma^2(F_0)$, $k = 3.06$ in the last cycle. The maximum ratio of shift to error was less than 0.005 in the last cycle. A final difference-Fourier synthesis showed maxima and minima of +1.13 e/Å^3 and −0.67 e/Å^3, respectively, with the highest peaks around the Ga atom and much smaller values elsewhere. Details of the data collection and refinement procedures, as well as the sources of the scattering factors used, have been published elsewhere [27]. Tables with additional crystal structure data, anisotropic temperature factors, H atom coordinates and observed and calculated structure factors have been deposited [28].

Acknowledgement

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