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Gallium and indium compounds containing three different substituents. Crystal and molecular structure of $[(Me_3CCH_2)ClGaPPh_2]_3$

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Abstract

Three new heavier group 13 element compounds containing three different substituents, $(Me_3CCH_2)ClGaPPh_2$, $(Me_3CCH_2)BrGaPPh_2$ and $(Me_3CCH_2)ClInPPh_2$, have been prepared and characterized. All compounds were characterized by partial elemental analysis, cryoscopic molecular weight studies in benzene solution, and NMR and IR spectroscopic data. All three compounds exist as trimeric molecules in solution. NMR spectral data were consistent with the presence of multiple isomers of the trimers. The compound $[(Me_3CCH_2)ClGaPPh_2]_3$ crystallizes in the acentric space group $Pn2_1a$ with $a = 17.741(9)$ Å, $b = 13.942(6)$ Å and $c = 21.574(8)$ Å. Diffraction data were collected on an Enraf-Nonius CAD-4 diffractometer, and the structure was refined to $R = 4.6\%$ and $R_w = 6.0\%$ for those 2971 reflections with $[F_0 \geq 5\sigma(F_0)]$. The GaP six-membered ring has a typical chair conformation with the bulky neopentyl groups occupying the E,A,A, positions. Distances of interest include Ga–Cl = 2.209(4), 2.219(4) and 2.220(4) Å and Ga–P(bridging) which range from 2.414(3) Å to 2.433(4) Å.

1. Introduction

Gallium and indium compounds which incorporate three different ligands in a single compound provide interesting challenges. Since these types of compounds have the potential to undergo ligand redistribution reactions to form symmetrized products as is common in Group 13 chemistry, these compounds must be fully characterized in order to prove their existence in both the solid phase and in solution. The compounds, $\{(^iPr)(Cl)In[N(H)(^tBu)]\}_2$ [1], $\{(Me_3C_6H_2)[(Me_3Si)_2N]InCl\}_2$ [1,2], $[(C_5Me_5)(Cl)InP(SiMe_3)_2]_2$ [3], $[(Me_3CCH_2)(Me_3SiCH_2)InCl]_2$ [4], $\{[(Me_3Si)_2CH][^iPr]InCl\}_2$ [5] and $\{(^tBu)[P(H)(^tBu_3C_6H_2)]GaCl\}_2$ [6], have been fully characterized by X-ray structural studies and by NMR spectral data. It is noteworthy all of these compounds are dimers and all, except $[(^iPr)(Cl)InN(H)(^tBu)]_2$ and $[(C_5Me_5)(Cl)InP(SiMe_3)_2]_2$, have bridging chlorine atoms according to the X-ray structural studies. Additional dimeric compounds with three different substituents which have been characterized in solution only include $[(Me)(Cl)GaPEt_2]_2$ [7], $[(Me)(Cl)GaAs(CH_2SiMe_3)_2]_2$ [8], $[(Ph)(Cl)GaAs(CH_2SiMe_3)_2]_2$ [8], $[(Me_3CCH_2)(C_6H_5)InCl]_2$ [4] and $[(Me_3SiCH_2)(Me_3CCH_2)InPEt_2]_2$ [4]. In contrast, the gallium compounds, $Ga(Me)(CH_2CMe_3)Cl$ [4] and $Ga(CH_2CMe_3)(CH_2CMe_2Ph)Cl$ [4], do not exist as pure compounds in solution. NMR spectroscopic data suggested the presence of symmetrized products due to the proposed occurrence of ligand redistribution reactions. Thus, the goal of the work reported herein was to prepare and characterize gallium and indium compounds with three different substituents which might be used to eventually prepare compounds with three different substituents including two different organic groups. We report the synthesis and characterization of $(Me_3CCH_2)(Cl)GaPPh_2$, $(Me_3CCH_2)(Br)GaPPh_2$ and $(Me_3CCH_2)(Cl)InPPh_2$. These new compounds have been characterized by elemental analyses, cryoscopic molecular weight studies and IR, ^1H and ^{31}P NMR

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spectroscopic data. In addition, $(Me_3CCH_2)(Cl)GaPPh_2$ was characterized by an X-ray structural study. The reaction of $(Me_3CCH_2)(Cl)GaPPh_2$ with $LiCMe_3$ in an attempt to prepare a gallium compound with three different substituents including two different organic groups is described elsewhere [9].

2. Experimental section

All compounds described in this investigation were extremely sensitive to oxygen and moisture and were manipulated in a standard vacuum line or under a purified argon atmosphere. Solvents were dried by conventional procedures. The compounds $Ga(CH_2CMe_3)Cl_2$ [10] and $In(CH_2CMe_3)Cl_2$ [11] were prepared and purified by literature methods. Diphenylphosphine was purchased from Strem Chemicals, Inc., and was purified by distillation prior to use. Potassium diphenylphosphide ($KPPh_2$) was prepared from excess diphenylphosphine and KH in diethyl ether. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY. Infrared spectra of Nujol mulls between CsI plates were recorded by means of a Perkin-Elmer 683 spectrometer. The ^1H NMR spectra were recorded at 300 MHz by using a Varian Gemini-300 spectrometer. Proton chemical shifts are reported in δ units (ppm) and are referenced to $SiMe_4$ at δ 0.00 ppm and C_6H_6 at δ 7.15 ppm. The ^{31}P NMR spectrum was recorded at 161.9 MHz on a Varian VXR-400 spectrometer. Proton-decoupled ^{31}P NMR spectra are referenced to 85% H_3PO_4 at δ 0.00 pm. All samples for NMR spectra were contained in sealed NMR tubes. Melting points were observed in sealed capillaries. Molecular weights were measured cryoscopically in benzene by using an instrument similar to that described by Shriver and Drezdzon [12].

2.1. Synthesis of $(Me_3CCH_2)ClGaPPh_2$

A side-arm dumper charged with $KPPh_2$ (1.35 g, 6.02 mmol) was fitted to a 100 ml two-neck flask charged with $Ga(CH_2CMe_3)Cl_2$ (1.27 g, 6.02 mmol). After the organogallium reagent was dissolved in 40 ml of Et_2O and cooled to -78°C, $KPPh_2$ was added slowly to the mixture. The resulting mixture was allowed to warm to ambient temperature on its own accord and stirred for 18 h. The Et_2O was removed by vacuum distillation, and the two-neck flask was fitted with a medium frit equipped with a 100 ml Schlenk flask. The assembly was evacuated and two extractions with 30 ml of benzene were performed. The benzene was removed by vacuum distillation and a colorless solid was isolated. The product was washed with anhydrous pentane to yield 1.13 g (5.12 mmol) of $(Me_3CCH_2)ClGaPPh_2$ in 85.1% yield. Crystals were grown by slow diffusion of anhydrous pentane into a benzene solution of $(Me_3CCH_2)ClGaPPh_2$.

2.1.1. $(Me_3CCH_2)ClGaPPh_2$

Mp 184–189°C (glass transition), 209–210°C (melting). ^1H NMR (C_6D_6, δ): 0.94, 0.97, 1.01, 1.04, 1.05 (s, 8.4H combined, $-CMe_3$), [1.09–1.33 (mbr), 1.46, 1.49, 1.62 (s), 1.76 (d, $^3J(PGaCH) = 2.8$ Hz), 1.80 (d, $^3J(PGaCH) = 2.8$ Hz) (2.0 H combined, $-CH_2-$)]. $^{31}P\{^1H\}$ NMR (C_6D_6, δ): -46.53 (s, 2.8), -46.83 (s, 5.6), -47.23 (s, 16.0), -47.27 (s, 20.5), -47.61 (s, 10.1), -48.01 (s, 5.9), -48.36 (s, 1.6), -48.75 (s, 1.00). Low temperature NMR data $^{31}P\{^1H\}$ NMR ($C_6D_5CD_3$, δ) (10°C): -46.7 (s, 1.5), -47.0 (s, 2.6), -47.4 (s, 12.1), -47.6 (s, 2.9), -48.4 (s, 1.1), -48.8 (s, 1.0). (0°C): -46.8 (s, 1.4), -47.2 (s, 4.7), -47.6 (s, 25.1), -47.8 (s, 12.8), -48.2 (s, 5.1), -48.4 (br, 1.0), -48.6 (br, 1.2), -48.9 (br, 1.0). (-10°C): -46.7 (s, 1.6), -47.3 (s, 2.8), -47.7 (s, 14.3), -47.9 (s, 6.9), -48.2 (s, 2.9), -48.7 (br, 1.3), -48.9 (br, 1.0). (-20°C): -47.1 (br, 2.4), -47.6 (br, 4.8), -47.9 (s, 26.5), -48.0 (s, 11.8), -48.3 (br, 3.5), -48.8 (br, 2.1), -49.1 (br, 1.0). (-30°C): -47.3 (br, 1.0), -47.8 (br, 4.0), -48.0 (s, 25.4), -48.4 (br, 1.8), -49.1 (br, 1.0). (-40°C): -48.3 (s, 12.7), -49.3 (br, 1.0). (-50°C): -48.2 (s, 12.6), -49.4 (br, 1.0). Anal. Calcd.: C, 56.32; H, 6.12; Cl, 9.88. Found: C, 56.43; H, 5.93; Cl, 10.13%. Cryoscopic molecular weight, formula weight 361.43 (obsd. molality, obsd. mol. wt., association): 0.0602, 1028, 2.84; 0.0463, 1027, 2.84; 0.0332, 1059, 2.94. IR (Nujol mull, cm^{-1}): 3057w, 2725vw, 1582w, 1568vw, 1305m, 1194w, 1185w, 1130vw, 1090w, 1067w, 1022m, 996m, 965vw, 912vw, 839vw, 739vs, 688vs, 672sh, 610vw, 567m, 505m, 480w, 472m, 448w, 334s.

2.2. Synthesis of $Ga(CH_2CMe_3)Br_2$

The compound $Ga(CH_2CMe_3)Br_2$ was prepared by a ligand redistribution reaction. Stoichiometric quantities of $Ga(CH_2CMe_3)_3$ (1.41 g, 4.99 mmol) and $GaBr_3$ (3.09 g, 9.99 mmol) were combined into a 100-ml Schlenk flask by using pentane and stirred for 20 h at room temperature. The pentane was removed by vacuum distillation, and a yellowish brown liquid was obtained. The product was purified by vacuum distillation at 50°C (0.001 mm, dynamic vacuum) by using a short-path microstill. Pure $Ga(CH_2CMe_3)Br_2$ was isolated as a colorless solid (3.068 g, 10.20 mmol, 68.07%).

2.2.1. $Ga(CH_2CMe_3)Br_2$

Mp 42–44°C. ^1H NMR (C_6D_6, δ): 0.93 (s, 9.1 H, $-CMe_3-$), 1.46 (s, 2.0 H, $-CH_2-$). Anal. Calcd.: C, 19.97; H, 3.69. Found: C, 19.91; H, 3.91%. Cryoscopic molecular weight, formula weight 300.68 (obsd. molality, obsd. mol. wt., association): 0.0801, 666, 2.21;

0.0590, 656, 2.18; 0.0441, 664, 2.21. IR (Nujol mull, cm^{-1}): 2715w, 1398m, 1361s, 1260w, 1233s, 1136s, 1092m, 1013m, 1000m, 910vw, 840w, 808w, 740sh, 724vs, 625s, 452m, 381m, 302s, 248m.

2.3. Synthesis of $(Me_3CCH_2)BrGaPPh_2$

The compound $(Me_3CCH_2)BrGaPPh_2$ (2.12 g, 5.22 mmol, 88.0% yield) was prepared from $Ga(CH_2CMe_3)Br_2$ (1.78 g, 5.93 mmol) and $KPPh_2$ (1.34 g, 5.99 mmol) by using the procedure previously described. Crystals were grown by slow diffusion of anhydrous pentane into a benzene solution of $(Me_3CCH_2)BrGaPPh_2$.

2.3.1. $(Me_3CCH_2)BrGaPPh_2$

Mp 200–203°C. ^1H NMR (C_6D_6, δ): 0.18, 0.27, 0.98, 1.03, 1.05, 1.07, 1.10, 1.12, 1.22 (s, 7.3 H combined, $-CMe_3$), [1.90(m), 1.58, 1.62, 1.64, 1.68, 1.72(br), 2.06 (d, $^3J(PGaCH) = 2.0$ Hz, $-CH_2-$), 1.80 (d, $^3J(PGaCH) = 2.8$ Hz) (2.0 H combined, $-CH_2-$)]. $^{31}P\{^1H\}$ NMR (C_6D_6, δ): −50.83 (s, 1.0), −50.44 (s, 1.3), −50.13 (s, 3.0), −49.74 (s, 7.1), −49.35 (s, 13.9), −49.30 (s, 10.8), −48.91 (s, 4.2), −48.65 (s, 2.8). Anal. Calcd.: C, 50.30; H, 5.22. Found: C, 50.46; H, 5.30%. Cryoscopic molecular weight, formula weight 406.07 (obsd. molality, obsd. mol. wt., association): 0.0619, 1137, 2.80; 0.0515, 1122, 2.76; 0.0362, 1109, 2.73. IR (Nujol mull, cm^{-1}): 1580vw, 1568vw, 1360s, 1300vw, 1257w, 1226w, 1140w, 1128w, 1098sh, 1086w, 1020vw, 1003vw, 800w, 732vs, 709m, 687s, 597w, 500m, 478w, 454vw, 441vw, 383w, 232m.

2.4. Synthesis of $(Me_3CCH_2)ClInPPh_2$

The compound $(Me_3CCH_2)ClInPPh_2$ (1.43 g, 3.51 mmol, 79.85% yield) was prepared from $In(CH_2CMe_3)Cl_2$ (1.13 g, 4.40 mmol) and $KPPh_2$ (0.987 g, 4.40 mmol) by using the procedure previously described. Crystals were grown by slow diffusion of anhydrous pentane into a benzene solution of $(Me_3CCH_2)ClInPPh_2$.

2.4.1. $(Me_3CCH_2)ClInPPh_2$

Mp 184–189°C (glass transition), 209–210°C (melting), ^1H NMR (C_6D_6, δ): 0.85, 0.93, 0.98, 1.55 (s, 8.7H combined, $-CMe_3$), 1.62, 1.65, 1.84, 1.87 (s), 2.06 (t, $^3J(PInCH) = 2.4$ Hz) (2.0 H combined, $-CH_2-$)]. $^{31}P\{^1H\}$ NMR (C_6D_6, δ): −41.06 (s, 2.3), −41.27 (s, 3.2), −41.66 (s, 10.5), −41.70 (s, 9.6), −42.19 (s, 8.0), −42.58 (s, 3.2), −42.83 (s, 1.6), −43.23 (s, 1.0). Anal. Calcd.: C, 50.22; H, 5.21. Found: C, 50.46; H, 5.37%. High temperature NMR data: $^{31}P\{^1H\}$ NMR ($C_6D_5CD_3$, δ) (20°C): −41.06 (s, 2.1), −41.26 (s, 2.9), −41.65 (s, 8.8), −41.70 (s, 8.2), −42.19 (s, 7.0), −42.58 (s, 2.8), −42.83 (s, 1.4), −43.23 (s, 1.0). (40°C): −40.9 (br, 1.5), −41.2 (br, 2.3), −41.6 (s, 10.9), −42.2 (s, 4.7), −42.5 (br, 1.9), −42.7 (br, 1.0), −42.8 (br, 1.0). (50°C): −41.1 (br, 1.1), −41.5 (s, 5.5), −42.1 (m, 2.2), −42.5 (br, 1.0). (60°C): −41.5 (s, 2.5), −42.1 (m, 1.0). Low temperature NMR data: (−20°C): −40.99 (s, 2.2), −41.21 (s, 3.5), −41.59 (s, 7.0), −41.64 (s, 8.7), −42.03 (s, 5.0), −42.41 (s, 2.3), −42.68 (s, 1.3), −43.05 (s, 1.0). (−30°C): −40.91 (s, 2.1), −41.14 (s, 3.1), −41.51 (s, 7.1), −41.56 (s, 7.6), −41.95 (s, 4.9), −42.32 (s, 2.4), −42.59 (s, 1.3), −42.97 (s, 1.0). (−40°C): −40.79 (s, 1.9), −41.01 (s, 2.7), −41.43 (s, 8.0), −41.84 (s, 4.7), −41.84 (s, 4.7), −42.22 (s, 2.3), −42.50 (s, 1.2), −42.87 (s, 1.0). (−65°C): −40.46 (s, 1.7), −40.65 (s, 2.2), −41.08 (s, 7.6), −41.61 (s, 3.9), −42.01 (s, 1.9), −42.25 (s, 1.3), −42.63 (s, 1.0). (−75°C): −40.33 (s, 12.0), −40.51 (s, 2.4), −40.94 (s, 8.4), −41.55 (s, 3.5), −41.95 (s, 1.7), −42.18 (br, 1.3), −42.58 (br, 1.0). Cryoscopic molecular weight, formula weight 406.60 (obsd. molality, obsd. mol. wt., association): 0.0436, 1330, 3.27; 0.0349, 1370, 3.37; 0.0236, 1447, 3.56. IR (Nujol mull cm^{-1}): 2724m, 1582w, 1302m, 1235m, 1185vw, 1155w, 1115w, 1090w, 1067w, 1023w, 1012w, 996w, 965w, 914vw, 887vw, 840vw, 732vs, 719s, 705m, 688s, 670s, 571w, 499m, 471w, 445w, 377w, 290m.

2.5. X-ray data collection, structure determination, and refinement for $[(Me_3CCH_2)ClGaPPh_2]_3$

A transparent single crystal of the title complex was mounted in a thin-walled glass capillary under Ar and transferred to the goniometer. The space group was determined to be either the centric *Pnma* or acentric $Pn2_1a$ from the systematic absences. Successful refinement of the structure was carried out in the acentric space group $Pn2_1a$. A summary of data collection parameters is given in Table 1.

Least-squares refinement with isotropic thermal parameters led to $R = 0.078$. The geometrically constrained hydrogen atoms were placed in calculated positions 0.95 Å from the bonded carbon atom and allowed to ride on that atom with B fixed at 5.5 $Å^2$. The methyl hydrogen atoms were included as a rigid group with rotational freedom at the bonded carbon atom (C–H = 0.95 Å, $B = 5.5$ $Å^2$). Refinement of non-hydrogen atoms with anisotropic temperature factors led to the final values of $R = 0.046$ and $R_W = 0.060$. The final values of the positional parameters are given in Table 2.

3. Results and discussion

Three new compounds containing three different substituents on the Group 13 metal, $(Me_3CCH_2)ClGaPPh_2$, $(Me_3CCH_2)BrGaPPh_2$ and $(Me_3CCH_2)ClInPPh_2$, have been prepared in high yield by metathetical reactions between the appropriate neopentyl Group 13

TABLE 1. Crystal data and summary of intensity data collection and structure refinement for $[(Me_3CCH_2)ClGaPPh_2]_3$

Compound	$[(Me_3CCH_2)ClGaPPh_2]_3$
Color/Shape	Colorless/parallelepiped
Mol. Wt.	1084.5
Space group	$Pn2_1a$
Temp. (°C)	22
Cell constants [a]	
a, Å	17.741(9)
b, Å	13.942(6)
c, Å	21.574(8)
Cell vol., $Å^3$	5336.2
Formula units/unit cell (2)	4
ρ_{calc}, g cm^{-3}	1.35
μ_{calc}, cm^{-1}	18.58
Diffractometer/Scan	Enraf-Nonius CAD-4/$\omega-2\theta$
Range of relative transm. factors, %	93/100
Radiation, graphite monochromator	Mo $K\alpha(\lambda = 0.71073)$
Max crystal dimensions, mm	$0.13 \times 0.15 \times 0.18$
Scan width, deg.	$0.80 + 0.35 \tan\theta$
Standard reflections	12,0,0; 0,10,0; 006
Decay of standards	±2%
Reflections measured	5213
2θ range, deg.	$2 \leq 2\theta \leq 50$
Range of h,k,l	+21, +16, +25
Reflections observed $[F_o \geqslant 5\sigma(F_o)]$ [b]	2971
Computer programs [c]	SHELX [13]
Structure solution	SHELXS [15]
No. of parameters varied	541
Weights	$[\sigma(F_o)^2 + 0.001\ F_o{}^2]^{-1}$
GOF	1.22
$R = \Sigma \lVert F_o \rvert - \lvert F_c \rVert / \Sigma \lvert F_o \rvert$	0.046
R_W	0.060
R inverse configuration	0.049
Largest feature final diff. map, e $Å^{-3}$	0.4 e^- $Å^3$

[a] Least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 25 reflections $\theta > 20°$; [b] corrections: Lorentz-polarization and absorption (empirical, psi scan); [c] neutral scattering factors and anomalous dispersion corrections from ref. 14.

dihalide and $KPPh_2$ in Et_2O at −78°C and characterized. The characterization data include partial elemental analyses, physical properties, cryoscopic molecular weight measurements, IR, ^1H NMR and ^{31}P NMR spectroscopic data. In addition, a single crystal X-ray structural study was used to define the nature of $(Me_3CCH_2)ClGaPPh_2$ in the solid state.

A crystal of $(Me_3CCH_2)ClGaPPh_2$ consisted of discrete trimeric units with the formula $[(Me_3CCH_2)ClGaPPh_2]_3$. There are no abnormally close contacts in

TABLE 2. Final fractional coordinates for $[(Me_3CCH_2)ClGaPPh_2]_3$

Atom	x	y	z	B_{eq} [a]
Ga(1)	0.67864(6)	0.7500	0.06075(6)	2.31
Ga(2)	0.76315(6)	0.6507(1)	−0.10666(5)	2.16
Ga(3)	0.75253(7)	0.9368(1)	−0.07193(5)	2.28
Cl(1)	0.5789(2)	0.7609(3)	−0.0011(2)	4.22
Cl(2)	0.8527(2)	0.5480(3)	−0.1341(2)	3.76
Cl(3)	0.8263(2)	1.0644(3)	−0.0755(2)	4.48
P(1)	0.7522(2)	0.6318(2)	0.0049(1)	1.97
P(2)	0.8203(2)	0.8075(2)	−0.1222(1)	2.30
P(3)	0.7399(2)	0.9004(2)	0.0377(1)	2.07
C(1)	0.6539(8)	0.704(1)	0.1445(5)	3.46
C(2)	0.621(1)	0.772(1)	0.1970(7)	4.41
C(3)	0.604(1)	0.707(1)	0.2537(9)	6.66
C(4)	0.680(1)	0.846(2)	0.2126(9)	7.24
C(5)	0.548(1)	0.819(2)	0.171(1)	7.01
C(6)	0.6598(6)	0.631(1)	−0.1394(5)	2.72
C(7)	0.6446(7)	0.554(1)	−0.1910(5)	3.04
C(8)	0.656(1)	0.455(1)	−0.1603(8)	4.81
C(9)	0.6928(9)	0.569(1)	−0.2462(6)	4.31
C(10)	0.5615(9)	0.563(1)	−0.2099(8)	5.19
C(11)	0.6484(6)	0.933(1)	−0.1146(5)	4.27
C(12)	0.6316(9)	1.037(1)	−0.1468(8)	4.71
C(13)	0.556(1)	1.023(2)	−0.1792(9)	7.91
C(14)	0.625(1)	1.127(2)	−0.1035(9)	7.67
C(15)	0.6890(9)	1.066(2)	−0.1981(9)	5.83
C(16)	0.8405(7)	0.6085(8)	0.0463(5)	2.36
C(17)	0.8398(7)	0.572(1)	0.1050(5)	2.98
C(18)	0.9057(7)	0.557(1)	0.1384(6)	3.28
C(19)	0.9737(8)	0.582(1)	0.1119(7)	4.18
C(20)	0.9741(7)	0.618(1)	0.0519(6)	3.32
C(21)	0.9111(6)	0.6316(9)	0.0181(5)	2.55
C(22)	0.7059(7)	0.5162(9)	0.0092(6)	2.49
C(23)	0.7448(7)	0.435(1)	−0.0008(6)	3.29
C(24)	0.7065(9)	0.342(1)	−0.0043(7)	4.05
C(25)	0.6288(9)	0.343(1)	0.0073(7)	4.55
C(26)	0.5917(8)	0.424(1)	0.0192(7)	4.00
C(27)	0.6257(6)	0.508(1)	0.0213(6)	2.98
C(28)	0.9216(6)	0.8010(9)	−0.1049(5)	2.17
C(29)	0.9679(7)	0.747(1)	−0.1433(6)	3.58
C(30)	1.0451(7)	0.740(1)	−0.1278(8)	4.27
C(31)	1.0732(7)	0.788(1)	−0.0790(9)	4.51
C(32)	1.0264(7)	0.842(1)	−0.0409(7)	3.79
C(33)	0.9508(6)	0.853(1)	−0.0560(6)	3.37
C(34)	0.8160(7)	0.8413(8)	−0.2037(5)	2.56
C(35)	0.7554(8)	0.818(1)	−0.2397(5)	3.52
C(36)	0.749(1)	0.849(1)	−0.3015(7)	4.96
C(37)	0.804(1)	0.898(1)	−0.3270(7)	4.64
C(38)	0.864(1)	0.925(1)	−0.2935(8)	6.03
C(39)	0.8702(9)	0.899(1)	−0.2311(7)	5.32
C(40)	0.8296(6)	0.9068(8)	0.0801(5)	2.14
C(41)	0.8794(7)	0.980(1)	0.0723(6)	3.33
C(42)	0.9486(7)	0.982(1)	0.1015(6)	3.18
C(43)	0.9699(8)	0.911(1)	0.1393(7)	3.82
C(44)	0.9198(8)	0.834(1)	0.1482(6)	3.98
C(45)	0.8491(7)	0.832(1)	0.1186(5)	3.19
C(46)	0.6817(7)	0.9985(9)	0.0672(5)	2.70
C(47)	0.6086(7)	1.0064(9)	0.0448(6)	3.02
C(48)	0.5639(8)	1.080(1)	0.0665(6)	3.74
C(49)	0.5890(9)	1.145(1)	0.1068(7)	4.40
C(50)	0.661(1)	1.134(1)	0.1309(8)	4.94
C(51)	0.7079(8)	1.063(1)	0.1087(7)	4.11

Notes to Table 2:

[a] $B_{eq} = 4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

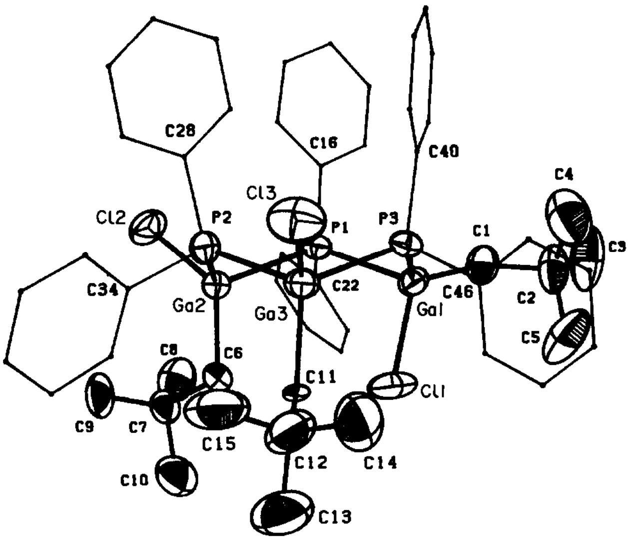

Fig. 1. Labelling of atoms in $[(Me_3CCH_2)ClGaPPh_2]_3$ (ORTEP diagram; 50% ellipsoids. The hydrogen atoms have been omitted and the phenyl rings are arbitarily reduced for clarity).

the unit cell. The labelling of the atoms in the molecule is depicted in Fig. 1. The interatomic distances and angles are provided in Tables 3 and 4.

The Ga_3P_3 six-membered ring has a typical chair conformation with the bulky neopentyl groups occupying the E,A,A positions. The only other gallium phosphide trimers investigated in the solid state are $(^tBu_2GaPH_2)_3$ [16] and $[Me_2GaP(^iPr)_2]_3$ [17]. The Ga_3P_3 six-membered ring for $(^tBu_2GaPH_2)_3$ had a planar conformation whereas the six-membered ring for $[Me_2GaP(^iPr)_2]_3$ adopted a distorted boat conformation. The internal ring angles of $[(Me_3CCH_2)ClGaPPh_2]_3$ range from 104.2(1)° to 109.0(1)° for P–Ga–P and from 113.6(1)° to 117.5(1)° for Ga–P–Ga, respectively.

TABLE 3. Interatomic distances (Å) for $[(Me_3CCH_2)ClGaPPh_2]_3$

(A) Gallium – phosphorus distances			
Ga(1) – P(1)	2.423(3)	Ga(1) – P(3)	2.414(3)
Ga(2) – P(2)	2.433(4)	Ga(2) – P(1)	2.429(3)
Ga(3) – P(3)	2.429(3)	Ga(3) – P(2)	2.423(4)
(B) Gallium – chlorine distances			
Ga(1) – Cl(1)	2.222(4)	Ga(2) – Cl(2)	2.219(4)
Ga(3) – Cl(3)	2.209(4)		
(C) Gallium – carbon distances			
Ga(1) – C(1)	1.97(1)	Ga(2) – C(6)	1.98(1)
Ga(3) – C(11)	2.06(1)		
(D) Phosphorus – carbon distances			
P(1) – C(16)	1.83(1)	P(1) – C(22)	1.81(1)
P(2) – C(28)	1.84(1)	P(2) – C(34)	1.82(1)
P(3) – C(40)	1.84(1)	P(3) – C(46)	1.83(1)

TABLE 4. Angles (deg) for $[(Me_3CCH_2)ClGaPPh_2]_3$

(A) Angles around the gallium atoms			
P(1) – Ga(1) – P(3)	104.2(1)	Cl(1) – Ga(1) – P(1)	100.2(1)
P(1) – Ga(2) – P(2)	105.5(1)	Cl(1) – Ga(1) – P(3)	100.1(1)
P(2) – Ga(3) – P(3)	109.0(1)	Cl(2) – Ga(2) – P(1)	104.6(1)
P(1) – Ga(1) – C(1)	111.0(4)	Cl(2) – Ga(2) – P(2)	104.2(1)
P(3) – Ga(1) – C(1)	124.8(4)	Cl(3) – Ga(3) – P(2)	106.8(1)
P(1) – Ga(2) – C(6)	105.3(3)	Cl(3) – Ga(3) – P(3)	104.8(1)
P(2) – Ga(2) – C(6)	117.5(4)	Cl(1) – Ga(1) – C(1)	113.4(4)
P(2) – Ga(3) – C(11)	103.0(5)	Cl(2) – Ga(2) – C(6)	118.4(4)
P(3) – Ga(3) – C(11)	110.3(3)	Cl(3) – Ga(3) – C(11)	122.3(5)
(B) Angles around the phosphorus atoms			
Ga(1) – P(1) – Ga(2)	117.5(1)	Ga(1) – P(1) – C(16)	109.8(4)
Ga(2) – P(1) – C(16)	115.7(4)	Ga(1) – P(1) – C(22)	109.6(4)
Ga(2) – P(1) – C(22)	100.6(4)	C(16) – P(1) – C(22)	101.8(6)
Ga(2) – P(2) – Ga(3)	113.6(1)	Ga(2) – P(2) – C(28)	109.6(4)
Ga(3) – P(2) – C(28)	115.5(5)	Ga(2) – P(2) – C(34)	110.4(4)
Ga(3) – P(2) – C(34)	102.6(4)	C(28) – P(2) – C(34)	104.4(5)
Ga(1) – P(3) – Ga(3)	115.1(1)	Ga(1) – P(3) – C(40)	109.2(4)
Ga(3) – P(3) – C(40)	113.2(3)	Ga(1) – P(3) – C(46)	108.9(4)
Ga(3) – P(3) – C(46)	103.6(4)	C(40) – P(3) – C(46)	106.3(5)
(C) Gallium – carbon – carbon angles			
Ga(1) – C(1) – C(2)	123(1)	Ga(2) – C(6) – C(7)	120.4(8)
Ga(3) – C(11) – C(12)	109(1)		
(D) Phosphorus – carbon – carbon angles			
P(1) – C(16) – C(17)	120.7(9)	P(1) – C(16) – C(21)	120.1(8)
P(1) – C(22) – C(23)	121(1)	P(1) – C(22) – C(27)	121.5(9)
P(2) – C(28) – C(29)	118.9(9)	P(2) – C(28) – C(33)	119.7(9)
P(2) – C(34) – C(35)	121.2(9)	P(2) – C(34) – C(39)	122(1)
P(3) – C(40) – C(41)	122.5(9)	P(3) – C(40) – C(45)	118.9(9)
P(3) – C(46) – C(47)	117.9(9)	P(3) – C(46) – C(51)	122(1)

There are no unusual bond lengths in $[(Me_3CCH_2)ClGaPPh_2]_3$. The Ga–P bond distances were in the range of 2.414(3) Å to 2.433(4) Å. These Ga–P bond distances are longer than the Ga–P bond distance of 2.360 Å for gallium phosphide [18], but are comparable to those of 2.439(3) Å for $(^tBu_2GaPH_2)_3$ [16] and of 2.419(3) to 2.457(3) Å for $[Me_2GaP(^iPr)_2]_3$ [17]. The Ga–Cl bond distances for $[(Me_3CCH_2)ClGaPPh_2]_3$ range from 2.209(4) to 2.222(4) Å. These Ga–Cl bond distances are comparable to the terminal Ga–Cl bond distances of 2.150(4) and 2.164(4) Å for $(GaMesCl_2)_n$ [19], but are substantially shorter than the bridging Ga–Cl bond distances of 2.363(3) and 2.369(3) Å for $(GaMesCl_2)_n$ [19], as would be expected. Furthermore, the Ga–C neopentyl bond distances in $[(Me_3CCH_2)ClGaPPh_2]_3$ are in the range of 1.97(1) to 2.06(1) Å. These Ga–C neopentyl bond lengths are comparable to those in $[(Me_3CCH_2)_2GaPPh_2]_2$ which range from 1.996(12) to 2.016(12) Å [20].

Cryoscopic molecular weight studies indicate that $(Me_3CCH_2)ClGaPPh_2$, $(Me_3CCH_2)ClInPPh_2$ and $(Me_3CCH_2)BrGaPPh_2$ are trimeric in benzene solution. The observations that the degrees of association of the three compounds do not change in a regular and the expected manner with concentration suggest that solutions of these compounds are not composed of species of multiple degrees of association. Furthermore, since the melting points of all three compounds are very sharp, it is unlikely that species other than trimers exist in the solid state either. Replacement of a neopentyl group on gallium in $(Me_3CCH_2)_2GaPPh_2$ [20] by a halogen, chlorine or bromine, changed the degree of association in solution from dimer to trimer. However, replacing the neopentyl group with a chloride on the corresponding indium species changed the degree of association in solution from a monomer-dimer equilibrium mixture to a trimer. The observation of the higher degree of association of $(Me_3CCH_2)XMPPh_2$ compared to $(Me_3CCH_2)_2MPPh_2$ might be related to steric and electronic effects. The halide substituents are sterically less demanding than the neopentyl group, which would be expected to favor a higher degree of association. Furthermore, calculations which use group electronegativities [21] indicate that a higher positive charge is located on the metallic center of the halogen derivatives, $(Me_3CCH_2)XMPPh_2$. Consequently, the halogen derivatives would be expected to have a higher Lewis acidity than the corresponding bisneopentyl analogs. Higher Lewis acidity would favor a higher degree of association.

The very complex ^1H and ^{31}P NMR spectral data of $(Me_3CCH_2)ClGaPPh_2$, $(Me_3CCH_2)ClInPPh_2$ and $(Me_3CCH_2)BrGaPPh_2$ are consistent with the existence of a mixture of isomers of trimeric species in solution. Isomers may arise from different conformations of the six-membered ring (chair, boat, twist boat) and/or different orientations of the neopentyl groups and the halides on the metal (axial and equatorial). The $^{31}P\{^1H\}$ NMR spectral data for all three compounds $(Me_3CCH_2)ClGaPPh_2$, $(Me_3CCH_2)ClInPPh_2$ and $(Me_3CCH_2)BrGaPPh_2$ were very similar and each had eight lines within a range of 2.25 ppm. This small range of ^{31}P chemical shifts is consistent with the presence of species of only one degree of association as was suggested by the molecular weight data. It was not possible to relate a specific ^{31}P NMR line to a given isomer due to the complexity of the system.

Variable temperature $^{31}P\{^1H\}$ NMR spectra of $[(Me_3CCH_2)ClInPPh_2]_3$ and $[(Me_3CCH_2)ClGaPPh_2]_3$ were studied in an attempt to elucidate the nature of these compounds in solution. The $^{31}P\{^1H\}$ NMR spectra of $[(Me_3CCH_2)ClInPPh_2]_3$ in d_8-toluene did not exhibit any significant changes from 20°C to −75°C. Thus, there are no significant changes in the various isomers of $[(Me_3CCH_2)ClInPPh_2]_3$ with temperature. However, when the solution was heated from 20°C to 60°C, the eight lines coalesced to two broad lines at −41.50 and −42.05 ppm. Thus, only two apparent isomers or one isomer with two unique phosphorus atoms exist at 60°C for $[(Me_3CCH_2ClInPPh_2]_3$. Temperatures above 60°C were not studied. In contrast, the low temperature $^{31}P\{^1H\}$ NMR spectra of $[(Me_3CCH_2)ClGaPPh_2]_3$ in d_8-toluene was very different from that observed for $[(Me_3CCH_2)ClInPPh_2]_3$. As the temperature was decreased, the eight lines broadened and eventually formed two broad lines at −40°C. The spectrum did not change significantly as the temperature was lowered further to −60°C. At −40°C the $^{31}P\{^1H\}$ NMR spectra exhibited two chemically nonequivalent phosphorus atoms at −48.2 ppm and −49.4 ppm with a relative peak height ratio of 12.3 to 1.0. Typically, lowering the temperature should reduce the exchange rate between different conformations of a species. Thus, more lines and more splitting might have been expected. The observation of fewer lines at lower temperature suggests that the phosphorus atoms have become more chemically equivalent. A planar six-membered ring might make the phosphorus atoms chemically equivalent. However, there must be more than one species in solution.

In conclusion, all three compounds $(Me_3CCH_2)ClGaPPh_2$, $(Me_3CCH_2)BrGaPPh_2$ and $(Me_3CCH_2)ClInPPh_2$ are trimeric in solution and their room temperature NMR spectral data are almost identical. These data suggest that all three compounds behave similarly in solution and the fluxionality of the six-membered rings are similar at ambient temperature. However, variable temperature ^{31}P NMR spectral data suggest that the fluxionality of the six-membered rings of the two closely related compounds, $[(Me_3CCH_2)ClGaPPh_2]_3$ and $[(Me_3CCH_2)ClInPPh_2]_3$, are significantly different. The reasons behind these observations are currently under investigation.

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