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μ-CHLOROBIS(DIETHYLALUMINIUM) BIS(DIPHENYLPHOSPHINO)-METHANIDE, A COMPLEX WITH WINDSHIELD WIPER FLUXIONALITY *

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Summary

Lithiated bis(diphenylphosphino)methane reacts with two equivalents of a dialkylchloro-alane or -gallane (R_2MCl; R = CH_3, C_2H_5; M = Al, Ga;) to form coordination compounds (**3**–**6**) which have peculiar structure and show unusual fluxional behaviour. A single crystal X-ray diffraction study of the compound $[(C_6H_5)_2P]_2CH[(C_2H_5)_2Al]_2Cl$ (**4**) reveals that these complexes can be described as the unsymmetrical adducts of the potential six-electron donor anion $[Ph_2\bar{P}-\bar{C}H-\bar{P}Ph_2]^-$ with the difunctional acceptor cation $[Et_2Al-Cl-AlEt_2]^+$. Through P→ Al and C→ Al donor/acceptor bonds a five-membered ring PCAlClAl is generated, which has an envelope conformation typical for this ring size and a center of chirality at the central carbon atom of the anion. Variable temperature ^1H, ^{13}C, and ^{31}P NMR spectroscopy (in toluene) indicates that the acceptor portion R_2MClMR_2 appears to undergo a rotation around the central P_2C–Al bond, thereby rendering the PPh_2 groups equivalent on the NMR time scale through breaking and re-formation of the Al–P bonds. The process is best regarded as a "windshield wiper" motion, which leaves the AlC bonds intact since complete dissociation of R_2MCl units is unlikely in the light of the low activation barriers for the fluxionality.

Introduction

Bis(diorganophosphino)-methanes and -amines are extremely versatile 1,3-difunctional donor molecules which have found increasing application (1) as tailor-made "frames" for binuclear complexes with short metal–metal distances [1,2], (2) as "small-bite" bis-phosphine chelating ligands in mononuclear complexes [1,2], and

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** X-ray analysis.

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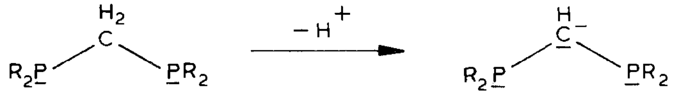
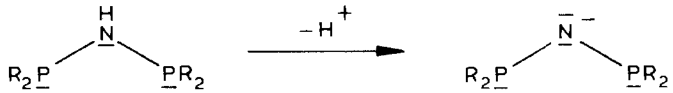
(3) as phosphine ligands with reactive sites (CH_2 or NH) in the bridging position [3,4] between the two phosphorus atoms. Deprotonation in these positions leads to extremely powerful six-electron donor anions containing three donor sites in the closest proximity:





A large number of transition metal complexes containing the above ligands has been described [1,2], mainly with the low-valent late transition elements as the preferred acceptor centers. (For a few leading references see refs. 1–4.) The anionic ligands are far less well represented than the neutral precursors [3–15], also much less is known generally for the analogous derivatives of the *p*-block metals. Lithiation of $Ph_2PCH_2PPh_2$ was carried out by Issleib and his collaborators [3] soon after the first synthesis of this important compound [15]. $Ph_2PNHPPh_2$ can be converted into alkali amides even more readily, and lithium, sodium, and potassium amides $(Ph_2P)_2NM$ have been reported (M = Li, Na, K) [16–18]. Earth alkali salts with these anions are, to the best of our knowledge, still unknown, but compounds containing Al–P or Ga–P bonds based on the bis(phosphino)-methane or -amine skeletons have recently attracted considerable interest [5,19]. $Ph_2PNHPPh_2$ was found to react with trialkyl-aluminium or -gallium compounds to give dimeric products with the anion Ph_2PNPPh_2 as a P,N- or P,P-difunctional ligand, respectively [19]. In contrast, $Ph_2PCH_2PPh_2$ was not deprotonated at the PCH_2P bridge, and only 1/1 or 1/2 addition compounds were obtained [20]. The complexes with 1/1 stoichiometry are fluxional in solution, with he site exchange $M\overline{P}\,\overline{P} \rightleftharpoons \overline{P}\,\overline{P}M$ rapid on the NMR time scale [20].

As an extension of this work we report here the results of experiments carried out in an attempt to screen the range of products available from a combination of the trifunctional $[Ph_2PCHPPh_2]^-$ ligand with R_2AlX or R_2GaX substrates. While only untractable materials were obtained for the clearcut 1/1 stoichiometry, a new class of compounds was detected serendipitously from higher molar ratios, preferably 1/2, with R = Me, Et and X = Cl. Because of the intriguing fluxional properties observed a detailed study of spectroscopic and structural features was undertaken.

Synthesis and properties of the title compounds

The reaction of lithiated $Ph_2PCHLiPPh_2$ with equimolar quantities of dimethylchloro-alane or -gallane in non-polar organic solvents yields colorless insoluble products of the expected composition $(Ph_2P)_2CH \cdot MMe_2$, where M = Al or Ga (**1** and **2**, respectively). The structure of these materials is unknown. They are slightly soluble in tetrahydrofuran, and the solutions show a singlet signal in the ^{31}P NMR spectra. Oligomeric compounds are probably present in the solid state, and are degraded by THF solvation.

$$\mathrm{Ph_2PCHLiPPh_2} \xrightarrow[-\mathrm{LiCl}]{\mathrm{Me_2MCl}} [(\mathrm{Ph_2P})_2\mathrm{CH}\cdot\mathrm{MMe_2}]_n$$

$$\begin{aligned}&(\mathbf{1}\text{: } \mathrm{M} = \mathrm{Al};\\ &\ \mathbf{2}\text{: } \mathrm{M} = \mathrm{Ga})\end{aligned}$$

In experiments with 1/2 molar ratios of the same reactants and their ethyl homologues, crystalline products (**3**–**6**) can be isolated in high yield from the reaction mixture after filtration from the LiCl by-product.

$$\mathrm{Ph_2PCHLiPPh_2} \xrightarrow[-\mathrm{LiCl}]{2\,\mathrm{R_2MCl}} (\mathrm{Ph_2P})_2\mathrm{CH}\cdot(\mathrm{MR_2})_2\mathrm{Cl}$$

$$\begin{aligned}&(\mathbf{3}\text{: } \mathrm{M} = \mathrm{Al},\ \mathrm{R} = \mathrm{Me};\\ &\ \mathbf{4}\text{: } \mathrm{M} = \mathrm{Al},\ \mathrm{R} = \mathrm{Et};\\ &\ \mathbf{5}\text{: } \mathrm{M} = \mathrm{Ga},\ \mathrm{R} = \mathrm{Me};\\ &\ \mathbf{6}\text{: } \mathrm{M} = \mathrm{Ga},\ \mathrm{R} = \mathrm{Et})\end{aligned}$$

As expected, the products are very sensitive to air and moisture, but are thermally stable well beyond their melting points. Solubility in most organic solvents is excellent. In the case of **3** and **5**, these solutions on standing slowly give a colorless precipitate of insoluble polymeric compounds of the same analytical composition. Such behaviour is not encountered with the ethyl derivatives **4** and **6**.

Nuclear magnetic resonance spectra

The ^{1}H, ^{13}C, and ^{31}P NMR spectra of compounds **3**–**6** are all very similar and show similar temperature dependency, with fully reversible spectral characteristics. It was therefore very likely that **3**–**6** would retain the same essential structure as observed for the ground state at low temperature, but with certain intra- or inter-molecular motions as the temperature is raised. The observation that the spectra of a given compound are largely independent of concentration and of the nature of the solvents rules out extensive dissociation into separate components. The observations suggested a fluxional behaviour for all four species in solution.

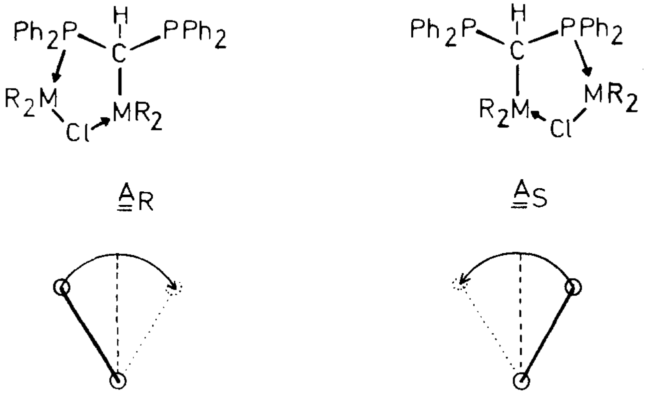
The low temperature extremes in the series of ^{31}P NMR spectra (in toluene) indicate two non-equivalent phosphorus atoms in the shift region of complexed and uncomplexed phosphines, respectively. With the exception of **5**, for which an AB splitting (^2J 25.5 Hz) was observed, the resonances were broad singlets, at least partly caused by quadrupole interaction between the phosphorus and the metal nuclei (Al: $s = \frac{5}{2}$; Ga: $s = \frac{9}{2}$).

Above the coalescence temperatures, which vary between −77°C (for **6**) and +44°C (for **4**), only singlet ^{31}P resonances are observed (^{1}H-decoupled).

In the ^{13}C NMR spectra, at low temperatures there are signals for four chemically non-equivalent alkyl groups R, the substituents at the metal atoms, along with an extremely complicated aryl region originating from several non-equivalent phenyl groups. The ^{13}C resonance of the P–*C*H–P bridge appears as a broadened doublet at low temperature. At high temperatures the R resonances collapse into two sets of equivalent R substituents, while the Ph resonances are also clearly simplified, and approach the patterns of virtually coupled equivalent phenyl groups (AXX′ for C(1), C(2), and C(3), singlets for C(4)). The P*C*HP signal is changed into a 1/2/1 triplet at high temperatures, clearly indicating equivalent PPh_2 groups as previously suggested by the Ph ^{13}C resonances. The ^1H coupled ^{13}C spectrum of **2** (at +82°C) confirmed the signal assignments through the additional splittings originating from $^1H-^{13}C$ coupling. The P–*C*H–P signal, in particular, is identified as associated with a carbon atom of *sp*^{3} hybridisation attached to two phosphorus and one hydrogen atoms: doublet of triplets, ^1J(HC) 115.2, ^1J(PC) 27.3 Hz. The latter is to be interpreted as the average of a large (^1J(PC) 52.7 Hz) and a very small coupling (^1J(PC) ca. 1 Hz) extracted from the broad low temperature doublet.

The ^1H NMR spectra, finally, are in agreement with the structural pattern derived from the ^{13}C and ^{31}P spectra. Signal overlap in the aliphatic region makes signal assignments much more difficult, however, and thus much less weight can be given to these results. Nevertheless, the high temperature triplet for the PC*H*P moiety (^2J(PH) 2.4 Hz) is a common feature for all four compounds, clearly corresponding to the P*C*P triplet in the ^{13}C spectra.

The above NMR data led to the proposal of the fluxional structure as shown in formula **A**, which is in full agreement with all the details of the complicated spectral patterns (Scheme 1). It is best regarded as a "windshield wiper" model, with the R_2MClMR_2 unit as the "wiper arm". A P–M bond is broken in the semicircular movement and re-formed to the second phosphorus atom after rotation about the central C–M axis.



SCHEME 1

In order to confirm this structure a single crystal X-ray diffraction study of compound **4** was undertaken.

The crystal and molecular structure of complex 4

The result of the structure determination is shown in Fig. 1, and the pertinent data are summarized in Tables 1 and 2. From Fig. 1 it is immediately obvious that the conclusions drawn from the analytical and spectroscopic data were correct at least for one species of the series in the crystal. The position of the unique hydrogen atom H(1) attached to the carbon atom C(1) bridging the two PPh_2 group was also localized in difference Fourier maps with sufficient accuracy.

One of the two aluminium atoms is attached to one of the two phosphorus atoms (*d*(Al(1)–P(1)) 2.431(2) Å), while the other is engaged in bonding with the phos-

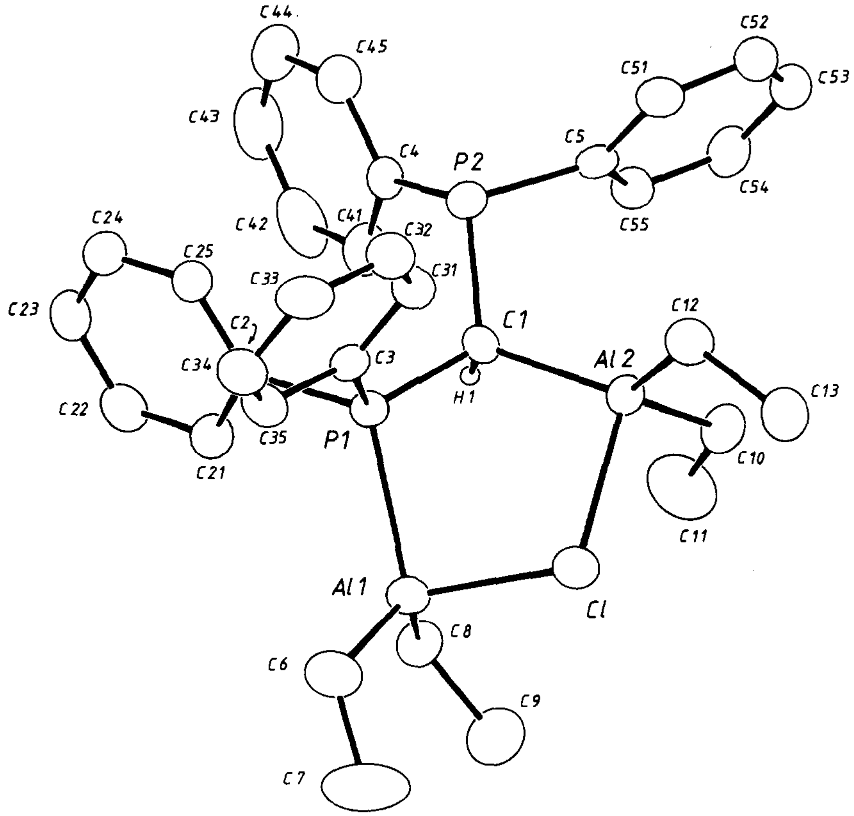
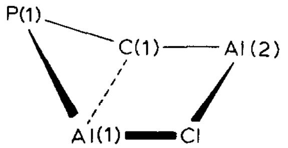


Fig. 1. Molecular structure of molecule 4 in the crystal. Hydrogen atoms are omitted for clarity, except for H(1). In the "windshield wiper" movement the bond P(1)–Al(1) is broken, and a bond P(2)–Al(1) is formed after rotation of the "wiper arm" C(1)Al(2)ClAl(1) around C(1)–Al(2).

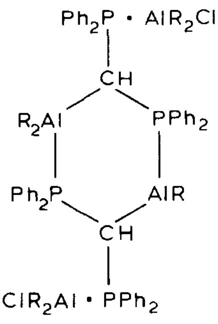
phorus-bridging carbon (*d*(Al(2)–C(1)) 2.047(4) Å). The second phosphorus atom (P(2)) thus represents a free donor center, which in solution is alternatingly occupied by the fluctuating Et_2Al group (Scheme 1). The two aluminium atoms are linked by a chloro-bridge with markedly different Al–Cl bond lengths (*d*(Al(1)–Cl) 2.273(2) and *d*(Al(2)–Cl) 2.392(2) Å, respectively).

While the distances and angles in the $Ph_2PCHPPh_2$ skeleton are wholly normal, the geometries at the two metal centers are somewhat irregular. The four substituents at each aluminium atom deviate strongly from a tetrahedral arrangement, as illustrated by extreme bond angles like ClAl(1)P(1) 91.3(1)° and C(6)Al(1)C(8) 123.0(2)° or ClAl(2)C(1) 99.2(1)° and C(1)Al(2)C(12) 121.7(2)°. This is reminiscent of the bonding situation in the related adduct $Ph_2PCH_2PPh_2 \cdot Me_2GaCl$, where similar deviations from the tetrahedral geometry were observed for the gallium environment [20]. The peculiar geometry of Al(2) can be accounted for by regarding the C(1), Al(2), C(10), C(12) moiety as a trialkylaluminium unit which becomes distorted from its original trigonal planar array towards an sp^3-geometry by the approaching chlorine donor.

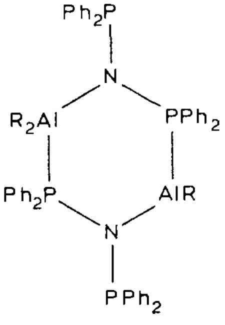
The Al(1)ClAl(2) angle of 106.8(1)° is an internal angle of a five-membered ring (Al(1)ClAl(2)C(1)P(1)). This ring system has an envelope conformation, with P(1) deviating markedly (0.92 Å) from the best plane through the remaining four atoms. The interplanar angle between the planes C(1)P(1)Al(1) and C(1)Al(1)ClAl(2) amounts to 46.6°.



The smallest internal angles of the heterocycle are found at Al(1) (91.3(1)°) and Al(2) (99.2(1)°), the largest at C(1) (114.4(2)°). With Al(1)P(1)C(1) 105.5(1)°, only the phosphorus atom is provided with an almost undistorted valence angle. Thus it appears that the aluminium atoms are the most readily deformed ring members. The various ring constituents with their very different geometrical requirements can presumably be best accommodated in a five-membered ring of the observed irregular structure. This is particularly surprising, since the formation of a six-membered ring dimer would appear to offer a more favourable solution (**B**):



(B)



(C)

The latter type of structure was found for an analogous nitrogen compound of 1/1 stoichiometry (**C**) [19].

The individual molecules have a centre of chirality at C(1). They can be presented as the optical isomers $\mathbf{A}_R$ and $\mathbf{A}_S$ (Scheme 1), and the windshield wiper movement transforms one isomer into the other. In the crystals both forms are present in equal amounts. Their sites in the unit cell are related by symmetry.

Experimental

Experiments were carried out under dry purified nitrogen. Solvents were dried and saturated with nitrogen. Glassware was oven-dried and filled with nitrogen.

Bis(diphenylphosphino)methyllithium was prepared from equimolar quantities of bis(diphenylphosphino)methane and n-butyllithium in benzene. After heating to reflux for 4 h a yellow precipitate was formed, and this was filtered off, washed with n-hexane, and dried in vacuo.

Bis(diphenylphosphino)methyl-dimethylaluminium and -dimethylgallium (1,2). A suspension of the above lithium compound in benzene was treated with one equivalent of dimethylaluminium chloride or dimethylgallium chloride. The mixtures were stirred for 1 h at room temperature before the products were isolated by filtration. Yields after washing with n-hexane and drying in vacuo were ca. 90%. The material in both cases contained the lithium chloride formed in the reaction, which could not be separated.

1, white solid, m.p. 230°C (dec.), Anal. Found: C, 64.15; H, 5.59; Al, 5.60; Cl, 7.34; P, 12.85; Li, 1.45. $C_{27}H_{27}AlClLiP_2$ calcd.: (482.45) C, 64.56; H, 5.36; Al, 5.90; Cl, 8.79; P, 11.68; Li, 1.50%.

2, white solid, m.p. 228°C (dec.), Anal. Found: C, 61.61; H, 5.13; Cl, 6.74; P, 11.79, Li, 1.33. $C_{27}H_{27}ClGaLiP_2$ (525.85) calcd.: C, 60.76; H, 5.24; Cl, 7.56; P, 11.62; Li, 1.38%.

[μ-Chlorobis(dimethylaluminium)][η^2(Al–C,Al–P)-bis(diphenylphosphino)methanide] (3) and the ethylaluminium, methylgallium, and ethylgallium analogues (4–6)

A suspension of $LiCH(PPh_2)_2$ in benzene was treated with two equivalents of the R_2MCl component (R = Me, Et; M = Al, Ga;). Evolution of heat was observed, and the reaction was completed by stirring for 1 h at room temperature. The solid in the original slurry was consumed and a new precipitate formed. This precipitate, identified as LiCl, was filtered off, and the filtrate was concentrated in vacuo. The remaining pale-yellow oil crystallized out when covered with a layer of a mixture of benzene and hexane (1/1). The products (yields ca. 70%) are colorless, very sensitive solids, soluble in benzene and toluene, diethyl ether and tetrahydrofuran. Solutions of **3** and **5** are unstable, however, and a precipitate is formed on standing.

3, m.p. 120°C, Anal. Found: C, 63.36; H, 6.24; Al, 10.12; Cl, 6.65; P, 11.62. $C_{29}H_{33}Al_2ClP_2$ (532.93) calcd.: C, 63.31; H, 6.09; Al, 9.90; Cl, 6.88; P, 11.17%.

4, m.p. 101°C, Anal. Found: C, 65.29; H, 7.01; Al, 9.16; Cl, 6.02; P, 10.51. $C_{33}H_{41}Al_2ClP_2$ (589.02) calcd.: C, 65.34; H, 6.88; Al, 9.40; Cl, 6.26; P, 10.21%.

5, m.p. 105°C, Anal. Found: C, 56.32; H, 5.38; Cl, 5.73; P, 10.01. $C_{29}H_{33}ClGa_2P_2$ (618.41) calcd.: C, 55.11; H, 5.45; Cl, 5.44; P, 10.13%.

6, m.p. 85°C, Anal. Found: C, 58.72; H, 6.12; Cl, 5.25; P, 9.17. $C_{33}H_{41}ClGa_2P_2$ (675.02) calcd.: C, 57.55; H, 6.03; Cl, 5.21; P, 9.23%.

X-ray structure determination of 4

Crystal data: $C_{33}H_{41}Al_2ClP_2$, $M_r = 589.06$, monoclinic, space group $P2_1/c$, a 14.348(3), b 11.311(3), c 19.903(4) Å, β 90.18(2)°, V 3230.05 Å^3, $D_{calcd.}$ 1.211 g/cm^3 for $Z = 4$ at −40°C; $F(000) = 1248$, μ(Mo-K_α) 2.88 cm^{-1}. A suitable single crystal of **4** was grown from toluene (room temperature), sealed under argon at dry ice temperature in a Lindemann glass capillary, and mounted on a Syntex P2$_1$ computer-controlled four-circle diffractometer equipped with a graphite monochromator and a scintillation counter.

Intensity data were collected by previously described procedures [21] (ω-scan, $\Delta\omega$ 0.9°, $0.9 \leq \dot{\omega} \leq 29.3°$ min^{-1}, $1 \leq \vartheta \leq 24°$, Mo-$K_\alpha$ radiation, λ 0.71069 Å, T −40 ± 5°C). Of a total of 5601 measured intensities 5046 were unique ($R_{int} = 0.062$, SHELX). After Lorentz and polarization corrections 3761 structure factors with $F_o \geq 4.0\sigma(F_o)$ were considered statistically significant and used for all subsequent calculations. The structure was solved by direct methods (SHELX 76) and completed by Fourier syntheses. After anisotropic refinement of the non-hydrogen atoms the positions of 23 out of the 41 hydrogen atoms were obtained from a difference map. The rest was calculated at idealized geometrical positions (d(C–H) 0.975 Å).

Full-matrix least-squares refinement of 343 parameters converged at $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o| = 0.051$; $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2} = 0.050$; ($w = k/\sigma^2(F_o)$ with $k = 3.15$ in the last cycle; the function minimized was $\Sigma w(|F_o| - |F_c|)^2$; non-H atoms anisotropic, H atoms fixed with $U = 0.05$ Å^2, SHELX 76). In the final refinement cycles, 7 structure factors out of the total of 3761 "observed" were omitted because they showed large F_o/F_c discrepancies due to erroneous diffractometer measurements. In the final cycle the maximum ratio of shift to error was less than 0.008. A final difference map revealed no anomalies in the unit cell, $\Delta\rho_{max/min} = +0.35/-$

TABLE 1

FRACTIONAL ATOMIC COORDINATES AND EQUIVALENT ISOTROPIC THERMAL PARAMETERS FOR **4** (U(eq.) $= (U_1 \cdot U_2 \cdot U_3)^{1/3}$, where U_1, U_2, U_3 are the eigenvalues of the U_{ij} matrix. E.s.d.'s in parentheses)

Atom	x/a	y/b	z/c	U(eq.)
Cl	0.6276(1)	0.0766(1)	0.4551(0)	0.0349
P(1)	0.7472(1)	0.3025(1)	0.3870(0)	0.0244
P(2)	0.8533(1)	0.1945(1)	0.2680(0)	0.0257
Al(1)	0.6011(1)	0.2741(1)	0.4463(1)	0.0297
Al(2)	0.7201(1)	0.0214(1)	0.3603(1)	0.0268
C(1)	0.7514(2)	0.1863(3)	0.3245(2)	0.0234
C(2)	0.7572(3)	0.4465(3)	0.3480(2)	0.0268
C(21)	0.6763(3)	0.5054(4)	0.3286(2)	0.0324
C(22)	0.6809(3)	0.6110(4)	0.2943(2)	0.0390
C(23)	0.7672(3)	0.6584(4)	0.2785(2)	0.0398
C(24)	0.8478(3)	0.6014(4)	0.2973(2)	0.0398
C(25)	0.8443(3)	0.4965(4)	0.3325(2)	0.0330
C(3)	0.8478(3)	0.2955(3)	0.4427(2)	0.0249
C(31)	0.9176(3)	0.2113(3)	0.4377(2)	0.0296
C(32)	0.9928(3)	0.2148(4)	0.4821(2)	0.0331
C(33)	0.9985(3)	0.3014(4)	0.5308(2)	0.0359
C(34)	0.9289(3)	0.3851(4)	0.5356(2)	0.0371
C(35)	0.8534(3)	0.3818(4)	0.4923(2)	0.0341
C(4)	0.8244(3)	0.3047(3)	0.2040(2)	0.0264
C(41)	0.7359(3)	0.3470(4)	0.1883(2)	0.0373
C(42)	0.7228(4)	0.4306(4)	0.1378(3)	0.0487
C(43)	0.7990(5)	0.4729(4)	0.1036(2)	0.0469
C(44)	0.8862(4)	0.4342(4)	0.1186(2)	0.0463
C(45)	0.8988(3)	0.3501(4)	0.1681(2)	0.0390
C(5)	0.8400(3)	0.0587(3)	0.2178(2)	0.0243
C(51)	0.9084(3)	−0.0265(4)	0.2231(2)	0.0330
C(52)	0.9058(3)	−0.1278(4)	0.1836(2)	0.0369
C(53)	0.8339(3)	−0.1448(4)	0.1387(2)	0.0379
C(54)	0.7644(3)	−0.0604(4)	0.1329(2)	0.0334
C(55)	0.7677(3)	0.0405(3)	0.1717(2)	0.0303
C(6)	0.6045(3)	0.3417(4)	0.5363(2)	0.0460
C(7)	0.5233(4)	0.3121(6)	0.5806(3)	0.0735
C(8)	0.4943(3)	0.2928(4)	0.3851(2)	0.0353
C(9)	0.4106(3)	0.2174(4)	0.4066(3)	0.0539
C(10)	0.6278(3)	−0.0614(4)	0.3050(2)	0.0361
C(11)	0.5459(4)	0.0054(5)	0.2785(3)	0.0594
C(12)	0.8142(3)	−0.0772(4)	0.4063(2)	0.0332
C(13)	0.7636(3)	−0.1824(4)	0.4424(2)	0.0405

0.41 $e/\text{Å}^3$. The thermal parameters are of the form $\exp(-2\pi^2(U_{11}h^2a^{\star 2} + U_{22}k^2b^{\star 2} + U_{33}l^2c^{\star 2} + 2\ U_{12}hka^\star b^\star + 2\ U_{13}hla^\star c^\star + 2\ U_{23}klb^\star c^\star))$. A list of the programs used as well as the sources of the scattering factors are also included in ref. [21].

Table 1 lists the final atomic coordinates of the non-H atoms and the equivalent isotropic thermal parameters; Table 2 lists important bond lengths and angles. Figure 1 gives a perspective view of the molecular structure. Additional crystal structure data, tables of H atom parameters and anisotropic thermal parameters, and lists of observed and calculated structure factor amplitudes have been deposited [22].

*NMR-Data of compounds **3**–**6** (in toluene-d_8)*

3: δ(P) −6.9 ppm, s, at +60°C; Coal. temp. +10°C; δ(P) −7.7 and −25.3 ppm, br. AB, not resolved at −42°C. δ(P*C*P) 14.5 ppm, t, ^1J(PC) 26.8 Hz, at 30°C; δ(P*C*P) 12.80, dd, J(PC) 50.8 and 1.4 Hz, at −20°C. δ(CH_3) −7.60 and −4.4 ppm, br. s, at 30°C; δ(CH_3) −7.53, −7.50, −4.94 and −3.77 at −20°C; δ(C_6H_5) 123.7 to 137.7, m. δ(PC*H*P) 2.4 ppm, t, ^2J(PH) 3.5 Hz, at 30°C; broadened resonance at −30°C, partly obscured; δ(CH_3) −0.5 and −0.9 ppm, s, at 30°C; δ(CH_3) −0.10, −0.80, −0.5(br.) at −30°C, Coal. temp. 2°C; δ(C_6H_5) 6.4 to 7.5 ppm, m.

4: δ(P) −11.6 ppm, s, at 83°C; Coal. temp. 44°C; δ(P) −7.4 and −23.9 ppm, br. AB, not resolved at −34°C. δ(P*C*P) 14.10 ppm, t, ^1J(PC) 27.3 Hz, at 82°C; δ(P*C*P) 11.7 ppm, dd, ^1J(PC) 52.7 and 1 Hz, at −35°C; hydrogen-coupled: ^1J(PH) 115.2 Hz. δ(CH_3) 2.08 and 4.68 ppm, s, at +82°C; δ(CH_3) 0.4, 1.5, 2.3 and 4.2 ppm, s, at −35°C. δ(CH_2) 9.87 and 9.09, s, at 82°C; δ(CH_2) 9.4 (br.), 10.2 and 10.5 ppm, s, at −35°C. δ(C_6H_5) 128.5 to 134.7 ppm, m, at 30°C. δ(PC*H*P) 2.35 ppm, t, ^2J(PH) 3.5 Hz, at 30°C; all other ^{1}H resonances are overlapping multiplets.

5: δ(P) −7.6 ppm, s, at 100°C; Coal. temp. 70°C; δ(P) 2.4 and −22.8 ppm, AB, ^2J(PP) 25.5 Hz, at −23°C. δ(P*C*P) 15.8 ppm, t, ^1J(PC) 26.8 Hz, at 68°C; δ(P*C*P)

TABLE 2

SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (deg.) FOR **4**

P(1)–Al(1)	2.431(2)	Al(1)–P(1)–C(2)	113.3(1)
P(1)–C(1)	1.811(4)	Al(1)–P(1)–C(3)	112.5(1)
P(1)–C(2)	1.811(4)	C(2)–P(1)–C(3)	103.7(2)
P(1)–C(3)	1.818(4)	P(1)–Al(1)–Cl	91.3(1)
P(2)–C(1)	1.850(4)	P(1)–Al(1)–C(6)	112.0(1)
P(2)–C(4)	1.829(4)	P(1)–Al(1)–C(8)	110.9(1)
P(2)–C(5)	1.842(4)	Cl–Al(1)–C(6)	108.1(2)
Cl–Al(1)	2.273(2)	Cl–Al(1)–C(8)	106.5(1)
Cl–Al(2)	2.392(2)	C(6)–Al(1)–C(8)	123.0(2)
Al(1)–C(6)	1.949(4)	Al(1)–Cl–Al(2)	106.8(1)
Al(1)–C(8)	1.964(4)	C(1)–Al(2)–Cl	99.2(1)
Al(2)–C(1)	2.047(4)	C(1)–Al(2)–C(10)	112.8(2)
Al(2)–C(10)	1.959(4)	C(1)–Al(2)–C(12)	121.7(2)
Al(2)–C(12)	1.974(4)	Cl–Al(2)–C(10)	101.1(1)
		Cl–Al(2)–C(12)	99.4(1)
P(1)–C(1)–Al(2)	114.4(2)	C(10)–Al(2)–C(12)	116.8(2)
P(1)–C(1)–P(2)	114.2(2)	C(1)–P(2)–C(4)	106.2(2)
P(2)–C(1)–Al(2)	115.6(2)	C(1)–P(2)–C(5)	102.0(2)
C(1)–P(1)–Al(1)	105.5(1)	C(4)–P(2)–C(5)	99.6(2)
C(1)–P(1)–C(2)	110.8(2)		
C(1)–P(1)–C(3)	111.1(2)		

14.2 ppm, dd, ^1J(PC) 49.8 and 1 Hz, at −22°C; $\delta(CH_3)$ 6.75 and 10.1, s, at 68°C; $\delta(CH_3)$ 6.0, 7.5, 9.7 and 10.9, s, at −22°C; $\delta(CH_2)$ 10.52 and 10.91, s, at 68°C; $\delta(CH_2)$ 10.9 (br), 11.2 and 11.5 ppm, s, at −22°C. $\delta(C_6H_5)$ 126.3 to 134.7 ppm, m, at 30°C.

6: δ(P) −9.9 ppm, s, at 29°C; δ(P) −5.6 and −14.7 ppm, br. AB, unresolved at −83°C. δ(PC*H*P) 2.60 ppm, t, ^2J(PH) 3.5 Hz, at 30°C; overlapping multiplets for the C_2H_5 and C_6H_5 resonances at 0.05 to −1.2 ppm and 6.4 to 7.7 ppm, respectively. δ(P*C*P) 16.6 ppm, t, ^1J(PC) 25.0 Hz, at 30°C; δ(P*C*P) 15.14, dd, ^1J(PC) 46.77 and 1 Hz, at −71°C.

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